

Preface

Magnetochemistry is situated on one of the interfaces between physics and chemistry. This discipline includes chemistry predominantly as a source of new objects to which the molecular systems or periodical aggregates, such as linear, planar or three-dimensional networking of certain entities, belong. It is mostly the chemistry of coordination compounds, which produces transition metal complexes having unpaired electrons as carriers of magnetic phenomena. Under the influence of physical fields these new materials exhibit a number of interesting properties, some of which may find technical exploitation. Therefore the interdisciplinary character of magnetochemistry is enriched also by its output to material science. Contemporary research trends include the investigation of molecular clusters, high-spin molecules, molecular magnets, spin-crossover systems as well as nano-scale magnetism. These systems adopt the properties of molecular devices with a perspective of the construction of units of very high integration.

An accumulation of a large amount of experimental data makes their theoretical interpretation and systemisation feasible. Although the general strategy of theoretical magnetochemistry has been known for decades, its performance for extended systems of interacting magnetic units can be very complicated. This is due to the fact that magnetic phenomena originate at the microscopic level by magnetic moments interacting with an external magnetic field. In this way the energy levels of chemical entities are altered. A complete description of the energy levels for a microobject, with and/or without the presence of the external magnetic field, can be obtained from the principles of quantum mechanics. Methods of quantum chemistry need to be applied but these are still subject to development and improvement. However, the usual non-relativistic formulation of quantum mechanics may be far from sufficient for the purposes of magnetochemistry. In many cases we need to pass from the Schrödinger formulation of quantum mechanics to the Dirac one which takes into account principles of the special theory of relativity.

When the energy levels of a system under investigation have been determined, their dependence upon the magnetic field or magnetic moments of atomic nuclei and electrons can be obtained. Derivation of magnetic parameters (like the tensor of a temperature-independent magnetic susceptibility) is achieved by differentiating the total molecular energy. Knowledge of the energy levels facilitates the application of the apparatus of statistical thermodynamics and, from the thermodynamic partition function, macroscopic

observables (such as the temperature-dependent magnetic susceptibility) can be obtained.

In describing the exchange coupling in clusters of high nuclearity a task of evaluating the matrix elements of matrices of order 10^6 or higher is met. The enumeration of energy levels by their diagonalisation becomes a very difficult, if not intractable, numerical problem.

Now one can realise that the mosaic of theoretical magnetochemistry has roots in the special theory of relativity, the theory of tensor operators, group theory, quantum mechanics, quantum chemistry, statistical thermodynamics, numerical mathematics, etc.

The present book first recapitulates all the necessary mathematical background (Chapter 1). An overview of macroscopic magnetic properties is then presented (Chapter 2). Formulation of magnetic parameters and methods of their calculation are given in Chapters 3–6. A brief summary of magnetic behaviour is presented (Chapter 7). The core of the book deals with the temperature dependence of magnetic susceptibility for mononuclear complexes, dimers and exchange-coupled clusters (Chapters 8–11).

Mathematical Background

1.1 SYMBOLICS

1.1.1 Notation

The notation according to Table 1.1 is used hereafter. For units and important definitions see Appendix 1.

1.1.2 Scalars, vectors and tensors

We will deal with scalar (single valued) quantities A , Cartesian (three component) vectors

$$\vec{A} = (A_x, A_y, A_z) = \vec{i}A_x + \vec{j}A_y + \vec{k}A_z$$

TABLE 1.1
Notation used

Meaning	Symbol
vector $\vec{A}$ components	A_a
tensor $\vec{A}$ components	A_{ab}
scalar product	$\vec{A} \cdot \vec{B}$
vector product	$\vec{A} \times \vec{B}$
tensor product	$\vec{A} \otimes \vec{B}$
Dirac function	$\delta(\vec{r}_i)$
Kronecker delta symbol	δ_{ij}
molecular orbitals	ϕ_i, ϕ_j
—occupied (occ) MOs	ϕ_o
—unoccupied (un) MOs	ϕ_u
atomic orbitals	$\chi_\mu, \chi_\nu, \chi_\lambda, \chi_\sigma$
Dirac “bra-ket” one-electron integral	$\langle \mu \hat{A}_1 \nu \rangle = \int \chi_\mu^*(1) \hat{A}(1) \chi_\nu(1) d\tau_1$
Dirac “bra-ket” two-electron integral	$\langle \mu\lambda \hat{g}_{12} \nu\sigma \rangle = \int \int \chi_\mu^*(1) \chi_\lambda^*(2) \hat{g}(1, 2) \chi_\nu(1) \chi_\sigma(2) d\tau_1 d\tau_2$

(where elementary Cartesian vectors occur) as well as with Cartesian (nine-components, 3×3 , second-rank) tensors

$$\bar{\bar{A}} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} = \left\{ \begin{array}{l} A_{xx}\vec{i}\vec{i} + A_{xy}\vec{i}\vec{j} + A_{xz}\vec{i}\vec{k} \\ + A_{yx}\vec{j}\vec{i} + A_{yy}\vec{j}\vec{j} + A_{yz}\vec{j}\vec{k} \\ + A_{zx}\vec{k}\vec{i} + A_{zy}\vec{k}\vec{j} + A_{zz}\vec{k}\vec{k} \end{array} \right\}$$

Here $\vec{i}\vec{j}$, etc., represent *diadic products* of the elementary Cartesian vectors.

The unit vector is

$$\vec{e} \equiv (1, 1, 1) = \vec{i} + \vec{j} + \vec{k}$$

and the identity tensor is

$$\bar{\bar{I}} \equiv \vec{i}\vec{i} + \vec{j}\vec{j} + \vec{k}\vec{k}$$

1.1.3 Vector algebra

The mean value (the length) of the vector is a scalar

$$A = |\vec{A}| = (A_x^2 + A_y^2 + A_z^2)^{1/2}$$

The scalar product of two vectors is a scalar

$$d = \vec{A} \cdot \vec{B} = A_x B_x + A_y B_y + A_z B_z = \vec{B} \cdot \vec{A}$$

The vector product of two vectors is a vector perpendicular to both of them

$$\begin{aligned} \vec{C} = \vec{A} \times \vec{B} &= \det \begin{pmatrix} \vec{i} & \vec{j} & \vec{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{pmatrix} \\ &= (A_y B_z - B_y A_z; A_z B_x - B_z A_x; A_x B_y - B_x A_y) = -\vec{B} \times \vec{A} \end{aligned}$$

It holds true that

$$(\vec{A} \times \vec{B}) \cdot \vec{C} = \vec{A} \cdot (\vec{B} \times \vec{C})$$

$$(\vec{A} \times \vec{B}) \cdot (\vec{C} \times \vec{D}) = (\vec{A} \cdot \vec{C})(\vec{B} \cdot \vec{D}) - (\vec{A} \cdot \vec{D})(\vec{B} \cdot \vec{C})$$

$$\vec{A} \times (\vec{B} \times \vec{C}) = (\vec{A} \cdot \vec{C})\vec{B} - (\vec{A} \cdot \vec{B})\vec{C}$$

The *diadic product* of two vectors is a second-rank tensor

$$\begin{aligned}\overline{\overline{C}} &= \vec{A}\vec{B} = (A_x\vec{i} + A_y\vec{j} + A_z\vec{k})(B_x\vec{i} + B_y\vec{j} + B_z\vec{k}) \\ &= \left\{ \begin{array}{l} A_xB_x\vec{ii} + A_xB_y\vec{ij} + A_xB_z\vec{ik} \\ + A_yB_x\vec{ji} + A_yB_y\vec{jj} + A_yB_z\vec{jk} \\ + A_zB_x\vec{ki} + A_zB_y\vec{kj} + A_zB_z\vec{kk} \end{array} \right\}\end{aligned}$$

The scalar product of a tensor with a vector results in a vector

$$\begin{aligned}\overline{\overline{C}} \cdot \vec{D} &= \left\{ \begin{array}{l} (C_{xx}\vec{ii} + C_{xy}\vec{ij} + C_{xz}\vec{ik} \\ + C_{yx}\vec{ji} + C_{yy}\vec{jj} + C_{yz}\vec{jk} \\ + C_{zx}\vec{ki} + C_{zy}\vec{kj} + C_{zz}\vec{kk}) \\ \cdot (D_x\vec{i} + D_y\vec{j} + D_z\vec{k}) \end{array} \right\} \\ &= \left\{ \begin{array}{l} (C_{xx}D_x + C_{xy}D_y + C_{xz}D_z)\vec{i} \\ + (C_{yx}D_x + C_{yy}D_y + C_{yz}D_z)\vec{j} \\ + (C_{zx}D_x + C_{zy}D_y + C_{zz}D_z)\vec{k} \end{array} \right\}\end{aligned}$$

But

$$\vec{D} \cdot \overline{\overline{C}} = \left\{ \begin{array}{l} (D_xC_{xx} + D_yC_{yx} + D_zC_{zx})\vec{i} \\ + (D_xC_{xy} + D_yC_{yy} + D_zC_{zy})\vec{j} \\ + (D_xC_{xz} + D_yC_{yz} + D_zC_{zz})\vec{k} \end{array} \right\}$$

1.1.4 The vector operator ‘nabla’

The differential operator

$$\vec{\nabla} \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

adopts frequent utilisation. This enters

(a) the *gradient* of a scalar function

$$\text{grad}A \equiv \vec{\nabla}A = \left(\frac{\partial A}{\partial x}, \frac{\partial A}{\partial y}, \frac{\partial A}{\partial z} \right)$$

(b) the *rotation* of a vector function

$$\text{rot} \vec{A} \equiv \text{curl} \vec{A} \equiv \vec{\nabla} \times \vec{A} = \det \begin{pmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{pmatrix}$$

(c) the *divergence* of a vector function

$$\text{div} \vec{A} \equiv \vec{\nabla} \cdot \vec{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$$

If the scalar S and the components of the vectors $\vec{A}, \vec{B}, \vec{C}, \vec{D}$ commute with one another, the following relations are satisfied

$$\vec{\nabla} \cdot (S\vec{A}) = (\vec{\nabla} S) \cdot \vec{A} + S(\vec{\nabla} \cdot \vec{A})$$

$$\vec{\nabla} \times (S\vec{A}) = (\vec{\nabla} S) \times \vec{A} + S(\vec{\nabla} \times \vec{A})$$

$$\vec{\nabla}(\vec{A} \cdot \vec{B}) = (\vec{B} \cdot \vec{\nabla})\vec{A} + (\vec{A} \cdot \vec{\nabla})\vec{B} + \vec{B} \times (\vec{\nabla} \times \vec{A}) + \vec{A} \times (\vec{\nabla} \times \vec{B})$$

$$\vec{\nabla} \cdot (\vec{A} \times \vec{B}) = (\vec{\nabla} \times \vec{A}) \cdot \vec{B} - \vec{A} \cdot (\vec{\nabla} \times \vec{B})$$

$$\vec{\nabla} \times (\vec{A} \times \vec{B}) = \vec{A}(\vec{\nabla} \cdot \vec{B}) - (\vec{A} \cdot \vec{\nabla})\vec{B} + (\vec{B} \cdot \vec{\nabla})\vec{A} - (\vec{\nabla} \cdot \vec{A})\vec{B}$$

$$\vec{\nabla} \times (\vec{\nabla} S) = 0$$

$$\vec{\nabla} \cdot (\vec{\nabla} \times \vec{A}) = 0$$

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{A}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{A}) - \vec{\nabla}^2 \vec{A}$$

The following relations involving the position vector $\vec{r}(x, y, z)$ hold true

$$\vec{\nabla} \cdot \vec{r} = \sum_a \nabla_a r_a = 3$$

$$\vec{\nabla} \times \vec{r} = \det \begin{pmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ x & y & z \end{pmatrix} = 0$$

The relations involving the reciprocal distance are more complex

$$\begin{aligned}
 \vec{\nabla}\left(\frac{1}{r}\right) &= \left(\vec{i}\frac{\partial}{\partial x} + \vec{j}\frac{\partial}{\partial y} + \vec{k}\frac{\partial}{\partial z}\right)(x^2 + y^2 + z^2)^{-1/2} \\
 &= -(x^2 + y^2 + z^2)^{-3/2}(\vec{i}x + \vec{j}y + \vec{k}z) = -\frac{\vec{r}}{r^3} \\
 \vec{\nabla}^2\left(\frac{1}{r}\right) &= \vec{\nabla} \cdot \vec{\nabla}\left(\frac{1}{r}\right) = -\vec{\nabla} \cdot \left(\frac{\vec{r}}{r^3}\right) \\
 &= -\left(\vec{i}\frac{\partial}{\partial x} + \vec{j}\frac{\partial}{\partial y} + \vec{k}\frac{\partial}{\partial z}\right) \cdot \frac{(\vec{i}x + \vec{j}y + \vec{k}z)}{(x^2 + y^2 + z^2)^{3/2}} = \begin{cases} 0 & \text{for } \vec{r} \neq 0 \\ \infty & \text{for } \vec{r} = 0 \end{cases} \\
 &= -4\pi\delta(\vec{r})
 \end{aligned}$$

Instead of the infinity symbol it is more appropriate to speak about a singular function. However, the operator $\nabla^2(1/r)$ occurs in integrals of the form

$$I = \int_{-\infty}^{\infty} \psi^*(\vec{r}) \nabla^2\left(\frac{1}{r}\right) \psi(\vec{r}) d\vec{r}$$

and the singularity of the operator does not imply the non-existence of the integral. Let us define the “function” $\delta(x)$ satisfying

$$\int_{-\infty}^{\infty} f(x) \delta(x) dx = f(0)$$

This is the definition of the *Dirac function* which is zero everywhere except at $x = 0$. It is infinite in such a way that the area under it is unity

$$\int_{-\infty}^{\infty} \delta(x) dx = 1$$

Then we can write

$$I = \int_{-\infty}^{\infty} \psi^*(\vec{r}) f(\vec{r}) \delta(\vec{r}) \psi(\vec{r}) d\vec{r} = f(\vec{r}_0) \psi^*(\vec{r}_0) \psi(\vec{r}_0); \text{ for } \vec{r}_0 = 0$$

The Dirac function is an eigenfunction of the operator of the position vector so that

$$\vec{r}\delta(\vec{r}) = \vec{r}_0\delta(\vec{r})$$

for $\vec{r}_0 = 0$, which means that the Dirac function is zero everywhere except at $\vec{r} = 0$. Some important properties of the Dirac function follow

$$\delta(\vec{r}) = \delta(x)\delta(y)\delta(z)$$

$$\int_{-\infty}^{\infty} f(x)\delta(x)dx = f(0)$$

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)dx = f(a)$$

$$\delta(cx) = \delta(x)/c$$

$$x\delta(x) = 0$$

$$\delta(-x) = \delta(x)$$

A representation of the Dirac function through usual functions is possible, e.g.

$$\delta(x) = \lim_{n \rightarrow \infty} (n/\pi)^{1/2} \exp(-nx^2)$$

Using the Dirac function we can write

$$\vec{\nabla}_i \cdot \frac{(\vec{r}_j - \vec{r}_i)}{|\vec{r}_j - \vec{r}_i|^3} = 4\pi\delta(\vec{r}_j - \vec{r}_i)$$

$$\sum_a \sum_b \nabla_a \left(\frac{r_b}{r^3} \right) = \sum_a \sum_b \left[\frac{4\pi}{3} \delta_{ab} \delta(\vec{r}) + \frac{1}{r^3} \delta_{ab} - \frac{3r_a r_b}{r^5} \right]$$

and in particular

$$\sum_a \sum_{b \neq a} \nabla_a \left(\frac{r_b}{r^3} \right) = \sum_a \sum_{b \neq a} \left[-\frac{3r_a r_b}{r^5} \right]$$

$$\sum_a \nabla_a \left(\frac{r_a}{r^3} \right) = 4\pi \delta(\vec{r})$$

The *Kronecker function* is defined as

$$\delta_{ij} = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases}$$

1.1.5 Matrix algebra

We define

$$\mathbf{a}, \text{ a column matrix, } \mathbf{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix},$$

$$\mathbf{a}^T, \text{ a row matrix, } \mathbf{a}^T = (a_x, a_y, a_z), \text{ representing the vector } \vec{A},$$

$$\mathbf{C}, \text{ a square matrix representing the second-rank tensor } \overline{\overline{C}}$$

Then the scalar product of vectors can be written as

$$\mathbf{a}^T \mathbf{b} = \mathbf{b}^T \mathbf{a} = \sum_a a_a b_a = d$$

and also the matrix product

$$\mathbf{a}^T \mathbf{C} \mathbf{b} = \sum_a \sum_b a_a C_{ab} b_b = d = \mathbf{b}^T \mathbf{C}^T \mathbf{a}$$

is a scalar. The products $\mathbf{C} \mathbf{b}$ and $\mathbf{a}^T \mathbf{C}$ are vectors.

Some matrix rules for square matrices are collected in Table 1.2.

TABLE 1.2
Some matrix rules

Symbol	Meaning	Property
$\mathbf{A} = \mathbf{B}$	matrix equality	$A_{ij} = B_{ij}$
$\mathbf{A} + \mathbf{B} = \mathbf{C}$	matrix addition	$C_{ij} = A_{ij} + B_{ij}$
$c\mathbf{A} = \mathbf{B}$	multiplication of $\mathbf{A}$ by scalar	$B_{ij} = cA_{ij}$
$\mathbf{AB} = \mathbf{C}$	matrix multiplication	$C_{ij} = \sum_{k=1}^n A_{ik} B_{kj}$
$ \mathbf{A} $	the determinant of the matrix	
$\mathbf{1}, \mathbf{I}$	the <i>unit</i> matrix	$I_{ij} = \delta_{ij}$
$\mathbf{D}$	the <i>diagonal</i> matrix	$D_{ij} = d_i \delta_{ij}$
$\mathbf{A}^{-1}$	the <i>inverse</i> of $\mathbf{A}$	$\mathbf{A}^{-1} \mathbf{A} = \mathbf{A} \mathbf{A}^{-1} = \mathbf{1}$
$\mathbf{B} = \mathbf{A}^*$	the <i>complex conjugate</i> of $\mathbf{A}$	$B_{ij} = A_{ij}^*$
$\mathbf{B} = \mathbf{A}^T$	the <i>transpose</i> of $\mathbf{A}$	$B_{ij} = A_{ji}$
	— <i>symmetric</i> if $\mathbf{A} = \mathbf{A}^T$	
	— <i>antisymmetric</i> if $\mathbf{A} = -\mathbf{A}^T$	
	— <i>orthogonal</i> if $\mathbf{A}^T = \mathbf{A}^{-1}$	
$\mathbf{B} = \mathbf{A}^+$	the <i>Hermitian adjoint</i> of $\mathbf{A}$	$B_{ij} = A_{ji}^*$
	— <i>Hermitian</i> if $\mathbf{A} = \mathbf{A}^+$	
	— <i>unitary</i> if $\mathbf{A}^{-1} = \mathbf{A}^+$	
$(\mathbf{AB})^* = \mathbf{A}^* \mathbf{B}^*$	complex conjugate of product	
$(\mathbf{AB})^T = \mathbf{B}^T \mathbf{A}^T$	transpose of product	
$(\mathbf{AB})^+ = \mathbf{B}^+ \mathbf{A}^+$	Hermitian adjoint of product	
$(\mathbf{AB})^{-1} = \mathbf{B}^{-1} \mathbf{A}^{-1}$	inverse of product	
$\mathbf{B} = \mathbf{U}^{-1} \mathbf{A} \mathbf{U}$	a similarity transformation	
	— <i>orthogonal</i> if $\mathbf{U}^{-1} = \mathbf{U}^T$	
	— <i>unitary</i> if $\mathbf{U}^{-1} = \mathbf{U}^+$	

1.2 PRINCIPLES OF QUANTUM MECHANICS

A microparticle is defined as a physical object whose wave properties can be registered. This class includes elementary particles, atomic nuclei, atoms (atomic ions), molecules (molecular ions) and more complex assemblies (like clusters and macromolecules). Some properties of microparticles belong to the universal physical constants (energy, mass, linear momentum, angular momentum, electric charge, magnetic moment); some, on the contrary, are exclusively specific for microparticles (spin, parity, life-time). Macroscopic state properties (such as temperature, pressure, volume, entropy, etc.) are irrelevant for a single microparticle.

For purposes of molecular magnetism two properties of microparticles are of key importance:

- (1) the energy of the bound states of molecules adopts only discrete values;
- (2) the angular momentum vector (orbital, spin, total) and its projection are quantised.

Thus a successful theory starts with the determination of the microscopic properties which are subsequently treated by statistical thermodynamics (Table 1.3).

1.2.1 Operators

The discrete character of some physical observables is introduced through operators. The operator $\hat{A}$ is a function defined on the set of functions; it is a recipe for how one set of functions, $f(x)$, is transformed to another one, $g(x)$

$$\hat{A}f(x) = g(x)$$

Some important operators can be classified according to Table 1.4.

Let us introduce, for instance, two column vectors

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Then the Pauli matrix operators acting on these vectors yield the results

$$\hat{\sigma}_x \alpha = \beta, \quad \hat{\sigma}_x \beta = \alpha$$

$$\hat{\sigma}_y \alpha = i\beta, \quad \hat{\sigma}_y \beta = -i\alpha$$

$$\hat{\sigma}_z \alpha = \alpha, \quad \hat{\sigma}_z \beta = -\beta$$

It can be easily proven that

$$\begin{aligned} \hat{\sigma}_x \hat{\sigma}_y + \hat{\sigma}_y \hat{\sigma}_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ &= \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} + \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \end{aligned}$$

TABLE 1.3

A link between microscopic and macroscopic properties

Discipline	Objects
quantum mechanics	Hamiltonian, $\hat{H}$; energy levels ε_i ; state vectors
statistical thermodynamics	partition function, Z
thermodynamics	state functions, H, S, G, F
magnetism	magnetisation, M ; magnetic susceptibility χ

TABLE 1.4
Some operators

Type	Example	Form or property	Note
multiplicative	$\hat{x}$	x	coordinate
differential	$\hat{p}_x$	$-i\hbar \frac{\partial}{\partial x}$	momentum
integral	$\hat{J}_l$	$\hat{J}_l \psi_k(1)\rangle = \int \psi_l^*(2)r_{12}^{-1}\psi_k(1)\psi_l(2)dV_2$	Coulomb
	$\hat{K}_l$	$\hat{K}_l \psi_k(1)\rangle = \int \psi_l^*(2)r_{12}^{-1}\psi_l(1)\psi_k(2)dV_2$	exchange
matrix	$\{\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z\}$	$\left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\}$	Pauli matrices
field	$\hat{A}^+$ $\hat{A}^-$	$\hat{A}^+ \psi_n\rangle = N_n^+ \psi_{n+1}\rangle$ $\hat{A}^- \psi_n\rangle = N_n^- \psi_{n-1}\rangle$	creation annihilation
combinatoric	$\hat{p}$	$\hat{p}\psi(x, y, z, t) = \pm\psi(-x, -y, -z, t)$	parity
	$\hat{T}_{ij}$	$\hat{T}_{ij}\psi(1, \dots, i, \dots, j, \dots, n) = \pm\psi(1, \dots, j, \dots, i, \dots, n)$	transposition

The operators possess a number of properties of which the following will be mentioned.

1. The operators, in general, do not commute. They obey these possibilities:
 - (a) non-commutation, when

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

so that the *commutator* is

$$[\hat{A}, \hat{B}] \equiv [\hat{A}, \hat{B}]_- \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$$

- (b) commutation, when

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

- (c) anticommutation, when

$$\hat{A}\hat{B} = -\hat{B}\hat{A}$$

or the *anticommutator* is

$$[\hat{A}, \hat{B}]_+ \equiv \hat{A}\hat{B} + \hat{B}\hat{A} = 0$$

2. By the *linear operator* we imply

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x)$$

where c_1 and c_2 are arbitrary (complex) numbers.

3. A *Hermitian* (or self-adjoint) *operator* fulfils

$$\int f^*(x)[\hat{A}g(x)]dx = \int g(x)[\hat{A}f(x)]^*dx$$

or more transparently

$$\langle f | \hat{A} | g \rangle = \langle g | \hat{A} | f \rangle^*$$

where $f(x)$ and $g(x)$ are arbitrary functions; an asterisk indicates the complex conjugate.

4. The most important case of a linear Hermitian operator is given by the *eigenvalue equation*

$$\hat{A}f(x) = a_n f(x)$$

The scalar a_n is termed the eigenvalue and the function $f(x)$ the eigenfunction of the given operator. There may be more than one eigenvalue and corresponding eigenfunction satisfying the eigenvalue equation for a given operator.

5. For the Hermitian operators it holds true that
- (a) their eigenvalues are real numbers;
 - (b) their eigenfunctions are mutually orthogonal, i.e.

$$\int f_n^*(x) f_m(x) dx = \langle f_n | f_m \rangle = \delta_{nm}$$

- (c) their eigenfunctions form a complete orthonormal set of functions;
 - (d) the degenerate eigenvalues ($a_n = a_m$) have associated different eigenfunctions $f_n(x) \neq f_m(x)$ which are not necessarily orthogonal; however, they can be orthogonalised.
6. The commuting operators $[\hat{A}, \hat{B}] = 0$ have a common set of eigenfunctions, so that

$$\hat{A}f_n(x) = a_n f_n(x)$$

$$\hat{B}f_n(x) = b_n f_n(x)$$

This is strictly valid only if the functions belong to different degrees of freedom.

7. The *Poisson bracket* $\{A, B\}$ in classical mechanics is given by the expression

$$\{A, B\} = \sum_{i=1}^{3n} \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right)$$

where A and B are two measurable quantities; p_i and q_i represent components of the momentum and position vectors, respectively. According to the *Dirac fundamental postulate* of quantum mechanics the relationship between the Poisson bracket and the commutator is

$$[\hat{A}, \hat{B}] = i\hbar\{A, B\}$$

Consequently we get the commutation relationships between canonical variables

$$[\hat{p}_i, \hat{p}_j] = 0$$

$$[\hat{q}_i, \hat{q}_j] = 0$$

$$[\hat{q}_i, \hat{p}_j] = i\hbar\delta_{ij}$$

This means that the measurement of a coordinate component (say q_x) does not interfere with the measurement of another component of momentum (say p_y); when p_i and q_i refer to the same degree of freedom, the measurements do interfere.

When, for several good reasons, the operator of the position is fixed simply as

$$\hat{q}_i \rightarrow q_i$$

then the operator of the momentum, which satisfies the above commutation relationships, becomes

$$\hat{p}_i \rightarrow -i\hbar \frac{\partial}{\partial q_i}$$

1.2.2 State vectors

Within the Dirac nomenclature of quantum mechanics the state vector is called *ket* and denoted as $|\psi\rangle$. Such a ket is analogous to a wave function but it need not be specified in an explicit form. The ket may often be represented as a column vector ($n \times 1$ matrix). Then the adjoint matrix—a row vector—represents the *bra* vector denoted as $\langle\psi|$, i.e.

$$|\psi\rangle^* = \langle\psi|$$

The bra and the ket define a scalar $\langle\psi_1|\psi_2\rangle$; this is analogous to the scalar product of ordinary vectors, to the matrix product of row and column matrices, or to the scalar product of two functions defined through the integral

$$\langle\psi_1|\psi_2\rangle = \int \psi_1^* \psi_2 dV$$

For a state vector one can define the length; the square of the length is

$$S = \langle \psi | \psi \rangle$$

which can be renormalised to unity. However, any ket may be multiplied by a phase factor $\exp(ik)$ without changing the direction or length of the state vector

$$S = \langle \psi | [\exp(ik)]^* \exp(ik) | \psi \rangle = \langle \psi | \psi \rangle$$

Thus the length and the phase of a ket are not physically meaningful.

Since the operators corresponding to all the components of the positions of the particles in the system commute, the coordinates form a complete set of commuting observables. Consequently any ket $|\psi\rangle$ can be expanded in terms of eigenkets of the complete set, i.e.

$$|\psi\rangle = \sum_i c_i |\chi_i\rangle$$

where $|\chi_i\rangle$ is the eigenket of all the commuting observables q_i simultaneously.

According to the first postulate of quantum mechanics the state of a system is completely described by the state vector $|\psi\rangle$ which, in the Schrödinger representation, is only a function of the coordinates and, eventually, time

$$|\psi\rangle = \psi(q_1, \dots, q_{3n}, \xi_1, \dots, \xi_n, t)$$

In addition to the spatial coordinates q_i in three Cartesian directions, also formal spin coordinates (variables) ξ_i have been introduced.

The time-independent states are characterised by the stationary state vector which is free of the time variable. The state vector can be represented by the (wave) function of the complex argument belonging to a Hilbert space. The wave function should be:

- (a) unique;
- (b) continuous;
- (c) finite;
- (d) square-integrable.

An arbitrary function $F(x)$ is square-integrable when the following integral exists

$$S = \int F^*(x) F(x) dV$$

A renormalisation can be performed as

$$F_n(x) = NF(x)$$

with

$$\int F_n^*(x)F_n(x)dV = N^2S = 1$$

so that the normalisation factor becomes

$$N = S^{-1/2}$$

A square-integrable function $F(x)$ can be expressed in the form of a linear combination of terms $f_n(x)$ forming a complete set of functions

$$F(x) = \sum_n c_n f_n(x)$$

The state vectors form a complete set of functions. They obey a *superposition principle*: when $|\psi_1\rangle$ and $|\psi_2\rangle$ are two possible kets of the system, then also the function

$$|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$$

is the possible ket of the system.

1.2.3 Schrödinger equation

The state vector is not physically observable. However, it bears all the information about the system. Such information is withdrawn through the eigenvalue equation. A good question is how the state vectors can be obtained.

Quantum mechanics postulates that to every observable property of a system there corresponds a linear Hermitian operator. Mechanical operators having a classical analogue can be constructed when the operator forms for coordinates and momenta are known.

The operator of key interest is the total energy operator—the *Hamiltonian* $\hat{H}$. It consists of the kinetic energy part $\hat{T}$ and the potential energy part $\hat{V}$

$$\hat{H} = \hat{T} + \hat{V}$$

The mechanical kinetic energy is expressed through the momenta of individual particles as follows

$$\hat{T} = \sum_i \hat{T}_i = \sum_i \frac{1}{2m_i} (\hat{p}_{i,x}^2 + \hat{p}_{i,y}^2 + \hat{p}_{i,z}^2)$$

and, after substitution for the momentum operators, one gets

$$\hat{T} = - \sum_i \frac{\hbar^2}{2m_i} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2$$

When the potential energy is given by electrostatic pair interactions (as in atoms and molecules) then

$$\hat{V} = \sum_i \sum_{j<i} \hat{V}_{ij} = \frac{e^2}{4\pi\epsilon_0} \sum_i \sum_{j<i} \frac{Z_i Z_j}{r_{ij}}$$

where the charges, in units of the elementary charge, are denoted by Z_i . Thus for a molecule the Hamiltonian takes the form of

$$\begin{aligned} \hat{H} = & - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_A \sum_i \frac{Z_A}{r_{Ai}} + \frac{e^2}{4\pi\epsilon_0} \sum_i \sum_{j<i} \frac{1}{r_{ij}} \\ & + \frac{e^2}{4\pi\epsilon_0} \sum_A \sum_{B<A} \frac{Z_A Z_B}{r_{AB}} \end{aligned}$$

Here the indices A and B run over atomic nuclei and those of i and j over electrons.

There are two fundamental kinds of operator equations.

1. In one case $|\psi\rangle$ is a pure eigenfunction of the operator $\hat{A}$; the result of the observations will always yield the same result, that is

$$\hat{A}|\psi\rangle = a|\psi\rangle$$

2. In the case when $|\psi\rangle$ is not an eigenket of the operator $\hat{A}$ a large number of measurements of the quantity $\hat{A}$ in the state $|\psi\rangle$ will give rise to a variety of different results. Although one cannot predict the results of any particular measurement, the average value of $\hat{A}$ in the state $|\psi\rangle$ is

$$\langle A \rangle = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle}$$

When $|\psi\rangle$ is normalised to unity, the denominator can be left out. However, not any value of $\hat{A}$ can be observed; the possible values for $\hat{A}$ may be discrete and limited.

The time evolution of a state is given by the *time-dependent Schrödinger equation*

$$\hat{H}(t)|\psi\rangle = i\hbar \frac{\partial}{\partial t} |\psi\rangle$$

When the Hamiltonian does not depend upon time, the *stationary Schrödinger equation* becomes

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

where E stands for the stationary energy value. This equation plays a key role in quantum mechanics since it serves as a basis for the determination of the state vectors and energy values of the system.

1.2.4 Antisymmetry

The state vector describing the system of identical particles is:

- (a) antisymmetric for particles of half-integral spin (like an electron);
- (b) symmetric for particles of integral spin.

Thus the transposition $\hat{T}_{ij}$ which interchanges the coordinates $(i) \equiv (\vec{r}_i, \xi_i)$ and $(j) \equiv (\vec{r}_j, \xi_j)$ of electrons yields the result

$$\hat{T}_{ij}|\psi(1, \dots, i, \dots, j, \dots, n)\rangle = -|\psi(1, \dots, j, \dots, i, \dots, n)\rangle$$

The many-particle state vector used to be constructed from simpler units—the electronic and nuclear wave functions—and the many-electron wave function consists of the one-electron wave functions, the *spinorbitals* $|\varphi_i\rangle$. The general expression for the many-electron wave function in terms of the products of spinorbitals is

$$|\psi'(1, 2, \dots, n)\rangle = |\varphi_1(1)\rangle|\varphi_2(2)\rangle \dots |\varphi_n(n)\rangle = |\varphi_1(1)\varphi_2(2) \dots \varphi_n(n)\rangle$$

Here the notation $|\varphi_i(k)\rangle$ means that the i th spinorbital, which is a function of the spatial coordinates and a spin variable, is occupied by the k th electron. The above expression, however, should accommodate for:

- (a) indistinguishability of electrons, which means that all permutations of electrons within the given set of occupied spinorbitals are possible;
- (b) the antisymmetry requirement, which determines the sign of the product functions;
- (c) normalisation to unity.

These requirements are achieved by the form

$$|\psi\rangle = \frac{1}{\sqrt{n!}} \sum_{\alpha} (-1)^{p(\alpha)} \hat{P}_{\alpha} |\varphi_1(1)\varphi_2(2) \dots \varphi_n(n)\rangle = \hat{A}_n |\varphi_1(1)\varphi_2(2) \dots \varphi_n(n)\rangle$$

where the sum extends over all the possible distinct permutations of the electrons, $\hat{P}_{\alpha}$ is a permutation operator expressed as a product of several transposition operators, and $p(\alpha)$ is the parity of the permutation (the number of elementary transpositions). This form is equivalent to the *Slater determinant*

$$|\psi\rangle = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(n) & \varphi_2(n) & \dots & \varphi_n(n) \end{vmatrix}$$

For a two-electron system one can write

$$|\psi\rangle = \frac{1}{\sqrt{2}} [\varphi_1(1)\varphi_2(2) - \varphi_1(2)\varphi_2(1)]$$

and when each spinorbital is written as a product of the spatial part, the orbital ϕ_i and the spin part η_i , we have

$$|\psi\rangle = \frac{1}{\sqrt{2}} [\phi_1(1)\eta_1(1)\phi_2(2)\eta_2(2) - \phi_1(2)\eta_1(2)\phi_2(1)\eta_2(1)]$$

The spin part, however, can adopt only two forms, denoted as

$$\eta_i(k) = \begin{cases} \alpha(k), & \text{for } s_z = +1/2 \\ \beta(k), & \text{for } s_z = -1/2 \end{cases}$$

Then, for a two-electron system, four different antisymmetric functions are possible

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)]\alpha(1)\alpha(2)$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2)\alpha(1)\beta(2) - \phi_1(2)\phi_2(1)\beta(1)\alpha(2)]$$

$$|\psi_3\rangle = \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2)\beta(1)\alpha(2) - \phi_1(2)\phi_2(1)\alpha(1)\beta(2)]$$

$$|\psi_4\rangle = \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)]\beta(1)\beta(2)$$

The true state vectors (denoted as $|S, M_S\rangle$), which are the eigenfunctions of the spin operators $\hat{S}^2$ and $\hat{S}_z$, are given by the linear combinations

$$|1, 1\rangle = |\psi_1\rangle = \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)]\alpha(1)\alpha(2)$$

$$\begin{aligned} |1, 0\rangle &= \frac{1}{\sqrt{2}}[|\psi_2\rangle + |\psi_3\rangle] \\ &= \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)][\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{aligned}$$

$$|1, -1\rangle = |\psi_4\rangle = \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)]\beta(1)\beta(2)$$

$$\begin{aligned} |0, 0\rangle &= \frac{1}{\sqrt{2}}[|\psi_2\rangle - |\psi_3\rangle] \\ &= \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \end{aligned}$$

All these functions are antisymmetric: the first three functions have an antisymmetric spatial part and a symmetric spin part; the last function has a symmetric spatial part and an antisymmetric spin part.

A consequence of the antisymmetry property of the determinantal wave functions is that the matrix elements can be evaluated according to the *Slater rules*. Before the application of the Slater rules the determinantal functions should be ordered in such a way that maximum coincidence among the positions of the spinorbitals is secured. Notice that each transposition in the position of spinorbitals alters the sign of the determinantal function.

Then the matrix elements of the one-electron and two-electron operators are easily evaluated (Table 1.5). The final expressions are given among the spinorbitals; a subsequent restriction results from integration over the spin functions, hence

$$\langle \varphi_i | \hat{h}_1 | \varphi_k \rangle = \langle \phi_i | \hat{h}_1 | \phi_k \rangle \delta_{\eta(i), \eta(k)}$$

$$\langle \varphi_i \varphi_j | \hat{g}_{12} | \varphi_k \varphi_l \rangle = \langle \phi_i \phi_j | \hat{g}_{12} | \phi_k \phi_l \rangle \delta_{\eta(i), \eta(k)} \delta_{\eta(j), \eta(l)}$$

1.2.5 Hierarchised approximation scheme

The construction of a Hamiltonian is normally an easy problem. The solution of the Schrödinger equation, on the contrary, represents a serious problem. It can be solved exactly for several model cases: a particle in a box (one-, two- or three-dimensional), harmonic oscillator, rigid rotor, a particle passing through a potential barrier, hydrogen atom, etc. In most applications only an approximate solution of the Schrödinger equation is attainable.

TABLE 1.5
Slater rules for the matrix elements of operators

	One-electron term	Two-electron term
Determinantal functions	$\left\langle \Phi_u \left \sum_i \hat{h}_1(i) \right \Phi_v \right\rangle$	$\left\langle \Phi_u \left \sum_i \sum_{j < i} \hat{g}_{12}(i, j) \right \Phi_v \right\rangle$
1. Determinants are equivalent		
$ \Phi_u\rangle = \varphi_1 \varphi_2 \dots \varphi_n $	$\sum_i \langle i \hat{h}_1 i \rangle$	$\sum_i \sum_{j < i} (\langle ij \hat{g}_{12} ij \rangle - \langle ij \hat{g}_{12} ji \rangle)$
$ \Phi_v\rangle = \varphi_1 \varphi_2 \dots \varphi_n $		
2. Determinants differ in one spinorbital		
$ \Phi_u\rangle = \varphi_1 \varphi_2 \dots \varphi_k \dots \varphi_n $	$\langle k \hat{h}_1 k' \rangle$	$\sum_i ((ik \hat{g}_{12} ik') - \langle ij \hat{g}_{12} k' i \rangle)$
$ \Phi_v\rangle = \varphi_1 \varphi_2 \dots \varphi'_k \dots \varphi_n $		
3. Determinants differ in two spinorbitals		
$ \Phi_u\rangle = \varphi_1 \varphi_2 \dots \varphi_k \dots \varphi_j \dots \varphi_n $	zero	$\langle kj \hat{g}_{12} k' j' \rangle - \langle kj \hat{g}_{12} j' k' \rangle$
$ \Phi_v\rangle = \varphi_1 \varphi_2 \dots \varphi'_k \dots \varphi'_j \dots \varphi_n $		
4. Determinants differ in three and more spinorbitals	zero	zero

The solution of the Schrödinger equation for a molecule follows a certain approximation scheme. It is assumed that (Table 1.6):

- (1) nuclear coordinates are separated from electronic ones (Born–Oppenheimer approximation);
- (2) the many-electron wave function is decomposed into one-electron spinorbitals (one-electron approximation);
- (3) molecular orbitals are expressed in terms of a linear combination of atomic orbitals (LCAO approximation).

A typical contemporary *ab initio* calculation is performed as follows.

1. For a given molecular structure characterised by initial nuclear coordinates the basis set functions are attributed to each atom. These simulate the behaviour of atomic orbitals and are given in terms of a (fixed) linear combination of the primitive (usually Gaussian type) functions ϑ_p as follows

$$\chi_i = \sum_p a_{ip} \vartheta_p$$

The combination (contraction) coefficients a_{ip} and the characteristics of primitive functions (exponents) were obtained from atomic calculations. Some more (diffuse, polarisation, bond) functions are added in order to better modulate the molecular space.

2. The molecular orbitals in the LCAO form

$$\phi_i = \sum_{\mu} c_{i\mu} \chi_{\mu}$$

are evaluated, so that the coefficients of the expansion are determined. For a specified molecular charge and spin multiplicity (number of α and β electrons) the Roothaan equations (Hartree–Fock equations in the LCAO approximation) are solved.

3. The one-electron approximation is improved via the configuration interaction (CI) where either the expansion coefficients C_{iu} are determined

$$\Psi_i^{\text{el}} = \sum_u C_{iu} \Phi_u$$

or, alternatively, the molecular energy is improved by direct evaluation of the correlation energy.

4. The molecular energy at the fixed geometry represents a point of the adiabatic potential (AP), E_i^{AP} . An optimum molecular structure is received after geometry optimisation (a systematic search for the AP minimum). In the minimum the gradient of the AP vanishes, and the

TABLE 1.6
Basic approximations in treating a chemical object

Feature	Nonadiabatic	Born–Oppenheimer	One-electron
wave function	molecular $\Psi_v = \sum_i f_{vi}^{\text{nuc}} \Psi_i^{\text{el}}$	electronic $\Psi_i^{\text{el}} = \sum_u C_{iu} \Phi_u$	determinantal $\Phi_u = \hat{A}_n \prod_k \varphi_k(k)$
energy operator	nonrelativistic Hamiltonian, $\hat{H}^{\text{mol}}$	electronic Hamiltonian, $\hat{H}^{\text{el}}$	Fock operator, $\hat{F}$
characteristic equation	molecular Schrödinger	electronic Schrödinger	Hartree–Fock equations
energy eigenvalues	molecular states	electronic energy, adiabatic potential	orbital energies
calculation method	off-diagonal corrections	configuration interaction	self-consistent field
physical model	moving nuclei	frozen nuclei	effective field of electrons

second derivatives with respect to nuclear displacements (the force constants forming a Hessian matrix) are all positive. The nuclear motions (molecular vibrations) are included by solving the Schrödinger equation of the form

$$(\hat{T}_{\text{nuc}} + E_i^{\text{AP}})f_{vi} = \varepsilon_{vi}f_{vi}$$

where the vibration energy ε_{vi} and the nuclear vibration functions f_{vi} appear.

For many applications the full molecular Hamiltonian is not necessary; it is sufficient to include only relevant energy terms into the model Hamiltonian. One of the model Hamiltonians is the *spin Hamiltonian* which includes only the angular momentum operators in their mutual interaction (orbit–orbit, spin–orbit, spin–spin interactions) as well as their interaction with a magnetic field (the Zeeman terms: orbit–magnetic field and spin–magnetic field).

1.3 APPROXIMATE METHODS OF QUANTUM MECHANICS

1.3.1 Linear variation method

We are looking for the solution of the Schrödinger equation

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

by considering the state vector expanded in the form of a restricted linear combination of the (known) basis set functions

$$|\psi\rangle \approx |\Phi\rangle = \sum_{i=1}^n c_i |\phi_i\rangle$$

The mean energy value is given by the relationship

$$\langle E \rangle = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

which, after expansion, gives the expression

$$\langle E \rangle = \frac{\sum_i \sum_j c_i^* c_j \langle \phi_i | \hat{H} | \phi_j \rangle}{\sum_i \sum_j c_i^* c_j \langle \phi_i | \phi_j \rangle} = \frac{\mathbf{c}^+ \mathbf{H} \mathbf{c}}{\mathbf{c}^+ \mathbf{S} \mathbf{c}}$$

Here we introduced a column vector $\mathbf{c}$ of the expansion coefficients c_i ; then $\mathbf{c}^+$ is the row vector of the coefficients c_i^* ; $\mathbf{H}$ is a Hamiltonian matrix with elements

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$$

and $\mathbf{S}$ is an overlap matrix with elements

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

The variational principle states that the mean energy value will be an upper estimate of the lowest eigenvalue E_0 of the Hamiltonian; hence

$$\langle E \rangle = f(c_1, c_2, \dots, c_n) \geq E_0$$

The problem can be formulated as an evaluation of the coefficients c_i which minimise the mean energy value $\langle E \rangle$. The above energy function should be minimised at the boundary condition

$$\langle \Phi | \Phi \rangle = 1$$

In such a case the method of Lagrangian multipliers is feasible: such a Lagrangian multiplier ε is chosen so that the functional

$$F(c_1, c_2, \dots, c_n) = \langle \Phi | \hat{H} | \Phi \rangle - \varepsilon \langle \Phi | \Phi \rangle = \sum_i \sum_j (H_{ij} - \varepsilon S_{ij}) c_i^* c_j$$

adopts a minimum value. The conditions for the minimum are

$$\frac{\partial F}{\partial c_i^*} = 0$$

which yield a homogeneous system of linear equations for the coefficients c_j

$$\sum_i \sum_j (H_{ij} - \varepsilon S_{ij}) c_j = 0, \quad \text{for } i = 1, 2, \dots, n$$

This can be rewritten into a matrix form

$$(\mathbf{H} - \varepsilon \mathbf{S})\mathbf{c} = \mathbf{0}$$

This equation has non-trivial solutions only for the vanishing determinant

$$\det(\mathbf{H} - \varepsilon \mathbf{S}) = 0$$

which is known as a *secular equation*. The second condition for the minimum of the functional

$$\frac{\partial F}{\partial c_i} = 0$$

yields exactly the same secular equation. This can be used for evaluation of the (unknown) Lagrangian multiplier as follows. By multiplying the above equation from the left by the vector $\mathbf{c}^+$ we get

$$\mathbf{c}^+(\mathbf{H} - \varepsilon \mathbf{S})\mathbf{c} = 0$$

which can be rearranged as

$$\mathbf{c}^+\mathbf{H}\mathbf{c} = \varepsilon \mathbf{c}^+\mathbf{S}\mathbf{c}$$

or

$$\varepsilon = \frac{\mathbf{c}^+\mathbf{H}\mathbf{c}}{\mathbf{c}^+\mathbf{S}\mathbf{c}}$$

so that the Lagrangian multiplier is just the mean value of the energy of the system.

After expansion of the determinant the secular equation reduces to an algebraic equation of n th order with respect to ε . It has, in general, n roots. The ground-state energy is equal to the minimum root

$$E_0 = \min\{\varepsilon_n\}$$

Extension of the basis set (by considering more than n terms) leads to a systematic shift of the eigenvalues. According to the *separation theorem* any basis set extension may lead only to lowering the energy eigenvalues

$$E_i(c_1, c_2, \dots, c_n) \geq E_i(c_1, c_2, \dots, c_n, c_{n+1}) \geq E_0$$

As far as the energy of the system is determined, it can be substituted into the equation

$$(\mathbf{H} - \varepsilon \mathbf{S})\mathbf{c} = \mathbf{0}$$

so that for each root ε_i we receive a different column vector of the coefficients $\mathbf{c}_i$.

A more general form for the expansion is

$$|\Phi_\mu\rangle = \sum_{i=1}^n c_{\mu i} |\phi_i\rangle$$

where the coefficients $c_{\mu i}$ form the matrix $\mathbf{C}$ so that

$$\Phi = \mathbf{C}\phi$$

Then the characteristic equation becomes

$$\mathbf{H}\mathbf{C}^+ = \mathbf{S}\mathbf{C}^+\mathbf{E}$$

($\mathbf{E}$ is a diagonal matrix of energy eigenvalues) and it can be solved through a diagonalisation procedure. Although the basis set functions are not orthogonal since

$$\mathbf{C}\mathbf{S}\mathbf{C}^+ = \mathbf{I}$$

they can be orthogonalised in the following way. Let us introduce the transformations

$$\mathbf{U} = \mathbf{S}^{1/2}\mathbf{C}^+$$

$$\mathbf{H}' = \mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{1/2}$$

We assume that both $\mathbf{S}^{1/2}$ and $\mathbf{S}^{-1/2}$ are Hermitian and real. Then it holds true that

$$\mathbf{U}^+\mathbf{U} = (\mathbf{C}\mathbf{S}^{1/2})(\mathbf{S}^{1/2}\mathbf{C}^+) = \mathbf{I}$$

$$\mathbf{U}^+\mathbf{H}'\mathbf{U} = (\mathbf{C}\mathbf{S}^{1/2})(\mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{1/2})(\mathbf{S}^{1/2}\mathbf{C}^+) = \mathbf{E}$$

The last equation can be interpreted that the unitary matrix $\mathbf{U}$ diagonalises the (transformed) Hamiltonian matrix $\mathbf{H}'$. For the diagonalisation of real

symmetric or complex Hermitian matrices several effective algorithms have been developed.

1.3.2 Partitioning technique

This method serves for the decomposition of a high-dimensional secular equation to the matrix equations of lower dimensions. We start from the transcription of the matrix equation

$$(\mathbf{H} - E\mathbf{I})\mathbf{c} = \mathbf{0}$$

to blocks of a lower dimension

$$\begin{pmatrix} \mathbf{H}^{AA} & \mathbf{H}^{AB} \\ \mathbf{H}^{BA} & \mathbf{H}^{BB} \end{pmatrix} \begin{pmatrix} \mathbf{c}^A \\ \mathbf{c}^B \end{pmatrix} = E \begin{pmatrix} \mathbf{c}^A \\ \mathbf{c}^B \end{pmatrix}$$

which is equivalent to a couple of matrix equations

$$\mathbf{H}^{AA}\mathbf{c}^A + \mathbf{H}^{AB}\mathbf{c}^B = E\mathbf{c}^A$$

$$\mathbf{H}^{BA}\mathbf{c}^A + \mathbf{H}^{BB}\mathbf{c}^B = E\mathbf{c}^B$$

We assume that a non-singular resolvent does exist

$$\mathbf{R} = (E\mathbf{I} - \mathbf{H}^{BB})^{-1}$$

so that the second matrix equation can be used in expressing the vector $\mathbf{c}^B$

$$\mathbf{c}^B = (E\mathbf{I} - \mathbf{H}^{BB})^{-1} \mathbf{H}^{BA} \mathbf{c}^A$$

Then we can solve the equation

$$\mathbf{H}^{\text{eff}} \mathbf{c}^A = E \mathbf{c}^A$$

with the effective Hamiltonian matrix defined as

$$\mathbf{H}^{\text{eff}} = \mathbf{H}^{AA} + \mathbf{H}^{AB}(E\mathbf{I} - \mathbf{H}^{BB})^{-1} \mathbf{H}^{BA}$$

Such a system of equations can be solved by an iterative procedure.

1.3.3 Perturbation method

The perturbation theory for stationary states is based on the following assumptions.

1. The Hamiltonian of the interest can be split into two parts:

$$\hat{H} = \hat{H}^0 + \hat{H}'$$

2. A Hermitian operator $\hat{H}^0$ comprises the dominant part of the total Hamiltonian, the solutions of which are already known, i.e.

$$\hat{H}^0 |\phi_i\rangle = E_i^0 |\phi_i\rangle$$

so that E_i^0 are the eigenvalues and $|\phi_i\rangle$ the eigenfunctions of the *unperturbed Hamiltonian* $\hat{H}^0$.

3. The operator $\hat{H}'$ —the *perturbation*—comprises the rest of the total Hamiltonian. The perturbation should be small in comparison with the eigenvalues of $\hat{H}$; this is expressed by the condition

$$\left| \langle \phi_i | \hat{H}' | \phi_j \rangle \right| \ll |E_i^0 - E_j^0|$$

4. The state vectors obey an *intermediate normalisation* condition which is

$$\langle \phi_i | \psi_n \rangle = 1$$

for the known unperturbed ket $|\phi_i\rangle$ which yields the best approximation to the perturbed function $|\psi_n\rangle$.

5. When the perturbation is switched off, the limiting conditions should be obeyed

$$\lim_{\hat{H}' \rightarrow 0} |\psi_n\rangle = |\phi_i\rangle$$

and

$$\lim_{\hat{H}' \rightarrow 0} E_n = E_i^0$$

Hereafter the subscript n will be omitted for the sake of clarity but the derived formulae will be valid for any state of the system.

First, we search for the shift of energy as an effect of the perturbation. We start from the characteristic equation in the form

$$(\hat{H}^0 + \hat{H}')|\psi\rangle = E|\psi\rangle$$

which, after multiplying from the left side by the bra $\langle\phi_i|$ and integrating, yields

$$\langle\phi_i|\hat{H}^0|\psi\rangle + \langle\phi_i|\hat{H}'|\psi\rangle = E\langle\phi_i|\psi\rangle$$

Since $\hat{H}^0$ is a Hermitian operator, it holds true that

$$\langle\phi_i|\hat{H}^0 = \langle\phi_i|E_i^0$$

Using the intermediate normalisation $\langle\phi_i|\psi_n\rangle = 1$, we arrive at the relationship of interest

$$E = E_i^0 + \langle\phi_i|\hat{H}'|\psi\rangle$$

Second, we search for the expression of the perturbed wave function. Again we start from the characteristic equation in a modified form

$$(\varepsilon - \hat{H}^0)|\psi\rangle = (\hat{H}' + \varepsilon - E)|\psi\rangle$$

where ε is an arbitrary number (a reference energy level). By introducing an inverse operator we get

$$|\psi\rangle = (\varepsilon - \hat{H}^0)^{-1}(\hat{H}' + \varepsilon - E)|\psi\rangle$$

Now we introduce a formal projection operator $\hat{P}$, as an effect of which the perturbation is switched off, i.e.

$$\hat{P}|\psi\rangle = |\phi_i\rangle$$

This equation can be transcribed as

$$|\psi\rangle = |\phi_i\rangle + (\hat{1} - \hat{P})|\psi\rangle$$

which, after combination with the above equation for $|\psi\rangle$, yields the formula of interest

$$|\psi\rangle = |\phi_i\rangle + (\hat{1} - \hat{P})(\varepsilon - \hat{H}^0)^{-1}(\hat{H}' + \varepsilon - E)|\psi\rangle$$

This equation is appropriate for an iterative solution. The final expression may be written as a series

$$|\psi\rangle = \sum_{n=1}^{\infty} \left\{ (\hat{1} - \hat{P})(\varepsilon - \hat{H}^0)^{-1}(\hat{H}' + \varepsilon - E) \right\}^n |\phi_i\rangle$$

According to the selection of the reference energy level ε two different forms of the perturbation theory are obtained:

- (1) the Brillouin–Wigner perturbation theory assumes $\varepsilon = E$;
- (2) the Rayleigh–Schrödinger perturbation theory postulates $\varepsilon = E_i^0$.

The form of the projection operator can be derived from the expansion of the perturbed state vector into a complete orthonormal basis set, say

$$|\psi\rangle = \sum_j c_j |\phi_j\rangle = |\phi_i\rangle + \sum_{j \neq i} c_j |\phi_j\rangle$$

Here the expansion coefficients satisfy

$$c_j = \langle \phi_j | \psi \rangle$$

and

$$c_i = \langle \phi_i | \psi \rangle = 1$$

Then it holds true that

$$(1 - \hat{P})|\psi\rangle = \sum_{j \neq i} c_j |\phi_j\rangle = \left\{ \sum_{j \neq i} \langle \phi_j | \phi_j \rangle \right\} |\psi\rangle$$

In order to evaluate the expansion coefficients the following procedure is applied. We start from the equation

$$(\varepsilon - \hat{H}^0)|\psi\rangle = (\hat{H}' + \varepsilon - E)|\psi\rangle$$

which, after multiplying by the bra $\langle \phi_j |$ and integrating yields

$$\varepsilon \langle \phi_j | \psi \rangle - \langle \phi_j | \hat{H}^0 | \psi \rangle = \langle \phi_j | \hat{H}' | \psi \rangle + (\varepsilon - E) \langle \phi_j | \psi \rangle$$

For further manipulation we can utilise

$$\langle \phi_i | \hat{H}^0 = \langle \phi_i | E_i^0$$

$$|\psi\rangle = |\phi_i\rangle + \sum_{k \neq i} c_k |\phi_k\rangle$$

and

$$c_k = \langle \phi_k | \psi \rangle$$

so that

$$(\varepsilon - E_i^0)c_j = \langle \phi_j | \hat{H}' | \phi_i \rangle + \sum_{k \neq i} \langle \phi_j | \hat{H}' | \phi_k \rangle c_k + (\varepsilon - E)c_j$$

which can be rearranged to the final formula

$$c_j = (\varepsilon - E_i^0)^{-1} \left\{ \langle \phi_j | \hat{H}' | \phi_i \rangle + \sum_{k \neq i} \langle \phi_j | \hat{H}' | \phi_k \rangle c_k + (\varepsilon - E)c_j \right\}$$

which is suitable for an iterative solution.

Explicit formulae for the energy and the state vector up to the second order of the Rayleigh–Schrödinger perturbation theory are presented in Table 1.7. Here the following series are assumed

TABLE 1.7
Perturbation theory formulae^a

Energy	State vector
$E^{(0)} = E^0$	$ \psi^{(0)}\rangle = \phi_i\rangle$
$E^{(1)} = H'_{ii}$	$ \psi^{(1)}\rangle = \sum_{j \neq i} \frac{H'_{ji}}{E_i^0 - E_j^0} \phi_j\rangle$
$E^{(2)} = \sum_{j \neq i} \frac{H'_{ij} H'_{ji}}{E_i^0 - E_j^0}$	$ \psi^{(2)}\rangle = \sum_{j \neq i} \sum_{k \neq i} \frac{H'_{jk} H'_{ki}}{(E_i^0 - E_j^0)(E_i^0 - E_k^0)} \phi_j\rangle - \sum_{j \neq i} \frac{H'_{ii} H'_{ji}}{(E_i^0 - E_j^0)^2} \phi_j\rangle$

^aMatrix elements of the perturbation operator are $H'_{ij} = \langle \phi_i | \hat{H}' | \phi_j \rangle$.

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

$$|\psi\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle + |\psi^{(2)}\rangle + \dots$$

Since in these formulae summation over all excited electronic states occurs, the present form of the perturbation theory used to be termed the *sum-over-states perturbation theory*.

1.3.4 Perturbation theory for degenerate states

When the energy levels are degenerate, they cannot be treated by the formulae of the Rayleigh–Schrödinger perturbation theory since the denominators $(E_i^0 - E_j^0)$ vanish. Therefore an alternative formulation is necessary which can handle degenerate states as well.

We will start from the characteristic equation

$$(\hat{H}^0 + \hat{H}')|\psi\rangle = E|\psi\rangle$$

which, after multiplying by the bra $\langle\phi_l|$ and integrating, yields

$$\langle\phi_l|\hat{H}^0|\psi\rangle + \langle\phi_l|\hat{H}'|\psi\rangle = E\langle\phi_l|\psi\rangle$$

or

$$(E_l^0 - E)\langle\phi_l|\psi\rangle + \langle\phi_l|\hat{H}'|\psi\rangle = 0$$

The state vector is expanded in the form

$$|\psi\rangle = |\phi_i\rangle + |\phi_j\rangle + \sum_{k \neq i,j} c_k |\phi_k\rangle$$

where we assume that $|\phi_i\rangle$ and $|\phi_j\rangle$ are degenerate states with $E_i^0 = E_j^0$. A combination of these equations yields the relationship

$$(E_l^0 - E)c_l + \langle\phi_l|\hat{H}'|\phi_i\rangle c_i + \langle\phi_l|\hat{H}'|\phi_j\rangle c_j = - \sum_{k \neq i,j} c_k \langle\phi_l|\hat{H}'|\phi_k\rangle$$

This equation is fulfilled for an arbitrary index l , so that for $l = i$ and $l = j$ we arrive at the system of two equations

$$(E_i^0 - E)c_i + H'_{ii}c_i + H'_{ij}c_j = - \sum_{k \neq i,j} c_k H'_{ik}$$

$$(E_j^0 - E)c_i + H'_{ji}c_i + H'_{jj}c_j = - \sum_{k \neq i,j} c_k H'_{jk}$$

Here we used a notation for the matrix elements of the perturbation operator

$$H'_{ij} = \langle \phi_i | \hat{H}' | \phi_j \rangle$$

In first-order perturbation theory (in the first iteration) the right side can be simply neglected. In other words, we search for such a combination of the degenerate state vectors which makes the perturbation diagonal. Then we can write

$$\begin{pmatrix} H'_{ii} + E_i^0 - E & H'_{ij} \\ H'_{ji} & H'_{jj} + E_j^0 - E \end{pmatrix} \begin{pmatrix} c_i \\ c_j \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

In the case of a strict degeneracy $E_i^0 = E_j^0$ we can introduce an energy shift

$$\Delta E = E - E_i^0$$

and the above equation becomes equivalent to the characteristic equation

$$(\mathbf{H}' - \mathbf{I}\Delta E)\mathbf{c} = \mathbf{0}$$

having a solution for the vanishing determinant, i.e.

$$\det(\mathbf{H}' - \mathbf{I}\Delta E) = 0$$

For a d -dimensional problem there is a number of d roots ΔE_d of the secular determinant and the energy shift owing to the perturbation becomes

$$E^{(1)} = E_i^0 + \Delta E_d$$

Since the roots are in general different, the degeneracy of energy levels is (partially) removed.

1.3.5 Ordering parameter perturbation theory

For the purposes of perturbation theory the total Hamiltonian can be split as follows

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)}$$

where λ is the ordering parameter having values $\lambda \in < 0, 1 >$. In a special case the third term can be removed. It is assumed that the solutions of the Schrödinger equations for the unperturbed Hamiltonian are known

$$\hat{H}^{(0)}|\phi_i\rangle = E_i^0|\phi_i\rangle$$

The energy and the state vector for the perturbed state are expanded as follows

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

$$|\psi\rangle = |\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \lambda^2 |\psi^{(2)}\rangle + \dots$$

By substituting these expansions into the Schrödinger equation

$$\hat{H}(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$$

one gets an equation where various orders of λ occur

$$\begin{aligned} & (\hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)}) \left[|\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \lambda^2 |\psi^{(2)}\rangle + \dots \right] \\ &= (E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots) \left[|\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \lambda^2 |\psi^{(2)}\rangle + \dots \right] \end{aligned}$$

Collecting terms of the same powers in λ leads to

$$\lambda^0 : \quad (\hat{H}^{(0)} - E^{(0)})|\psi^{(0)}\rangle = 0$$

$$\lambda^1 : \quad (\hat{H}^{(1)} - E^{(1)})|\psi^{(0)}\rangle + (\hat{H}^{(0)} - E^{(0)})|\psi^{(1)}\rangle = 0$$

$$\lambda^2 : \quad (\hat{H}^{(2)} - E^{(2)})|\psi^{(0)}\rangle + (\hat{H}^{(1)} - E^{(1)})|\psi^{(1)}\rangle + (\hat{H}^{(0)} - E^{(0)})|\psi^{(2)}\rangle = 0$$

etc. After multiplying these equations by the bra $\langle \psi^{(0)} |$ we get

$$\lambda^1 : \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(0)} \rangle - E^{(1)} \langle \psi^{(0)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | (E^{(0)} - E^{(0)}) | \psi^{(1)} \rangle = 0$$

or

$$E^{(1)} = \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(0)} \rangle$$

which is a formula identical to the energy in the first order of the Rayleigh–Schrödinger perturbation theory. Analogously,

$$\begin{aligned} \lambda^2 : \langle \psi^{(0)} | \hat{H}^{(2)} | \psi^{(0)} \rangle - E^{(2)} \langle \psi^{(0)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(1)} \rangle - E^{(1)} \langle \psi^{(0)} | \psi^{(1)} \rangle \\ + \langle \psi^{(0)} | (E^{(0)} - E^{(0)}) | \psi^{(2)} \rangle = 0 \end{aligned}$$

or

$$E^{(2)} = \langle \psi^{(0)} | \hat{H}^{(2)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(1)} \rangle$$

which is a formula analogous to the second order of the Rayleigh–Schrödinger perturbation energy, but here an additional term $\langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(1)} \rangle$ occurs.

By multiplying the equation in λ^1 by the bra $\langle \phi_j |$ one obtains

$$\lambda^1 : \langle \phi_j | \hat{H}^{(1)} | \phi_i \rangle - E^{(1)} \langle \phi_j | \phi_i \rangle + (E_j^0 - E_i^0) \langle \phi_j | \psi^{(1)} \rangle = 0$$

The expansion of the state vector $|\psi^{(1)}\rangle$ into a complete set of orthonormal unperturbed functions $|\phi_i\rangle$ is written as

$$|\psi^{(1)}\rangle = \sum_{j \neq i} c_j^{(1)} |\phi_j\rangle$$

with

$$c_j^{(1)} = \langle \phi_j | \psi^{(1)} \rangle$$

The combination of these equations yields

$$\lambda^1 : \langle \phi_j | \hat{H}^{(1)} | \phi_i \rangle + (E_j^0 - E_i^0) c_j^{(1)} = 0$$

so that the first-order perturbation coefficients are

$$c_j^{(1)} = \frac{H'_{ji}}{E_i^0 - E_j^0}$$

and

$$|\psi^{(1)}\rangle = \sum_{j \neq i} \frac{H'_{ji}}{E_i^0 - E_j^0} |\phi_j\rangle$$

Then the expression for the second-order energy is straightforward

$$\begin{aligned} E^{(2)} &= \langle \psi^{(0)} | \hat{H}^{(2)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(1)} \left[\sum_{j \neq i} c_j^{(1)} |\phi_j\rangle \right] \\ &= \langle \phi_i | \hat{H}^{(2)} | \phi_i \rangle + \langle \psi^{(0)} | \hat{H}^{(1)} \left[\sum_{j \neq i} \frac{H'_{ji}}{E_i^0 - E_j^0} |\phi_j\rangle \right] \\ &= \langle \phi_i | \hat{H}^{(2)} | \phi_i \rangle + \sum_{j \neq i} \frac{H'_{ij} H'_{ji}}{E_i^0 - E_j^0} \end{aligned}$$

This expression is similar to the second-order energy given by the Rayleigh–Schrödinger perturbation theory with addition of the first term.

1.3.6 Double perturbation theory

The ordering parameter perturbation theory can be extended to the case of more perturbations simultaneously present. The new assumption is the following form of the Hamiltonian

$$\hat{H}(\lambda, \kappa) = \hat{H}^{(0)} + \lambda \hat{H}^{(1,0)} + \lambda^2 \hat{H}^{(2,0)} + \kappa \hat{H}^{(0,1)} + \kappa \lambda \hat{H}^{(1,1)} + \kappa^2 \hat{H}^{(0,2)}$$

This has a close relationship to the evaluation of magnetic parameters; for example, λ may be a component of the magnetic field and κ may represent a component of the spin magnetic moment.

One expands the energy and the state vector as

$$E = E^{(0)} + \lambda E^{(1,0)} + \lambda^2 E^{(2,0)} + \kappa E^{(0,1)} + \kappa \lambda E^{(1,1)} + \kappa^2 E^{(0,2)} + \dots$$

$$|\psi\rangle = |\psi^{(0)}\rangle + \lambda |\psi^{(1,0)}\rangle + \lambda^2 |\psi^{(2,0)}\rangle + \kappa |\psi^{(0,1)}\rangle + \kappa \lambda |\psi^{(1,1)}\rangle + \kappa^2 |\psi^{(0,2)}\rangle + \dots$$

and, after substituting into the Schrödinger equation and collecting the terms of the same power, we get

$$\lambda^0, \kappa^0 : (\hat{H}^{(0)} - E^{(0)})|\psi^{(0)}\rangle = 0$$

$$\lambda^1, \kappa^0 : (\hat{H}^{(1,0)} - E^{(1,0)})|\psi^{(0)}\rangle + (\hat{H}^{(0)} - E^{(0)})|\psi^{(1,0)}\rangle = 0$$

$$\begin{aligned} \lambda^2, \kappa^0 : (\hat{H}^{(2,0)} - E^{(2,0)})|\psi^{(0)}\rangle + (\hat{H}^{(1,0)} - E^{(1,0)})|\psi^{(1,0)}\rangle \\ + (\hat{H}^{(0)} - E^{(0)})|\psi^{(2,0)}\rangle = 0 \end{aligned}$$

$$\lambda^0, \kappa^1 : (\hat{H}^{(0,1)} - E^{(0,1)})|\psi^{(0)}\rangle + (\hat{H}^{(0)} - E^{(0)})|\psi^{(0,1)}\rangle = 0$$

$$\begin{aligned} \lambda^0, \kappa^2 : (\hat{H}^{(0,2)} - E^{(0,2)})|\psi^{(0)}\rangle + (\hat{H}^{(0,1)} - E^{(0,1)})|\psi^{(0,1)}\rangle \\ + (\hat{H}^{(0)} - E^{(0)})|\psi^{(0,2)}\rangle = 0 \end{aligned}$$

and

$$\begin{aligned} \lambda^1, \kappa^1 : (\hat{H}^{(1,1)} - E^{(1,1)})|\psi^{(0)}\rangle + (\hat{H}^{(1,0)} - E^{(1,0)})|\psi^{(0,1)}\rangle \\ + (\hat{H}^{(0,1)} - E^{(0,1)})|\psi^{(1,0)}\rangle + (\hat{H}^{(0)} - E^{(0)})|\psi^{(1,1)}\rangle = 0 \end{aligned}$$

After elementary manipulations similar to those followed above, the energy formulae result

$$E^{(1,0)} = \langle \psi^{(0)} | \hat{H}^{(1,0)} | \psi^{(0)} \rangle$$

$$E^{(0,1)} = \langle \psi^{(0)} | \hat{H}^{(0,1)} | \psi^{(0)} \rangle$$

$$E^{(2,0)} = \langle \psi^{(0)} | \hat{H}^{(2,0)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(1,0)} | \psi^{(1,0)} \rangle$$

$$E^{(0,2)} = \langle \psi^{(0)} | \hat{H}^{(0,2)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(0,1)} | \psi^{(0,1)} \rangle$$

$$\begin{aligned} E^{(1,1)} &= \langle \psi^{(0)} | \hat{H}^{(1,1)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(1,0)} | \psi^{(0,1)} \rangle \\ &= \langle \psi^{(0)} | \hat{H}^{(1,1)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(0,1)} | \psi^{(1,0)} \rangle \end{aligned}$$

The last term is given by two equivalent expressions. The only need which survives is the expression for the first-order corrections to the state vector, which are

$$|\psi^{(1,0)}\rangle = \sum_{j \neq i} c_j^{(1,0)} |\phi_j\rangle = \sum_{j \neq i} \frac{\langle \phi_j | \hat{H}^{(1,0)} | \phi_i \rangle}{E_i^0 - E_j^0} |\phi_j\rangle$$

and

$$|\psi^{(0,1)}\rangle = \sum_{j \neq i} c_j^{(0,1)} |\phi_j\rangle = \sum_{j \neq i} \frac{\langle \phi_j | \hat{H}^{(0,1)} | \phi_i \rangle}{E_i^0 - E_j^0} |\phi_j\rangle$$

1.4 ANGULAR MOMENTUM

1.4.1 Basic properties

The angular momentum of a massive particle about the origin is introduced as the vector normal to the plane of motion

$$\vec{l} = \vec{r} \times \vec{p}$$

In a three-dimensional space (having $\vec{i}, \vec{j}, \vec{k}$ unit vectors) $\vec{l}$ can be written in the determinantal form

$$\vec{l} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

If we apply the operator expression for $\vec{p}$ in its differential form

$$\vec{p} = -i\hbar \vec{\nabla}$$

the Cartesian components of the angular momentum operator become

$$\hat{l}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{l}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{l}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Now using

$$\frac{\partial}{\partial a}\left(b\frac{\partial}{\partial c}\right) = \left(\frac{\partial b}{\partial a}\right)\frac{\partial}{\partial c} + b\frac{\partial^2}{\partial a\partial c}$$

the following commutation relations are straightforward

$$\hat{l}_x\hat{l}_y - \hat{l}_y\hat{l}_x = i\hbar\hat{l}_z$$

$$\hat{l}_y\hat{l}_z - \hat{l}_z\hat{l}_y = i\hbar\hat{l}_x$$

$$\hat{l}_z\hat{l}_x - \hat{l}_x\hat{l}_z = i\hbar\hat{l}_y$$

or, in a more compressed form

$$[\hat{l}_a, \hat{l}_b] = \hat{l}_a\hat{l}_b - \hat{l}_b\hat{l}_a = i\hbar\hat{l}_c$$

with the cyclic permutation of $a, b, c = x, y, z$; this means that the angular momentum components do not commute with each other.

1.4.2 Common set of eigenfunctions

Let the square of the angular momentum be introduced

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$$

It obeys the commutation relations

$$[\hat{l}^2, \hat{l}_a] = 0$$

for $a = x, y, z$, which implies that the operators $\hat{l}^2$ and one component $\hat{l}_a$ (only a single component, say $\hat{l}_z$) have an identical set of eigenstates $|\Psi_i\rangle$

$$\hat{l}_z |\Psi_i\rangle = \mu_i |\Psi_i\rangle$$

$$\hat{l}^2 |\Psi_i\rangle = \lambda_i |\Psi_i\rangle$$

Because the remaining components do not commute with $\hat{l}_z$, they have not the same set of eigenstates and thus they cannot be determined simultaneously. Moreover, $\hat{l}_z$ and $\hat{l}^2$ both commute with the Hamiltonian $\hat{H}$

$$[\hat{H}, \hat{l}_z] = 0$$

$$[\hat{H}, \hat{l}^2] = 0$$

so that the eigenstates $|\Psi_i\rangle$ simultaneously obey the Schrödinger equation

$$\hat{H} |\Psi_i\rangle = E_i |\Psi_i\rangle$$

Thus we can use an indexation $|\Psi_i\rangle \equiv |E, \lambda, \mu\rangle$ for a set of eigenstates which simultaneously are eigenstates of the operators $\hat{H}$, $\hat{l}^2$ and $\hat{l}_z$. This result plays a key role in the theory of the electronic structure of atoms: one can expand an arbitrary eigenfunction as a sum over eigenfunctions common for the operators $\hat{H}$, $\hat{l}^2$ and $\hat{l}_z$

$$|\Psi_i\rangle = \sum_i C_i |E, \lambda, \mu\rangle_i$$

1.4.3 Shift operators

We introduce shift operators (escalator operators), namely the step-up (raising) operator

$$\hat{l}_+ = \hat{l}_x + i\hat{l}_y$$

and its complex conjugate, the step-down (lowering) operator

$$\hat{l}_- = \hat{l}_x - i\hat{l}_y$$

The former obeys the relationship

$$[\hat{l}_z, \hat{l}_+] = \hat{l}_z(\hat{l}_x + i\hat{l}_y) - (\hat{l}_x + i\hat{l}_y)\hat{l}_z = [\hat{l}_z, \hat{l}_x] - i[\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_y - i(i\hbar\hat{l}_x) = \hbar\hat{l}_+$$

and hence

$$\begin{aligned}\hat{l}_+\hat{l}_+|E, \lambda, \mu\rangle &= \{\hat{l}_+\hat{l}_z + [\hat{l}_z, \hat{l}_+]\}|E, \lambda, \mu\rangle = \{\hat{l}_+\mu + \hbar\hat{l}_+\}|E, \lambda, \mu\rangle \\ &= (\mu + \hbar)\hat{l}_+|E, \lambda, \mu\rangle\end{aligned}$$

This means that the eigenstate common for the operators $\hat{l}^2$ and $\hat{l}_z$ is shifted into another which has the eigenvalue for $\hat{l}_z$ shifted “up” by the amount of $\hbar$ (the eigenvalue for the $\hat{l}^2$ operator remains unchanged).

Analogously,

$$[\hat{l}_z, \hat{l}_-] = -\hbar\hat{l}_-$$

and

$$\hat{l}_z\hat{l}_-|E, \lambda, \mu\rangle = (\mu - \hbar)\hat{l}_-|E, \lambda, \mu\rangle$$

1.4.4 Quantum numbers

The shift operations can be repeated n times, yielding

$$\hat{l}_z(\hat{l}_\pm)^n|E, \lambda, \mu\rangle = (\mu \pm n\hbar)(\hat{l}_\pm)^n|E, \lambda, \mu\rangle$$

Thus the eigenvalues of $\hat{l}_z$ can alter only as integer multiples of $\hbar$ so that $\mu - n\hbar, \dots, \mu - \hbar, \mu, \mu + \hbar, \dots, \mu + n\hbar$ are allowed. This series has its lowest member, $\mu_{\min}$, and the highest member, $\mu_{\max}$, restricted by the shift operators

$$\hat{l}_-|E, \lambda, \mu_{\min}\rangle = 0$$

$$\hat{l}_+|E, \lambda, \mu_{\max}\rangle = 0$$

Consequently

$$\hat{l}_+\hat{l}_-|E, \lambda, \mu_{\min}\rangle = \hat{l}_+|0\rangle = 0$$

$$\hat{l}_-\hat{l}_+|E, \lambda, \mu_{\max}\rangle = \hat{l}_-|0\rangle = 0$$

hold true. Expressing explicitly

$$\begin{aligned}\hat{l}_+\hat{l}_- &= (\hat{l}_x + i\hat{l}_y)(\hat{l}_x - i\hat{l}_y) \\ &= (\hat{l}_x^2 + \hat{l}_y^2) - i[\hat{l}_x, \hat{l}_y] = (\hat{l}^2 - \hat{l}_z^2) - i[\hat{l}_x, \hat{l}_y] = \hat{l}^2 - \hat{l}_z^2 + \hbar\hat{l}_z\end{aligned}$$

we obtain

$$\begin{aligned}\hat{l}_+\hat{l}_-|E, \lambda, \mu_{\min}\rangle &= (\hat{l}^2 - \hat{l}_z^2 + \hbar\hat{l}_z)|E, \lambda, \mu_{\min}\rangle \\ &= (\lambda - \mu_{\min}^2 + \hbar\mu_{\min})|E, \lambda, \mu_{\min}\rangle = 0\end{aligned}$$

and thus we arrive at the first condition

$$\lambda - \mu_{\min}^2 + \hbar\mu_{\min} = 0$$

Likewise, from the identity

$$\hat{l}_-\hat{l}_+ = \hat{l}^2 - \hat{l}_z^2 - \hbar\hat{l}_z$$

and

$$\begin{aligned}\hat{l}_-\hat{l}_+|E, \lambda, \mu_{\max}\rangle &= (\hat{l}^2 - \hat{l}_z^2 - \hbar\hat{l}_z)|E, \lambda, \mu_{\max}\rangle \\ &= (\lambda - \mu_{\max}^2 - \hbar\mu_{\max})|E, \lambda, \mu_{\max}\rangle = 0\end{aligned}$$

we get the second condition

$$\lambda - \mu_{\max}^2 - \hbar\mu_{\max} = 0$$

These restrictions can be combined

$$\lambda = \mu_{\max}^2 + \hbar\mu_{\max} = \mu_{\min}^2 - \hbar\mu_{\min} \pm \mu_{\min} \pm \mu_{\max}$$

to yield

$$(\mu_{\max} + \mu_{\min})(\mu_{\max} - \mu_{\min} - \hbar) = 0$$

which implies

$$\mu_{\min} = -\mu_{\max}$$

since $\mu_{\min} \leq \mu_{\max}$. Now let the quantum number be introduced

$$l = 0, 1/2, 1, 3/2, 2, \dots$$

Hence

$$\mu_{\max} = l\hbar$$

$$\mu_{\min} = -l\hbar$$

and

$$\lambda = \mu_{\max}(\mu_{\max} + 1)\hbar = \mu_{\min}(\mu_{\min} - 1)\hbar = l(l + 1)\hbar^2$$

Finally we arrive at the eigenvalue equations

$$\hat{l}_z|E, \lambda, \mu\rangle = m\hbar|E, \lambda, \mu\rangle$$

$$\hat{l}^2|E, \lambda, \mu\rangle = l(l + 1)\hbar^2|E, \lambda, \mu\rangle$$

where

$$m = -l, -l + 1, \dots, +l$$

takes values in steps of unity. The eigenstates can be indexed by their quantum numbers, i.e. $|l, m\rangle$. The interpretation of the properties of the (microscopic) angular momentum in quantum mechanics is as follows: the angular momentum vector can adopt only certain, quantised values and its orientation again is limited to only certain positions, namely those having quantised projections of $\hat{l}_z$.

1.4.5 Eigenvalues of $\hat{l}_x$ and $\hat{l}_y$

The derivation of the eigenequations for $\hat{l}_x$ and $\hat{l}_y$ operators needs some more elaboration. First we have

$$\begin{aligned}\hat{l}_+\hat{l}_-|l, m\rangle &= (\hat{l}^2 - \hat{l}_z^2 + \hbar\hat{l}_z)|l, m\rangle = [l(l + 1) - m^2 + m]\hbar^2|l, m\rangle \\ &= [(l - m + 1)(l + m)]\hbar^2|l, m\rangle\end{aligned}$$

and hence

$$\hat{l}_-|l, m\rangle = [(l - m + 1)(l + m)]^{1/2}\hbar|l, m - 1\rangle$$

Analogously we have

$$\hat{l}_-\hat{l}_+|l, m\rangle = (\hat{l}^2 - \hat{l}_z^2 - \hbar\hat{l}_z)|l, m\rangle = [(l - m)(l + m + 1)]\hbar^2|l, m\rangle$$

and

$$\hat{l}_+|l, m\rangle = [(l-m)(l+m+1)]^{1/2}\hbar|l, m+1\rangle$$

The back transformations of the shift operators are

$$\hat{l}_x = \frac{1}{2}(\hat{l}_+ + \hat{l}_-)$$

$$\hat{l}_y = \frac{1}{2i}(\hat{l}_+ - \hat{l}_-)$$

and then we obtain

$$\begin{aligned}\hat{l}_x|l, m\rangle &= \frac{1}{2}[(l-m)(l+m+1)]^{1/2}\hbar|l, m+1\rangle \\ &\quad + \frac{1}{2}[(l-m+1)(l+m)]^{1/2}\hbar|l, m-1\rangle\end{aligned}$$

$$\begin{aligned}\hat{l}_y|l, m\rangle &= \frac{1}{2i}[(l-m)(l+m+1)]^{1/2}\hbar|l, m+1\rangle \\ &\quad - \frac{1}{2i}[(l-m+1)(l+m)]^{1/2}\hbar|l, m-1\rangle\end{aligned}$$

This result is nothing else but the statement quoted above: the eigenfunctions of $\hat{l}_x$ and $\hat{l}_y$ operators are expanded as a sum over eigenfunctions common for the operators $\hat{H}$, $\hat{l}^2$ and $\hat{l}_z$, i.e. $|l, m\rangle$.

1.4.6 Spherical harmonics

In atoms the Coulomb forces refer to a centre and thus we speak about the central field. In this important case the introduction of *polar coordinates* (r, ϑ, φ) is helpful. They are related to Cartesian coordinates through formulae

$$x = u \cos \varphi = r \sin \vartheta \cos \varphi$$

$$y = u \sin \varphi = r \sin \vartheta \sin \varphi$$

$$z = u \cos \vartheta$$

with $0 < r$; $0 \leq \vartheta \leq \pi$; $0 \leq \varphi \leq 2\pi$. The volume element is

$$dV = dx dy dz = r^2 \sin \vartheta dr d\vartheta d\varphi$$

In these coordinates the angular momentum operators adopt the forms

$$\hat{l}_x = i\hbar \left(\sin \vartheta \frac{\partial}{\partial \vartheta} + \cot \vartheta \sin \varphi \frac{\partial}{\partial \varphi} \right)$$

$$\hat{l}_y = i\hbar \left(-\cos \varphi \frac{\partial}{\partial \vartheta} + \cot \vartheta \sin \varphi \frac{\partial}{\partial \varphi} \right)$$

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

and

$$\hat{l}^2 = -\hbar^2 \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) - \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right] = -\hbar^2 \nabla^2(\vartheta, \varphi)$$

Making use of

$$\sin \varphi \pm i \cos \varphi = e^{\pm i\varphi}$$

the shift operators become

$$\hat{l}_+ = \hbar e^{i\varphi} \left(\frac{\partial}{\partial \vartheta} + i \cot \vartheta \frac{\partial}{\partial \varphi} \right)$$

$$\hat{l}_- = \hbar e^{-i\varphi} \left(-\frac{\partial}{\partial \vartheta} + i \cot \vartheta \frac{\partial}{\partial \varphi} \right)$$

The characteristic equation for $\hat{l}_z$ represents a simple differential equation

$$-i\hbar \frac{\partial}{\partial \varphi} |l, m\rangle = m\hbar |l, m\rangle$$

having solutions in the form of

$$|l, m\rangle = \Theta N_m e^{im\varphi} = \Theta \Phi_m(\varphi)$$

where Θ is not a function of the polar angle φ . The normalisation constant N_m is readily determined from the condition

$$\langle \Phi_m | \Phi_m \rangle = N_m^2 \int_0^{2\pi} e^{-im\varphi} e^{+im\varphi} d\varphi = N_m^2 (2\pi) = 1$$

so that

$$N_m = 1/\sqrt{2\pi}$$

and

$$\Phi_m(\varphi) = (1/\sqrt{2\pi})e^{im\varphi}$$

At this stage we must apply a constraint which secures that the wave function $|l, m\rangle$ is a single-valued function of position. Rotation by an angle α , $\hat{R}(\alpha)$, gives

$$\hat{R}(\alpha)|l, m\rangle = e^{-i\alpha m}|l, m\rangle$$

In particular

$$\hat{R}(2\pi)|l, m\rangle = e^{-i2\pi m}|l, m\rangle$$

and for a rotation by $\varphi = 2\pi$ about the z -axis we have the wave function unchanged only if m is an integer. Instead, for a half-integral value of $m = \pm 1/2, \pm 3/2, \dots$

$$\hat{R}(2\pi)|l, m\rangle = -|l, m\rangle$$

Therefore in the central field it holds that

$$\mu = m\hbar \quad [m \text{ integer}]$$

The integral values of m imply that l is an integer as well.

The characteristic equation for the $\hat{L}^2$ operator is

$$-\hbar^2 \nabla^2(\vartheta, \varphi)|l, m\rangle = l(l+1)\hbar^2|l, m\rangle$$

and has solutions called the *spherical harmonics*

$$|l, m\rangle = Y_{lm}(\vartheta, \varphi) = \Theta_{lm}(\vartheta)\Phi_m(\varphi)$$

Application of the raising operator to the function $|l, l\rangle$ results in the zero

$$\hat{l}_+ |l, l\rangle = \hat{l}_+ \Theta_{ll}(\vartheta) \Phi_m(\varphi) = 0$$

Using expressions in polar coordinates, this can be rewritten as

$$\hbar e^{i\varphi} \left(\frac{\partial}{\partial \vartheta} + i \cot \vartheta \frac{\partial}{\partial \varphi} \right) \Theta_{ll}(\vartheta) (1/\sqrt{2\pi}) e^{il\varphi} = 0$$

which reduces to a simple differential equation

$$\left(\frac{\partial}{\partial \vartheta} - l \cot \vartheta \right) \Theta_{ll}(\vartheta) = 0$$

and thus the particular solution results

$$\Theta_{ll}(\vartheta) = N_l (\sin \vartheta)^l$$

Application of the normalisation

$$\langle \Theta_{ll}(\vartheta) | \Theta_{ll}(\vartheta) \rangle = N_l^2 \int_0^\pi (\sin \vartheta)^{2l+1} d\vartheta = 1$$

yields the normalised form

$$\Theta_{ll}(\vartheta) = \left[(-1)^l \sqrt{\frac{(2l+1)!}{2}} \frac{1}{2^l l!} \right] (\sin \vartheta)^l$$

The constant factor $(-1)^l$ is the phase choice (see later).

The general solution for the $\Theta_{lm}(\vartheta)$ function is

$$\Theta_{lm}(\vartheta) = (-1)^l \left[\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \right]^{1/2} \frac{1}{2^l l!} \frac{1}{(\sin \vartheta)^m} \frac{d^{l-m}}{(d \cos \vartheta)^{l-m}} (\sin \vartheta)^{2l}$$

More frequently the solutions are expressed in terms of *Legendre polynomials* introduced through

$$P_l(a) = \frac{1}{2^l l!} \frac{d^l}{da^l} (a^2 - 1)^l$$

or associated Legendre polynomials

$$P_l^m(a) = \frac{1}{2^l l!} (1 - a^2)^{m/2} \frac{d^{l+m}}{da^{l+m}} (a^2 - 1)^l$$

of the argument a . Then

$$\begin{aligned} \Theta_{lm}(\vartheta) &= (-1)^m \left[\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \vartheta) \\ &= (-1)^m \left[\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \right]^{1/2} (\sin \vartheta)^m \frac{d^m}{(d \cos \vartheta)^m} P_l(\cos \vartheta) \end{aligned}$$

for $m \geq 0$ and

$$\Theta_{lm}(\vartheta) = (-1)^m \Theta_{l,-m}(\vartheta)$$

for $m < 0$.

The phase choice (sign) is referred to the *Condon–Shortley convention*: the factor -1 occurs only for positive odd values of m . Another phase choice, according to the *Fano–Racah convention*, can be met in literature and hence

$$Y'_{lm}(\vartheta, \varphi) = i^l Y_{lm}(\vartheta, \varphi)$$

Although the above formulae seem complicated, for the common values of $l = 0$ to 3 they reduce to the functions listed in Table 1.8.

The spherical harmonics are complex functions difficult to visualise and also their handling is impractical. A simple unitary transformation exists, yielding the real, normalised and orthogonal functions—*angular wave functions* $Y_{lm}^{\pm}$ for m positive only. They are collected in Table 1.9, using the Condon–Shortley phase convention.

The back transformations are provided by the formula

$$Y_{lm} = (-1)^{(m+|m|)/2} [(1 + \delta_{m,0})]^{1/2} [Y_{lm}^+ + i \cdot \text{sign}(m) Y_{lm}^-]$$

For the alternative Fano–Racah phase convention there is

$$Y_{lm}^+ = \frac{1}{\sqrt{2}} (Y'_{lm} + Y'_{l,-m})$$

$$Y_{lm}^- = \frac{1}{i\sqrt{2}} (Y'_{lm} - Y'_{l,-m})$$

TABLE 1.8
Normalised spherical harmonics

l	m	$Y_{l,m}$
0	0	$1/\sqrt{4\pi}$
1	0	$\sqrt{3/4\pi} \cos \vartheta$
1	± 1	$(-1)[\pm\sqrt{3/8\pi} \sin \vartheta \exp(\pm i\varphi)]$
2	0	$\sqrt{5/16\pi} (2 \cos^2 \vartheta - \sin^2 \vartheta)$
2	± 1	$(-1)[\pm\sqrt{15/8\pi} \cos \vartheta \sin \vartheta \exp(\pm i\varphi)]$
2	± 2	$\sqrt{15/32\pi} \sin^2 \vartheta \exp(\pm 2i\varphi)$
3	0	$\sqrt{7/16\pi} (2 \cos^3 \vartheta - 3 \cos \vartheta \sin^2 \vartheta)$
3	± 1	$(-1)[\pm\sqrt{21/64\pi} (4 \cos^2 \vartheta \sin \vartheta - \sin^3 \vartheta) \exp(\pm i\varphi)]$
3	± 2	$\sqrt{105/32\pi} \cos \vartheta \sin^2 \vartheta \exp(\pm 2i\varphi)$
3	± 3	$(-1)[\pm\sqrt{35/64\pi} \sin^3 \vartheta \exp(\pm 3i\varphi)]$
4	0	$3/\sqrt{256\pi} (35 \cos^4 \vartheta - 30 \cos^2 \vartheta + 3)$
4	± 1	$(-1)[\pm\sqrt{45/64\pi} \sin \vartheta (7 \cos^3 \vartheta - 3 \cos \vartheta) \exp(\pm i\varphi)]$
4	± 2	$\sqrt{65/128\pi} \sin^2 \vartheta (7 \cos^2 \vartheta - 1) \exp(\pm 2i\varphi)$
4	± 3	$(-1)[\pm\sqrt{315/64\pi} \sin^3 \vartheta \cos \vartheta \exp(\pm 3i\varphi)]$
4	± 4	$\sqrt{315/512\pi} \sin^4 \vartheta \exp(\pm 4i\varphi)$

TABLE 1.9
Real angular wave functions

Symbol	Y_{lm}^+
s	$Y_{0,0} = 0, 0\rangle$
p_x	$Y_{1,1}^+ = -(1/\sqrt{2})[1, 1\rangle - 1, -1\rangle]$
p_y	$Y_{1,1}^- = (i/\sqrt{2})[1, 1\rangle + 1, -1\rangle]$
p_z	$Y_{1,0} = 1, 0\rangle$
d_{xz}	$Y_{2,1}^+ = -(1/\sqrt{2})[2, 1\rangle - 2, -1\rangle]$
d_{yz}	$Y_{2,1}^- = (i/\sqrt{2})[2, 1\rangle + 2, -1\rangle]$
$d_{x^2-y^2}$	$Y_{2,2}^+ = (1/\sqrt{2})[2, 2\rangle + 2, -2\rangle]$
d_{xy}	$Y_{2,2}^- = -(i/\sqrt{2})[2, 2\rangle - 2, -2\rangle]$
d_{z^2}	$Y_{2,0} = 2, 0\rangle$

1.4.7 Coupling of two angular momenta

As the angular momentum is a physical vector, two angular momenta, say $\vec{l}_1$ and $\vec{l}_2$, obey vector addition yielding an angular momentum $\vec{L}$

$$\vec{L} = \vec{l}_1 + \vec{l}_2$$

In the role of the components either the orbital angular momenta or the spin angular momenta can operate, both at the same centre or at different centres.

It is assumed that the eigenstates of each component are known and fulfil characteristic equations such as

$$\hat{l}_{z1}|l_1m_1\rangle = m_1\hbar|l_1m_1\rangle$$

$$\hat{l}_1^2|l_1m_1\rangle = l_1(l_1 + 1)\hbar^2|l_1m_1\rangle$$

and

$$\hat{l}_{z2}|l_2m_2\rangle = m_2\hbar|l_2m_2\rangle$$

$$\hat{l}_2^2|l_2m_2\rangle = l_2(l_2 + 1)\hbar^2|l_2m_2\rangle$$

The compound angular momentum should obey similar equations

$$\hat{L}_z|LM\rangle = M\hbar|LM\rangle$$

$$\hat{L}^2|LM\rangle = L(L + 1)\hbar^2|LM\rangle$$

where the quantum numbers are restricted by the conditions

$$|l_1 - l_2| \leq L \leq l_1 + l_2$$

and

$$-L \leq M \leq +L$$

The tensor (direct) product of the $(2l_1 + 1)$ kets of the system 1 and $(2l_2 + 1)$ kets of the system 2 gives a space of $(2l_1 + 1)(2l_2 + 1)$ kets, labelled as

$$|l_1l_2m_1m_2\rangle = |l_1m_1\rangle|l_2m_2\rangle$$

which are simultaneous eigenvectors of the operators $\hat{l}_1^2$, $\hat{l}_2^2$, $\hat{l}_{1z}$ and $\hat{l}_{2z}$. Since the operators $\hat{l}_1^2$, $\hat{l}_2^2$, $\hat{L}^2$ and $\hat{L}_z$ are all commuting (as is easily proven), there exists a set of eigenstates $|l_1l_2LM\rangle$ common to them. A unitary transformation $\mathbf{U}$ can be found which transforms the eigenstates $|l_1l_2m_1m_2\rangle$ to $|l_1l_2LM\rangle$, viz.

$$|l_1l_2LM\rangle = \mathbf{U}|l_1l_2m_1m_2\rangle$$

The coefficients of the transformation depend on all six independent indices (variables)

$$|l_1 l_2 LM\rangle = \sum_{m_1} \sum_{m_2} U_{l_1, l_2, L, m_1, m_2, M} |l_1 l_2 m_1 m_2\rangle$$

and it is customary to call them *Clebsch–Gordan coefficients*. However, one can meet several equivalent definitions of the coupling coefficients with different (and shortened) notations and sometimes a different phase choice and a different constant factor:

- (1) $\langle l_1 l_2 m_1 m_2 | LM \rangle$, according to Bencini and Gatteschi [1];
- (2) $\langle l_1 m_1 l_2 m_2 | l_1 l_2 LM \rangle$, according to Condon and Shortley [2];
- (3) $C_{m_1 m_2 M}^{l_1 l_2 L}$, according to Biedenharn [3];
- (4) $C(l_1 l_2 L; m_1 m_2)$, according to Rose [4];
- (5) $S_{L m_1 m_2}^{l_1 l_2}$, according to Wigner [5];
- (6) $\langle l_1 l_2 m_1 m_2 | l_1 l_2 LM \rangle$, according to Griffith [6];
- (7) $C_{m_1, m_2, L, M}$, according to Slater [7];
- (8) the (Wigner) $3j$ -symbols $\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix}$, according to [8];
- (9) the Racah V -coefficients $V(l_1 l_2 L; m_1 m_2 M)$.

We will use the first notation with the fixation of the phase of kets $|l_1 l_2 LM\rangle$ so that $\langle l_1, l_2, l_1, L - l_1 | LL \rangle$ is real and positive. (The advantage of the V -coefficients and especially the $3j$ -symbols is that they have a considerably higher symmetry than the Clebsch–Gordan coefficients.)

The Clebsch–Gordan coefficients have the following properties:

- (1) they are real and form an orthogonal matrix;
- (2) non-zero coefficients are only for

$$m_1 + m_2 = M$$

and

$$|l_1 - l_2| \leq L \leq l_1 + l_2$$

- (3) they fulfil

$$\langle l_1 l_2 m_1 m_2 | LM \rangle = (-1)^{l_1 + l_2 - L} \langle l_2 l_1 m_2 m_1 | LM \rangle$$

(4) they are interrelated with the $3j$ -symbols through a constant factor

$$\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} = \langle l_1 l_2 m_1 m_2 | LM \rangle (-1)^{l_1 - l_2 + M} (2L + 1)^{-1/2}$$

For the direct evaluation of the $3j$ -symbol the *Racah formula* [8, 9] (equivalent to the Wigner formula [5, 6]) is helpful

$$\begin{aligned} \begin{pmatrix} a & b & c \\ A & B & C \end{pmatrix} &= (-1)^{a-b-c} \left[\frac{(a+b-c)!(b+c-a)!(c+a-b)!}{(a+b+c+1)!} \right]^{1/2} \\ &\times [(a+A)!(a-A)!(b+B)!(b-B)!(c+C)!(c-C)!]^{1/2} \\ &\times \sum_{n=n_{\min}}^{n_{\max}} (-1)^n [n!(c-b+n+A)!(c-a+n-B)!(a+b-c-n)! \\ &\times (a-n-A)!(b-n+B)!]^{-1} \end{aligned}$$

Necessarily it holds true that

$$A + B + C = 0$$

and

$$|a - b| \leq c \leq a + b$$

The summation runs over all indices n for which the factorials are defined (i.e. arguments are ≥ 0). Thus

$$n_{\min} = \max\{0; -c + b - A; -c + a + B\}$$

$$n_{\max} = \min\{a + b - c; b + B; a - A\}$$

Although tabulations of these coefficients can be found in literature [8], their computer generation is an easy task at present. For instance, if a spin angular momentum is added to the orbital angular momentum we arrive at

$$\vec{j} = \vec{l} + \vec{s}$$

and since the spin projections are characterised by the quantum number $m_s = \pm 1/2$ the only required Clebsch–Gordan coefficients are those of $\langle l, 1/2, m - m_s, m_s | jm \rangle$, presented in Table 1.10.

TABLE 1.10
Selected Clebsch–Gordan coefficients

j	m_s	$\langle l, 1/2, m - m_s, m_s jm \rangle$
$l + 1/2$	$1/2$	$[(l + m + 1/2)/(2l + 1)]^{1/2}$
$l - 1/2$	$1/2$	$-[(l - m + 1/2)/(2l + 1)]^{1/2}$
$l + 1/2$	$-1/2$	$[(l - m + 1/2)/(2l + 1)]^{1/2}$
$l - 1/2$	$-1/2$	$[(l + m + 1/2)/(2l + 1)]^{1/2}$

For some hand calculations, however, it is advantageous to have the relevant Clebsch–Gordan coefficients or the $3j$ -symbols at one's disposal (Appendix 3). Notice that the transformation of the local basis to the compound basis is represented by a unitary (orthogonal) matrix

$$|l_1 l_2 LM\rangle = \mathbf{U} |l_1 l_2 m_1 m_2\rangle$$

with

$$\mathbf{U}\mathbf{U}^T = \mathbf{1}$$

For example, the coupling of two spins $s_1 = s_2 = 1/2$ is represented by a transformation matrix $\mathbf{U}^{(12)}$ of dimension 4×4

$$|SM\rangle = \mathbf{U}^{(12)} |m_1 m_2\rangle$$

or

$$\begin{pmatrix} |0, 0\rangle \\ |1, -1\rangle \\ |1, 0\rangle \\ |1, +1\rangle \end{pmatrix} = \mathbf{U}^{(12)} \begin{pmatrix} |-1/2, -1/2\rangle \\ |-1/2, +1/2\rangle \\ |+1/2, -1/2\rangle \\ |+1/2, +1/2\rangle \end{pmatrix}$$

with

$$\mathbf{U}^{(12)} = \begin{pmatrix} 0 & -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

For coupling of two spins $s_1 = s_2 = 5/2$ the transformation matrix has the dimension of 36×36 .

1.4.8 Coupling of three angular momenta

The coupling of three angular momenta can be done by several routes:

- (1) the third component is added to the result of the coupling of the first and the second component

$$\vec{l}_1 + \vec{l}_2 = \vec{l}_{12}$$

$$\vec{L} \equiv \vec{l}_{123} = \vec{l}_{12} + \vec{l}_3$$

with the intermediate kets

$$|l_1 l_2 l_{12} m_{12}\rangle = \sum_{m_1} \sum_{m_2} \langle l_1 l_2 m_1 m_2 | l_{12} m_{12} \rangle |l_1 l_2 m_1 m_2\rangle$$

and the resulting kets are

$$\begin{aligned} |A; LM\rangle &= |l_1 l_2 l_{12} l_3 LM\rangle = \sum_{m_{12}} \sum_{m_3} \langle l_{12} l_3 m_{12} m_3 | LM \rangle |l_1 l_2 l_{12} m_{12}\rangle \\ &= \sum_{m_1} \sum_{m_2} \sum_{m_3} \sum_{m_{12}} \langle l_{12} l_3 m_{12} m_3 | LM \rangle \langle l_1 l_2 m_1 m_2 | l_{12} m_{12} \rangle |l_1 l_2 l_3 m_1 m_2 m_3\rangle \end{aligned}$$

- (2) the order of the coupling components is interchanged, e.g.

$$\vec{l}_2 + \vec{l}_3 = \vec{l}_{23}$$

$$\vec{L} \equiv \vec{l}_{132} = \vec{l}_{23} + \vec{l}_1$$

with

$$\begin{aligned} |B; LM\rangle &= |l_1 l_2 l_3 l_{23} LM\rangle = \sum_{m_{23}} \sum_{m_1} \langle l_1 l_{23} m_1 m_{23} | LM \rangle |l_2 l_3 l_{23} m_{23}\rangle \\ &= \sum_{m_1} \sum_{m_2} \sum_{m_3} \sum_{m_{23}} \langle l_1 l_{23} m_1 m_{23} | LM \rangle \langle l_2 l_3 m_2 m_3 | l_{23} m_{23} \rangle |l_1 l_2 l_3 m_1 m_2 m_3\rangle \end{aligned}$$

However, the final states $|A; LM\rangle$ and $|B; LM\rangle$ are dependent on the coupling path: the different states of a system may correspond to the same values $|LM\rangle$. In other words, for a full description of the states of a system two quantum numbers $|LM\rangle$ are not sufficient; intermediate quantum numbers should be included to form a complete set. This can be exemplified by

the coupling of spins $\{s_1 = 1/2, s_2 = 1/2, s_3 = 1\}$ and $\{s_1 = 1/2, s_2 = 1, s_3 = 1/2\}$, as demonstrated by Table 1.11.

Since the kets $|A; LM\rangle$ and $|B; LM\rangle$ span the same vector space as $|l_1 l_2 l_3 m_1 m_2 m_3\rangle$, they are related by a unitary transformation such as

$$|A; LM\rangle = U|B; LM\rangle = \sum_B |B; LM\rangle \langle B; LM|A; LM\rangle$$

or, more specifically,

$$|l_1 l_2 l_3 LM\rangle = \sum_{l_{23}} |l_1 l_2 l_{23} LM\rangle \langle l_1 l_2 l_{23} LM|l_1 l_2 l_3 LM\rangle$$

The recoupling coefficients just introduced are independent of the projections of angular momenta M (they appear as a scalar product and we know that the scalar product does not depend upon the coordinate system). The recoupling coefficients can be arranged into 6j-symbols (having a number of symmetry properties) through

$$\left\{ \begin{matrix} l_1 & l_2 & l_{12} \\ l_3 & L & l_{23} \end{matrix} \right\} = (-1)^{l_1+l_2+l_3+L} [(2l_{12}+1)(2l_{23}+1)]^{-1/2} \langle l_1 l_2 l_{12} l_3 LM | l_1 l_2 l_3 l_{23} LM \rangle$$

These are interrelated to *Racah W-coefficients* via a different phase factor [8,11]

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{matrix} \right\} = (-1)^{j_1+j_2+j_4+j_5} W(j_1 j_2 j_5 j_4; j_3 j_6)$$

A 6j-symbol is non-zero if the elements of the following triads

$$(a, b, c) = \left\{ \begin{matrix} (j_1, j_2, j_3) \\ (j_1, j_5, j_6) \\ (j_4, j_2, j_6) \\ (j_4, j_5, j_3) \end{matrix} \right.$$

- (1) have an integral sum;
- (2) satisfy the triangular condition

$$|a - b| \leq c \leq a + b$$

The 6j-symbols can be evaluated through an expansion via associated 3j-symbols [8]

TABLE 1.11
Two coupling coefficient matrices for addition of three angular momenta

(a) $\mathbf{U}(1/2, 1/2, 1)$

[illegible]

(b) $U(1/2, 1, 1/2)$

[illegible]

$$\begin{aligned}
\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{matrix} \right\} &= \sum_{m_1} \sum_{m_2} \sum_{m_3} \sum_{m_4} \sum_{m_5} \sum_{m_6} (-1)^{j_4+j_5+j_6+m_4+m_5+m_6} \\
&\times \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_5 & j_6 \\ m_1 & m_5 & -m_6 \end{pmatrix} \\
&\times \begin{pmatrix} j_4 & j_2 & j_6 \\ -m_4 & m_1 & m_6 \end{pmatrix} \begin{pmatrix} j_4 & j_5 & j_3 \\ m_4 & -m_5 & m_6 \end{pmatrix}
\end{aligned}$$

The three magnetic quantum numbers in each $3j$ -symbol must sum to zero (instead this vanishes) and consequently only two of the six summation indices are independent. If only m_1 and m_2 are summed over, then the above formula collapses to

$$\begin{aligned}
\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{matrix} \right\} &= (2j_3 + 1) \sum_{m_1} \sum_{m_2} (-1)^{j_4+j_5+j_6+m_4+m_5+m_6} \\
&\times \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_5 & j_6 \\ m_1 & m_5 & -m_6 \end{pmatrix} \\
&\times \begin{pmatrix} j_4 & j_2 & j_6 \\ -m_4 & m_1 & m_6 \end{pmatrix} \begin{pmatrix} j_4 & j_5 & j_3 \\ m_4 & -m_5 & m_6 \end{pmatrix}
\end{aligned}$$

A direct evaluation of the $6j$ -symbol is possible through the *Racah formula* [8]

$$\begin{aligned}
\left\{ \begin{matrix} a & b & c \\ A & B & C \end{matrix} \right\} &= (-1)^{a+b+A+B} f(abc) f(ABc) f(AbC) f(aBC) \\
&\times \sum_{n=n_{\min}}^{n_{\max}} (-1)^n (a+b+A+B+1-n)! / [n!(a+b-c-n)! \\
&\times (A+B-c-n)! \\
&\times (a+B-C-n)!(A+b-C-n)! \\
&\times (-a-A+c+C+n)!(-b-B+c+C+n)!]
\end{aligned}$$

with

$$f(abc) = \left[\frac{(a+b-c)!(a-b+c)!(-a+b+c)!}{(a+b+c+1)!} \right]^{1/2}$$

The sum must be taken over all the integer values of n for which the factorials are meaningful (non-negative arguments). Thus

$$n_{\min} = \max\{0; a + A - c - C; b + B - c - C\}$$

$$n_{\max} = \min\{a + b + A + B + 1; a + b - c; A + B - c; a + B - C; A + b - C\}$$

1.4.9 Coupling of four and more angular momenta

The coupling of four angular momenta again can be performed by different routes using a different set of intermediate spins. For example, we can select two coupling schemes:

- (1) scheme A with the final ket $|A; LM\rangle = |l_1 l_2 l_{12} l_3 l_4 l_{34} LM\rangle$; and
- (2) scheme B with the final ket $|B; LM\rangle = |l_1 l_3 l_{13} l_2 l_4 l_{24} LM\rangle$.

These two states are interrelated through the recoupling coefficients

$$|A; LM\rangle = U |B; LM\rangle = \sum_B |B; LM\rangle \langle B; LM | A; LM\rangle$$

$$= \sum_B |B; LM\rangle \langle A; LM | B; LM\rangle$$

$$|l_1 l_2 l_{12} l_3 l_4 l_{34} LM\rangle = \sum_{l_{13}} \sum_{l_{24}} |l_1 l_3 l_{13} l_2 l_4 l_{24} LM\rangle$$

$$\langle l_1 l_2 l_{12} l_3 l_4 l_{34} LM | l_1 l_3 l_{13} l_2 l_4 l_{24} LM\rangle$$

which can be expressed via $9j$ -symbols as

$$\langle l_1 l_2 l_{12} l_3 l_4 l_{34} LM | l_1 l_3 l_{13} l_2 l_4 l_{24} LM\rangle$$

$$= [(2l_{12} + 1)(2l_{34} + 1)(2l_{13} + 1)(2l_{24} + 1)]^{1/2} \begin{Bmatrix} l_1 & l_2 & l_{12} \\ l_3 & l_4 & l_{34} \\ l_{13} & l_{24} & L \end{Bmatrix}$$

A 9j-symbol can be expressed in terms of 3j-symbols

$$\begin{aligned} \begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{Bmatrix} &= \sum_{\text{all } m} \begin{pmatrix} j_{11} & j_{12} & j_{13} \\ m_{11} & m_{12} & m_{13} \end{pmatrix} \begin{pmatrix} j_{21} & j_{22} & j_{23} \\ m_{21} & m_{22} & m_{23} \end{pmatrix} \\ &\times \begin{pmatrix} j_{31} & j_{32} & j_{33} \\ m_{31} & m_{32} & m_{33} \end{pmatrix} \begin{pmatrix} j_{11} & j_{21} & j_{31} \\ m_{11} & m_{21} & m_{31} \end{pmatrix} \\ &\times \begin{pmatrix} j_{12} & j_{22} & j_{32} \\ m_{12} & m_{22} & m_{32} \end{pmatrix} \begin{pmatrix} j_{13} & j_{23} & j_{33} \\ m_{13} & m_{23} & m_{33} \end{pmatrix} \end{aligned}$$

or 6j-symbols

$$\begin{aligned} \begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{Bmatrix} &= \sum_j (-1)^{2j} (2j+1) \begin{Bmatrix} j_{11} & j_{21} & j_{31} \\ j_{32} & j_{33} & j \end{Bmatrix} \begin{Bmatrix} j_{12} & j_{22} & j_{32} \\ j_{21} & j & j_{23} \end{Bmatrix} \\ &\times \begin{Bmatrix} j_{13} & j_{23} & j_{33} \\ j & j_{11} & j_{12} \end{Bmatrix} \end{aligned}$$

In the last formula the index j runs over all the meaningful values for which the triangular conditions of 6j-symbols are satisfied. For better transparency we use the property that the 6j-symbol remains invariant under the interchange of columns so that

$$\begin{aligned} \begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{Bmatrix} &= \sum_{j=j_{\min}}^{j_{\max}} (-1)^{2j} (2j+1) \begin{Bmatrix} j_{11} & j_{21} & j_{31} \\ j_{32} & j_{33} & j \end{Bmatrix} \begin{Bmatrix} j_{12} & j_{32} & j_{22} \\ j_{21} & j_{23} & j \end{Bmatrix} \\ &\times \begin{Bmatrix} j_{33} & j_{23} & j_{13} \\ j_{12} & j_{11} & j \end{Bmatrix} \end{aligned}$$

The application of all triangular conditions implies that

$$j_{\min} = \min\{|j_{11} - j_{33}|; |j_{32} - j_{21}|; |j_{12} - j_{23}|\}$$

$$j_{\max} = \max\{j_{11} + j_{33}; j_{32} + j_{21}; j_{12} + j_{23}\}$$

The evaluation of Clebsch–Gordan coefficients, 3j-, 6j- and 9j-symbols can be performed on the basis of special formulae (Appendix 3) or a computer program (Appendix 5).

In coupling of five, six, etc. angular momenta the 12j-, 15j-, etc. symbols may appear but these are not used here.

1.4.10 Recursion coupling scheme

We have seen that the coupling of more angular momenta results in an appearance of the $3j$ -symbols (or Clebsch–Gordan coefficients) which bear all the fundamental information about the coupling route.

The basis set

$$|l_1 l_2 m_1 m_2\rangle = |l_1 m_1\rangle |l_2 m_2\rangle$$

can be viewed as a tensor (direct) product of vector spaces like

$$\begin{pmatrix} A \\ B \end{pmatrix} \otimes \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} Aa \\ Ab \\ Ba \\ Bb \end{pmatrix}$$

For the coupling of three angular momenta we have the basis set

$$|l_1 l_2 l_3 m_1 m_2 m_3\rangle = |l_1 m_1\rangle |l_2 m_2\rangle |l_3 m_3\rangle$$

which can be viewed as a direct products expansion like

$$\begin{pmatrix} A \\ B \end{pmatrix} \otimes \begin{pmatrix} a \\ b \end{pmatrix} \otimes \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} Aa \\ Ab \\ Ba \\ Bb \end{pmatrix} \otimes \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} Aa\alpha \\ Aa\beta \\ Ab\alpha \\ Ab\beta \\ Ba\alpha \\ Ba\beta \\ Bb\alpha \\ Bb\beta \end{pmatrix}$$

The coupling can be done in two steps:

- (1) using appropriate Clebsch–Gordan coefficients the first transformation matrix is generated

$$|l_{12} m_{12}\rangle = U^{(12)}(|l_1 m_1\rangle \otimes |l_2 m_2\rangle)$$

- (2) then

$$|l_{123} m_{123}\rangle = U^{(123)}(|l_{12} m_{12}\rangle \otimes |l_3 m_3\rangle)$$

The second transformation matrix $U^{(123)}$ is an expansion of the matrix of the previous generation $U^{(12)}$ and Clebsch–Gordan coefficients for a new set of

indices of coupled angular momenta. If the new set of Clebsch–Gordan coefficients is indexed as follows

$$C_{m_{12}, m_3, M} \equiv \langle l_{12} l_3 m_{12} m_3 | LM \rangle$$

then

$$U_{M,i}^{(123)} = \sum_{m_3} C_{m_{12}, m_3, M} U_{m_{12},j}^{(12)}$$

where the column index i of the new expanded matrix $U^{(123)}$ runs over $j \times m_3$. This formulation is useful for the derivation of a *recursion formula* in which the new generation of the (expanded) coupling matrix is created from the previous generation of the coupling matrix and a new set of Clebsch–Gordan coefficients

$$U_{M,i}^{(k)} = \sum_{m_k} C_{m_{k-1}, m_k, M} U_{m_{k-1},j}^{(k-1)} \quad [i = 1, 2, \dots, j \times m_k]$$

The initial “coupling” matrix becomes a unit matrix of the order $(2l_1 + 1)$

$$U_{M,i}^{(1)} = \delta_{ij}$$

For example, the coupling of three spins $s_1 = s_2 = s_3 = 1/2$ results in the transformation of the column vectors

$$\begin{pmatrix} |1/2, -1/2\rangle \\ |1/2, +1/2\rangle \\ |1/2, -1/2\rangle \\ |1/2, +1/2\rangle \\ |3/2, -3/2\rangle \\ |3/2, -1/2\rangle \\ |3/2, +1/2\rangle \\ |3/2, +3/2\rangle \end{pmatrix} = U^{(123)} \begin{pmatrix} |-1/2, -1/2, -1/2\rangle \\ |-1/2, -1/2, +1/2\rangle \\ |-1/2, +1/2, -1/2\rangle \\ |-1/2, +1/2, +1/2\rangle \\ |+1/2, -1/2, -1/2\rangle \\ |+1/2, -1/2, +1/2\rangle \\ |+1/2, +1/2, -1/2\rangle \\ |+1/2, +1/2, +1/2\rangle \end{pmatrix}$$

or

$$|SM\rangle = U^{(123)} |m_1 m_2 m_3\rangle$$

TABLE 1.12

Non-zero Clebsch–Gordan coefficients for coupling of spin states $s_{12} = 0, 1$ and $s_3 = 1/2$

State	s_{12}	S	m_{12}	m_3	M	$C_{m_{12}, m_3, M} \equiv \langle s_{12} s_3 m_{12} m_3 SM \rangle$
1	0	1/2	0	-1/2	-1/2	1
2	0	1/2	0	+1/2	+1/2	1
3	1	1/2	-1	+1/2	-1/2	$-\sqrt{2/3}$
3	1	1/2	0	-1/2	-1/2	$+\sqrt{1/3}$
4	1	1/2	0	+1/2	+1/2	$-\sqrt{1/3}$
4	1	1/2	+1	-1/2	+1/2	$+\sqrt{2/3}$
5	1	3/2	-1	-1/2	-3/2	1
6	1	3/2	-1	+1/2	-1/2	$+\sqrt{1/3}$
6	1	3/2	0	-1/2	-1/2	$+\sqrt{2/3}$
7	1	3/2	0	+1/2	+1/2	$+\sqrt{2/3}$
7	1	3/2	+1	-1/2	+1/2	$+\sqrt{1/3}$
8	1	3/2	+1	+1/2	+3/2	1

Just this matrix is generated from the previous generation of the coupling matrix $U^{(12)}$ and the new set of Clebsch–Gordan coefficients listed in Table 1.12. The resulting transformation matrix is

$$U^{(123)} = \begin{pmatrix} 0 & 0 & -\sqrt{1/2} & 0 & \sqrt{1/2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{1/2} & 0 & \sqrt{1/2} & 0 & 0 \\ 0 & -\sqrt{2/3} & \sqrt{1/6} & 0 & \sqrt{1/6} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{1/6} & 0 & -\sqrt{1/6} & \sqrt{2/3} & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{1/3} & \sqrt{1/3} & 0 & \sqrt{1/3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{1/3} & 0 & \sqrt{1/3} & \sqrt{1/3} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

1.5 TENSOR PROPERTIES

Each second-rank tensor represented by the square matrix can be transformed by the similarity transformation to its *diagonal form*

$$\mathbf{D} = \mathbf{U}^{-1} \mathbf{T} \mathbf{U}$$

where $\mathbf{D}$ is a diagonal matrix. The eigenvalues (“latent roots”) are preserved in such a transformation.

1.5.1 Deconvolution of tensors

Any second-rank tensor, $\overline{\overline{T}}$, can be decomposed into the sum of a symmetric, $\overline{\overline{S}}$, and an antisymmetric, $\overline{\overline{A}}$, tensor, i.e. in matrix notation

$$T_{ij} = S_{ij} + A_{ij}$$

with

$$S_{ij} = (1/2)(T_{ij} + T_{ji}) = S_{ji}$$

$$A_{ij} = (1/2)(T_{ij} - T_{ji}) = -A_{ji}$$

Evidently, the antisymmetric tensor is traceless. The symmetric tensor can be made traceless by subtracting one-third of the trace

$$t = \frac{1}{3} \text{Tr}(\mathbf{T}) = \frac{1}{3}(T_{xx} + T_{yy} + T_{zz})$$

from the diagonal elements

$$\mathbf{S}_0 = \mathbf{S} - t\mathbf{I}$$

where $\mathbf{I}$ stands for the identity (unit) matrix. Hence the decomposition of the tensor is

$$\mathbf{T} = \mathbf{S} + \mathbf{A} = t\mathbf{I} + \mathbf{S}_0 + \mathbf{A}$$

Nine components of the tensor $\mathbf{T}$ have been transformed into three independent components of $\mathbf{A}$ (i.e. A_{yz}, A_{zx}, A_{xy}), five independent components of $\mathbf{S}_0$ (i.e. $S_{yz}, S_{xz}, S_{xy}, S_{xx}, S_{yy}$; S_{zz} is a dependent component since $S_{xx} + S_{yy} + S_{zz} = 0$), and the last component is the trace $3t$.

The scalar product

$$c = \vec{X} \cdot \overline{\overline{T}} \cdot \vec{Y}$$

can be rewritten as

$$c = t\vec{X} \cdot \vec{Y} + \vec{a} \cdot (\vec{X} \times \vec{Y}) + \vec{X} \cdot \overline{\overline{S}}_0 \cdot \vec{Y}$$

where t is a scalar, $\vec{a}$ the polar vector (A_{yz}, A_{zx}, A_{xy}), and $\overline{\overline{S}}_0$ the symmetric traceless tensor. Here the first term is called the *isotropic*, the second *antisymmetric* and the third *asymmetric* contribution.

1.5.2 Rotation of vectors

Suppose that we rotate the Cartesian axes counterclockwise through an angle α . A two-dimensional vector $\mathbf{v} = (x, y)$ is transformed in this way to $\mathbf{v}' = (x', y')$ through the relationship

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

or

$$\mathbf{v}' = \mathbf{R}_1 \mathbf{v}$$

where $\mathbf{R}_1$ is a *rotation matrix*. If we were to rotate counterclockwise and then clockwise by the same angle (the $\sin \alpha$ alters the sign and thus $\mathbf{R}_2 = \mathbf{R}_1^T$) we arrive at the original vector

$$\mathbf{v} = \mathbf{R}_2 \mathbf{v}' = \mathbf{R}_2 \mathbf{R}_1 \mathbf{v}$$

so that it should be fulfilled that

$$\mathbf{R}_1^T \mathbf{R}_1 = \mathbf{1}$$

and the rotation matrix is found to be orthogonal.

Any ordinary vector (e.g. a three-component Cartesian vector) transforms in a similar way

$$v'_a = \sum_b R_{ab} v_b$$

Any rotation in three dimensions can be specified by three angles. It is customary to use the *Euler angles* α , β and γ , defining the rotation in three steps:

- (1) a rotation by α about the z axis, $0 \leq \alpha \leq 2\pi$;
- (2) a rotation by β about the y' axis, $0 \leq \beta \leq \pi$;
- (3) a rotation by γ about z'' axis, $0 \leq \gamma \leq 2\pi$.

Then the effect of rotation is characterised by the rotation matrix

$$\mathbf{R}(\alpha\beta\gamma) = \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

which is orthogonal, $\mathbf{R}^T = \mathbf{R}^{-1}$.

A scalar quantity is invariant under rotation. Other (vector, tensor) quantities transform like products of coordinates, e.g. x^2 , xy , etc.

1.5.3 Irreducible tensors

A general tensor $\mathbf{T}$ of degree n is defined as a set of quantities labelled by n indices which transform linearly among themselves under rotation as follows

$$T'_{a_1 a_2 \dots a_n} = \sum_{b_1, b_2, \dots, b_n} R_{a_1 b_1} R_{a_2 b_2} \dots R_{a_n b_n} T_{b_1 b_2 \dots b_n}$$

A scalar is a zero-rank tensor; an ordinary vector is a first-rank tensor. A Cartesian tensor $\mathbf{T}$ consists of 3^n quantities. If the index sets are denoted as

$$A \equiv (a_1, \dots, a_n)$$

and

$$B \equiv (b_1, \dots, b_n)$$

then the transformation of the tensor can be written as follows

$$T'_A = \sum_B R_{AB} T_B$$

with the transformation matrix

$$R_{AB}(\alpha\beta\gamma) = \prod_{i=1}^n R_{a_i b_i}(\alpha\beta\gamma)$$

The matrices $R_{AB}(\alpha\beta\gamma)$ provide a *representation* of the *rotation group*. However, this representation is reducible and thus its decomposition into

irreducible representations is possible. A second-rank tensor having nine independent Cartesian components can be decomposed into three parts

$$\mathbf{T} = \mathbf{T}^{(0)} + \mathbf{T}^{(1)} + \mathbf{T}^{(2)}$$

having the properties

$$T_{ab}^{(0)} = t\delta_{ab}, \quad t = \frac{1}{3} \sum_a T_{aa}, \quad \text{one quantity}$$

$$T_{ab}^{(1)} = -T_{ba}^{(1)}, \quad \text{three quantities}$$

$$T_{ab}^{(2)} = T_{ba}^{(2)}, \quad \sum_a T_{aa}^{(2)} = 0, \quad \text{five quantities}$$

Each subset transforms only within itself under rotation and thus these subsets are *irreducible tensors*; they provide bases for irreducible representations of the rotation group of dimension 1, 3 and 5, respectively (see Table 1.13).

Instead of Cartesian tensors one can introduce *spherical tensors* in the following way. An ordinary Cartesian vector can be replaced by the spherical components

$$v_{1,1} = -\frac{1}{\sqrt{2}}(v_x + iv_y)$$

$$v_{1,0} = v_z$$

$$v_{1,-1} = \frac{1}{\sqrt{2}}(v_x - iv_y)$$

These components transform under rotation like the spherical harmonic functions Y_{lm} . In general, an irreducible spherical tensor T_{lm} transforms like the function Y_{lm} . The spherical components of a second-rank tensor are again collected in Table 1.13.

A more precise definition is that a spherical tensor is called an *irreducible spherical tensor* if its $(2m+1)$ components transform under a rotation R of the coordinate system according to

$$RT_{lm}R^{-1} = \sum_{n=-l}^{+l} T_{ln}R_{mn}^k$$

where the Wigner rotation matrix $\mathbf{R}^k$ spans the k th irreducible representation of the real orthogonal rotation group $SO(3)$.

TABLE 1.13
Components of a second-rank tensor

Irreducible Cartesian components	Spherical components
$T_{ab}^{(0)} = t\delta_{ab}$	$T_{0,0} = -(1/\sqrt{3})t$
$T_{ab}^{(1)} = \frac{1}{2}(T_{ab} - T_{ba})$	$T_{1,1} = -\frac{1}{2}[(T_{xz} - T_{zx}) + i(T_{yz} - T_{zy})]$
	$T_{1,0} = \frac{i}{\sqrt{2}}(T_{xy} - T_{yx})$
	$T_{1,-1} = -\frac{1}{2}[(T_{xz} - T_{zx}) - i(T_{yz} - T_{zy})]$
$T_{ab}^{(2)} = \frac{1}{2}(T_{ab} + T_{ba}) - t\delta_{ab}$	$T_{2,2} = \frac{1}{2}[(T_{xx} - T_{yy}) + i(T_{xy} + T_{yx})]$
	$T_{2,1} = -\frac{1}{2}[(T_{xz} + T_{zx}) + i(T_{yz} + T_{zy})]$
	$T_{2,0} = \frac{1}{\sqrt{6}}(2T_{zz} - T_{xx} - T_{yy})$
	$T_{2,-1} = \frac{1}{2}[(T_{xz} + T_{zx}) - i(T_{yz} + T_{zy})]$
	$T_{2,-2} = \frac{1}{2}[(T_{xx} - T_{yy}) - i(T_{xy} + T_{yx})]$

The *tensor (direct) product* of two irreducible tensors (tensor operators) of rank l and k is defined as a set of $(2l+1)(2k+1)$ quantities

$$T_k \otimes T_l = \{T_{kn}T_{lm}\}$$

This set of operators is in general reducible but a proper linear combination of them can be taken as irreducible. It can be used in constructing an *irreducible tensor product* of order K with $(2K+1)$ elements, indexed as $-K \leq M \leq K$, by using Clebsch–Gordan coefficients

$$\{T_k \otimes T_l\}_{KM} = \sum_n \sum_m \langle klm | KM \rangle T_{kn}T_{lm}$$

or 3j-symbols

$$\{T_k \otimes T_l\}_{KM} = \sum_n \sum_m (2K+1)^{1/2} (-1)^{l-k-K} \begin{pmatrix} k & l & K \\ n & m & M \end{pmatrix} T_{kn}T_{lm}$$

with the constraint $|k-l| \leq K \leq (k+l)$.

From the tensor product of two irreducible tensor operators of rank $k = l = 1$ (i.e. ordinary vectors) one gets three sets of irreducible tensor operators corresponding to $K = 0, 1$ and 2 (Table 1.14).

TABLE 1.14

Compound irreducible tensor operators

$K = 0$	zero-rank tensor operators (scalar operators) $\{A_1 \otimes B_1\}_{0,0} = (1/\sqrt{3})(A_{1,1}B_{1,-1} - A_{1,0}B_{1,0} + A_{1,-1}B_{1,1})$
$K = 1$	first-rank tensor operators (vector operators) $\{A_1 \otimes B_1\}_{1,1} = (1/\sqrt{2})A_{1,1}B_{1,0} - (1/\sqrt{2})A_{1,0}B_{1,1}$ $\{A_1 \otimes B_1\}_{1,0} = (1/\sqrt{2})A_{1,1}B_{1,-1} - (1/\sqrt{2})A_{1,-1}B_{1,1}$ $\{A_1 \otimes B_1\}_{1,-1} = (1/\sqrt{2})A_{1,0}B_{1,-1} - (1/\sqrt{2})A_{1,-1}B_{1,0}$
$K = 2$	second-rank tensor operators $\{A_1 \otimes B_1\}_{2,2} = A_{1,1}B_{1,1}$ $\{A_1 \otimes B_1\}_{2,1} = (1/\sqrt{2})A_{1,1}B_{1,0} + (1/\sqrt{2})A_{1,0}B_{1,1}$ $\{A_1 \otimes B_1\}_{2,0} = (\sqrt{2/3})A_{1,0}B_{1,0} + (1/\sqrt{6})(A_{1,1}B_{1,-1} + A_{1,-1}B_{1,1})$ $\{A_1 \otimes B_1\}_{2,-1} = (1/\sqrt{2})A_{1,-1}B_{1,0} + (1/\sqrt{2})A_{1,0}B_{1,-1}$ $\{A_1 \otimes B_1\}_{2,-2} = A_{1,-1}B_{1,-1}$

The usual scalar product of two vector operators

$$(\vec{A} \cdot \vec{B}) = A_x B_x + A_y B_y + A_z B_z$$

is related to the tensor product as

$$\{A_1 \otimes B_1\}_{0,0} = -(1/\sqrt{3})(\vec{A} \cdot \vec{B})$$

A combination of frequent interest is

$$c = \vec{A} \cdot \vec{\bar{T}} \cdot \vec{B}$$

where $\vec{A}$ and $\vec{B}$ are physical vectors (spins, fields) and $\vec{\bar{T}}$ is a second-rank tensor. In terms of the irreducible spherical tensor components it becomes

$$\begin{aligned} \vec{A} \cdot \vec{\bar{T}} \cdot \vec{B} &= \sum_{l=0}^2 (2l+1)^{1/2} (T_l \cdot \{A \otimes B\}_l) \\ &= (T_0 \cdot \{A \otimes B\}_0) + \sqrt{3}(T_1 \cdot \{A \otimes B\}_1) + \sqrt{5}(T_2 \cdot \{A \otimes B\}_2) \end{aligned}$$

The components of T_l and $\{A \otimes B\}_l$ are given in Table 1.14.

The irreducible tensor operators obey the following properties [13]:

- (1) commutation relation with the third component of the total angular momentum operator

$$[\hat{J}_z, \hat{T}_{lm}] = m\hbar \hat{T}_{lm}$$

(2) commutation relation with shift operators

$$[\hat{J}_{\pm}, \hat{T}_{lm}] = \sqrt{(l \mp m)(l \pm m + 1)} \hbar \hat{T}_{l, m \pm 1}$$

(3) adjoint tensor operators are

$$\tilde{T}_{lm} = (-1)^m (T_{l, -m})^+$$

(4) the *Wigner–Eckart theorem* states that the matrix element of a tensor operator can be expressed through a more fundamental quantity—the *reduced matrix element* (which is free of projections of angular momenta)—and a coupling coefficient (e.g. 3j-symbol)

$$\langle \alpha j m | \hat{T}_{KM} | \alpha' j' m' \rangle = \langle \alpha j || \hat{T}_K || \alpha' j' \rangle (-1)^{j-m} \begin{pmatrix} j & K & j' \\ -m & M & m' \end{pmatrix}$$

The conjugate of a reduced matrix element is

$$\langle \alpha j || \hat{T}_K || \alpha' j' \rangle^* = (-1)^{j'-j} \langle \alpha' j' || \hat{T}_K^+ || \alpha j \rangle$$

Having determined the reduced matrix element, one can easily evaluate all the matrix elements of a tensor operator.

As a consequence of the Wigner–Eckart theorem the *replacement theorem* holds true: a matrix element of any irreducible tensor operator can be expressed with the help of the matrix elements formed from the angular momenta and a ratio of the reduced matrix elements, hence

$$\langle \alpha j m | \hat{J}_{KM} | \alpha' j' m' \rangle = \langle \alpha j || \hat{J}_K || \alpha' j' \rangle (-1)^{j-m} \begin{pmatrix} j & K & j' \\ -m & M & m' \end{pmatrix}$$

and

$$\langle \alpha j m | \hat{T}_{KM} | \alpha' j' m' \rangle = \langle \alpha j m | \hat{J}_{KM} | \alpha' j' m' \rangle \frac{\langle \alpha j || \hat{T}_K || \alpha' j' \rangle}{\langle \alpha j || \hat{J}_K || \alpha' j' \rangle}$$

An advantage of this expression lies in the fact that the reduced matrix elements formed from the angular momenta $\langle \alpha j || \hat{J}_K || \alpha' j' \rangle$ are well known and tabulated.

One important note: there are several different transcriptions of the Wigner–Eckart theorem. The above formulation, used hereafter, is equivalent to the use of the Clebsch–Gordan coefficients

$$\langle \alpha j m | \hat{T}_{KM} | \alpha' j' m' \rangle = \langle \alpha j | \hat{T}_K | \alpha' j' \rangle (2j+1)^{-1/2} \langle j' K m' M | j m \rangle$$

and matches with the conventions of Judd [14] and Wybourne [15]. An alternative formulation was used by Brink and Satchler [16]

$$\langle \alpha j m | \hat{T}_{KM} | \alpha' j' m' \rangle = \langle \alpha j | \hat{T}_K | \alpha' j' \rangle' (-1)^{2K} \langle j' K m' M | j m \rangle$$

and Rose [4]

$$\langle \alpha j m | \hat{T}_{KM} | \alpha' j' m' \rangle = \langle \alpha j | \hat{T}_K | \alpha' j' \rangle'' \langle j' K m' M | j m \rangle$$

Thus the reduced matrix elements according to Rose, and followers [17], contain a constant factor $(2j+1)^{-1/2}$.

1.5.4 Reduced matrix elements of tensor operators

Of frequent interest is the need to evaluate matrix elements for a tensor product of two irreducible tensor operators

$$Z \equiv \langle j_1 j_2 J_{12} M_{12} | \{ \hat{T}_k \otimes \hat{T}_l \}_{KM} | j'_1 j'_2 J'_{12} M'_{12} \rangle$$

which can be converted into a reduced matrix element by applying the Wigner–Eckart theorem as

$$Z = \langle j_1 j_2 J_{12} | \{ \hat{T}_k \otimes \hat{T}_l \}_K | j'_1 j'_2 J'_{12} \rangle (-1)^{J_{12}-M_{12}} \begin{pmatrix} J_{12} & K & J'_{12} \\ -M_{12} & M & M'_{12} \end{pmatrix}$$

The reduced matrix element (free of projections of angular momenta) is evaluable according to the following *decoupling formula*

$$\begin{aligned} X_{kl;K} &\equiv \langle j_1 j_2 J_{12} | \{ \hat{T}_k \otimes \hat{T}_l \}_K | j'_1 j'_2 J'_{12} \rangle \\ &= \langle j_1 | \hat{T}_k | j'_1 \rangle \langle j_2 | \hat{T}_l | j'_2 \rangle [(2J_{12}+1)(2J'_{12}+1)(2K+1)]^{1/2} \\ &\quad \times \begin{Bmatrix} j_1 & j'_1 & k \\ j_2 & j'_2 & l \\ J_{12} & J'_{12} & K \end{Bmatrix} \end{aligned}$$

(Owing to the symmetry properties of the $9j$ -symbol another ordering of its indices may be equivalent.) This formula, in fact, represents a decoupling of the angular momenta because on the left side we have coupled angular

momenta (J_{12}, J'_{12}, K) whereas on the right side only reduced matrix elements among uncoupled angular momenta (j_1, k, j'_1) and (j_2, l, j'_2) are present. The main advantage of this formula is that, for the evaluation of matrix elements, we do not need an explicit form of the coupled wave functions. Moreover, this formula can be simplified or extended to some important cases. The coupling coefficients on the right side can be easily evaluated by standard techniques. It is assumed hereafter that the first irreducible tensor operator, $\hat{T}_k(j_1)$, acts on the vector space $|j_1 m_1\rangle$ and the second one, $\hat{T}_l(j_2)$, on the $|j_2 m_2\rangle$.

The matrix elements of a unit operator (of rank zero) are reduced as

$$\begin{aligned}\langle j_1 m_1 | \hat{1} | j_1 m_1 \rangle &= \langle j_1 \| \hat{1} \| j_1 \rangle (-1)^{2(j_1 - m_1)} \begin{pmatrix} j_1 & 0 & j_1 \\ -m_1 & 0 & m_1 \end{pmatrix} \\ &= \langle j_1 \| \hat{1} \| j_1 \rangle (2j_1 + 1)^{-1/2} = 1\end{aligned}$$

and thus the reduced matrix element of a unit operator is

$$\langle j_1 \| \hat{1} \| j_1 \rangle = (2j_1 + 1)^{1/2}$$

The reduced matrix elements of uncoupled angular momenta are collected in Table 1.15.

Let us apply the decoupling formula to several important cases.

Case 1. If the first tensor operator is a unit operator, ($\hat{T}_k = \hat{1}$, $k = 0$, $K = l$), then

$$\begin{aligned}X_{0l;l} &\equiv \langle j_1 j_2 J_{12} \| \hat{T}_l(j_2) \| j'_1 j'_2 J'_{12} \rangle \\ &= \langle j_1 \| \hat{1} \| j'_1 \rangle \langle j_2 \| \hat{T}_l(j_2) \| j'_2 \rangle [(2J_{12} + 1)(2J'_{12} + 1)(2l + 1)]^{1/2} \\ &\quad \times \begin{Bmatrix} j_1 & j'_1 & 0 \\ j_2 & j'_2 & l \\ J_{12} & J'_{12} & l \end{Bmatrix}\end{aligned}$$

TABLE 1.15
Some reduced matrix elements

Tensor rank	Matrix element $\langle J \ \hat{T}_k(J) \ J' \rangle$
$\hat{T}_0 = \hat{1}$	$\langle J \ \hat{1} \ J' \rangle = \delta_{J,J'} (2J + 1)^{1/2}$
$\hat{T}_1 = \vec{J}$	$\langle J \ \vec{J} \ J' \rangle = \delta_{J,J'} [J(J + 1)(2J + 1)]^{1/2} [\hbar]$
$\hat{T}_2 = \{\vec{J} \otimes \vec{J}\}_2$	$\langle J \ \{\vec{J} \otimes \vec{J}\}_2 \ J' \rangle = \delta_{J,J'} [(2J + 1)(2J + 3)(2J - 1)J(J + 1)/6]^{1/2} [\hbar^2]$

Now we can use a property that the $9j$ -symbol containing one zero collapses to the $6j$ -symbol

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & 0 \end{Bmatrix} = (-1)^{j_2+j_4+j_3+j_7} \delta_{j_3 j_6} \delta_{j_7 j_8} [(2j_3 + 1)(2j_7 + 1)]^{-1/2} \\ \times \begin{Bmatrix} j_1 & j_2 & j_3 \\ j_5 & j_4 & j_7 \end{Bmatrix}$$

(A $9j$ -symbol is invariant in the even permutation of rows and columns and in a reflection through one of the diagonals. A $6j$ -symbol is invariant by interchange of any two columns or by switching the upper and lower members of any two rows.) For the above arrangement of indices it holds true that

$$\begin{Bmatrix} f & f & 0 \\ d & c & e \\ b & a & e \end{Bmatrix} = (-1)^{b+c+e+f} [(2e + 1)(2f + 1)]^{-1/2} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix}$$

and then

$$X_{0l;l} = \delta_{j_1 j'_1} \langle j_1 \| \hat{1} \| j_1 \rangle \langle j_2 \| \hat{T}_l(j_2) \| j'_2 \rangle [(2J_{12} + 1)(2J'_{12} + 1)(2l + 1)]^{1/2} \\ \times [(2l + 1)(2j_1 + 1)]^{-1/2} (-1)^{j_1+j'_2+J_{12}+l} \begin{Bmatrix} J'_{12} & J_{12} & l \\ j_2 & j'_2 & j_1 \end{Bmatrix}$$

Taking into account the result for the reduced matrix element of a unit operator, a further simplification of this formula is possible

$$X_{0l;l} = \langle j_1 j_2 J_{12} \| \hat{T}_l(j_2) \| j'_1 j'_2 J'_{12} \rangle \\ = \delta_{j_1 j'_1} \langle j_2 \| \hat{T}_l(j_2) \| j'_2 \rangle [(2J_{12} + 1)(2J'_{12} + 1)]^{1/2} (-1)^{j_1+j'_2+J_{12}+l} \\ \times \begin{Bmatrix} J'_{12} & J_{12} & l \\ j_2 & j'_2 & j_1 \end{Bmatrix}$$

Case 2. When the indices of the angular momenta are interchanged ($\hat{T}_l = 1, l = 0, K = k$) then

$$\begin{aligned} X_{k0;k} &= \langle j_1 j_2 J_{12} \| \hat{T}_k(j_1) \| j'_1 j'_2 J'_{12} \rangle \\ &= \delta_{j_2 j'_2} \langle j_1 \| \hat{T}_k(j_1) \| j'_1 \rangle [(2J_{12} + 1)(2J'_{12} + 1)]^{1/2} (-1)^{j_1 + j_2 + J'_{12} + k} \\ &\quad \times \left\{ \begin{matrix} J'_{12} & J_{12} & k \\ j_1 & j'_1 & j_2 \end{matrix} \right\} \end{aligned}$$

Case 3. When both tensor operators are the unit operators ($\hat{T}_k = \hat{T}_l = \hat{1}, k = l = 0$) we get

$$\begin{aligned} X_{00;0} &\equiv \langle j_1 j_2 J_{12} \| \hat{1} \| j'_1 j'_2 J'_{12} \rangle \\ &= \delta_{j_1 j'_1} \delta_{j_2 j'_2} \langle j_1 \| \hat{1} \| j_1 \rangle \langle j_2 \| \hat{1} \| j_2 \rangle \\ &\quad \times [(2J_{12} + 1)(2J_{12} + 1)]^{1/2} [2j_1 + 1]^{-1/2} (-1)^{j_1 + j_2 + J_{12}} \\ &\quad \times \left\{ \begin{matrix} J_{12} & J_{12} & 0 \\ j_2 & j_2 & j_1 \end{matrix} \right\} \end{aligned}$$

and a special formula for the 6j-symbol containing one zero is applicable

$$\left\{ \begin{matrix} c & c & 0 \\ b & b & a \end{matrix} \right\} = (-1)^{a+b+c} [(2b+1)(2c+1)]^{-1/2}$$

Then it holds true that

$$\begin{aligned} X_{00;0} &= \delta_{j_1 j'_1} \delta_{j_2 j'_2} \langle j_1 \| \hat{1} \| j_1 \rangle \langle j_2 \| \hat{1} \| j_2 \rangle \\ &\quad \times [(2J_{12} + 1)(2J_{12} + 1)]^{1/2} [2j_1 + 1]^{-1/2} (-1)^{2(j_1 + j_2 + J_{12})} \\ &\quad \times [(2j_2 + 1)(2J_{12} + 1)]^{-1/2} \\ &= \delta_{j_1 j'_1} \delta_{j_2 j'_2} \langle j_1 \| \hat{1} \| j_1 \rangle \langle j_2 \| \hat{1} \| j_2 \rangle [2J_{12} + 1]^{1/2} [(2j_1 + 1)(2j_2 + 1)]^{-1/2} \end{aligned}$$

and consequently we get the final expression

$$X_{00;0} = \langle j_1 j_2 J_{12} \| \hat{1} \| j'_1 j'_2 J'_{12} \rangle = \delta_{j_1 j'_1} \delta_{j_2 j'_2} [2J_{12} + 1]^{1/2}$$

Case 4. When the first-rank tensor is an angular momentum operator ($\hat{T}_k = \hat{1}, k = 0, \hat{T}_l = \hat{J}(j_2), l = 1$) then its reduced matrix elements become

$$\begin{aligned}
X_{01;1} &= \langle j_1 j_2 J_{12} \| \vec{J}(j_2) \| j'_1 j'_2 J'_{12} \rangle \\
&= \delta_{j_1 j'_1} \langle j_2 \| \vec{J}(j_2) \| j'_2 \rangle [(2J_{12} + 1)(2J'_{12} + 1)]^{1/2} (-1)^{j_1 + j'_2 + J_{12} + 1} \\
&\quad \times \begin{Bmatrix} J'_{12} & J_{12} & 1 \\ j_2 & j'_2 & j_1 \end{Bmatrix}
\end{aligned}$$

After insertion of the reduced matrix elements for uncoupled angular momenta according to Table 1.15 a further simplification is obtained

$$\begin{aligned}
X_{01;1} &= \delta_{j_1 j'_1} \delta_{j_2 j'_2} [j_2(j_2 + 1)(2j_2 + 1)]^{1/2} [(2J_{12} + 1)] (-1)^{j_1 + j_2 + J_{12} + 1} \\
&\quad \times \begin{Bmatrix} J'_{12} & J_{12} & 1 \\ j_2 & j_2 & j_1 \end{Bmatrix} [\hbar]
\end{aligned}$$

For the given 6j-symbol a special closed formula exists [8]. The triangular condition for the non-zero 6j-symbol yields a restriction $J'_{12} = J_{12}, J_{12} \pm 1$.

Case 5. For the squared angular momentum operator ($\hat{T}_k = \hat{1}, k = 0$, $\hat{T}_2(j_2) = \{\vec{j}_2 \otimes \vec{j}_2\}_2, l = 2$) we get

$$\begin{aligned}
X_{02;2} &= \langle j_1 j_2 J_{12} \| \hat{T}_2(j_2) \| j'_1 j'_2 J'_{12} \rangle \\
&= \delta_{j_1 j'_1} \langle j_2 \| \hat{T}_2(j_2) \| j'_2 \rangle [(2J_{12} + 1)(2J'_{12} + 1)]^{1/2} (-1)^{j_1 + j'_2 + J_{12} + 2} \\
&\quad \times \begin{Bmatrix} J'_{12} & J_{12} & 2 \\ j_2 & j'_2 & j_1 \end{Bmatrix}
\end{aligned}$$

which after the substitution

$$\langle j_2 \| \hat{T}_2(j_2) \| j'_2 \rangle = \delta_{j_2 j'_2} [(2j_2 + 1)(2j_2 + 3)(2j_2 - 1)j_2(j_2 + 1)/6]^{1/2} [\hbar^2]$$

transforms to

$$\begin{aligned}
X_{02;2} &= \langle j_1 j_2 J_{12} \| \hat{T}_2(j_2) \| j'_1 j'_2 J'_{12} \rangle \\
&= \delta_{j_1 j'_1} \delta_{j_2 j'_2} [(2j_2 + 1)(2j_2 + 3)(2j_2 - 1)j_2(j_2 + 1)/6]^{1/2} \\
&\quad \times [(2J_{12} + 1)(2J'_{12} + 1)]^{1/2} (-1)^{j_1 + j'_2 + J_{12} + 2} \begin{Bmatrix} J'_{12} & J_{12} & 2 \\ j_2 & j'_2 & j_1 \end{Bmatrix} [\hbar^2]
\end{aligned}$$

For the given 6j-symbol again a special closed formula exists [8]. The triangular condition for the non-zero 6j-symbol yields a restriction $J'_{12} = J_{12}, J_{12} \pm 1, J_{12} \pm 2$.

Case 6. A scalar product ($K = 0$) of two angular momenta (first-rank tensors, $k = l = 1$) is symbolised as follows

$$\vec{J}(A) \cdot \vec{J}(B) = -\sqrt{3}\{J_1(A) \otimes J_1(B)\}_{0,0}$$

and can be met in the isotropic exchange interaction for two centres

$$\hat{H}_{AB}^{\text{ex}} = -J_{AB} \vec{S}(A) \cdot \vec{S}(B) [\hbar^{-2}]$$

or the spin-orbit coupling at the same centre

$$\hat{H}_i^{\text{so}} = \xi \vec{l}_i \cdot \vec{s}_i [\hbar^{-2}]$$

Its matrix element is reduced via the formula

$$\begin{aligned} Z_{11;0} &= \langle j_A j_B J_{AB} M_{AB} | \{J_1(A) \otimes J_1(B)\}_{0,0} | j_A j_B J'_{AB} M'_{AB} \rangle \\ &= \langle j_A j_B J_{AB} \| \{J_1(A) \otimes J_1(B)\}_0 \| j_A j_B J'_{AB} \rangle \\ &\quad \times \delta_{J_{AB}, J'_{AB}} \delta_{M_{AB}, M'_{AB}} (-1)^{J_{AB} - M_{AB}} \begin{pmatrix} J_{AB} & 0 & J_{AB} \\ -M_{AB} & 0 & M_{AB} \end{pmatrix} \end{aligned}$$

where the special $3j$ -symbol yields a result

$$\begin{pmatrix} J_{AB} & 0 & J_{AB} \\ -M_{AB} & 0 & M_{AB} \end{pmatrix} = (2J_{AB} + 1)^{-1/2}$$

The corresponding reduced matrix element is decoupled using a $9j$ -symbol as

$$\begin{aligned} X_{11;0} &\equiv \langle j_A j_B J_{AB} \| \{J_1(A) \otimes J_1(B)\}_0 \| j_A j_B J'_{AB} \rangle \\ &= \langle j_A \| J_1(A) \| j_A \rangle \langle j_B \| J_1(B) \| j_B \rangle [(2J_{AB} + 1)(2J'_{AB} + 1)]^{1/2} \\ &\quad \times \begin{Bmatrix} j_A & j_A & 1 \\ j_B & j_B & 1 \\ J_{AB} & J'_{AB} & 0 \end{Bmatrix} \end{aligned}$$

Since the $9j$ -symbol contains one zero, it is simplified to a $6j$ -symbol

$$\left\{ \begin{matrix} j_A & j_A & 1 \\ j_B & j_B & 1 \\ J_{AB} & J'_{AB} & 0 \end{matrix} \right\} = \delta_{J_{AB}, J'_{AB}} (-1)^{j_A+j_B+J_{AB}+1} [(2 \cdot 1 + 1)(2J_{AB} + 1)]^{-1/2} \\ \times \left\{ \begin{matrix} j_A & j_A & 1 \\ j_B & j_B & J_{AB} \end{matrix} \right\}$$

The latter can be rearranged and expressed through a special formula as

$$\left\{ \begin{matrix} j_A & j_A & 1 \\ j_B & j_B & J_{AB} \end{matrix} \right\} = \left\{ \begin{matrix} 1 & j_A & j_A \\ J_{AB} & j_B & j_B \end{matrix} \right\} = \left\{ \begin{matrix} J_{AB} & j_A & j_B \\ 1 & j_B & j_A \end{matrix} \right\} \\ = (-1)^{J_{AB}+j_A+j_B} \frac{2[J_{AB}(J_{AB}+1) - j_A(j_A+1) - j_B(j_B+1)]}{[2j_A(2j_A+1)(2j_A+2)2j_B(2j_B+1)(2j_B+2)]^{1/2}}$$

Then we end up with the expression for the reduced matrix element

$$X_{11;0} = (-1) \langle j_A \| J_1(A) \| j_A \rangle \langle j_B \| J_1(B) \| j_B \rangle [(2J_{AB} + 1)/3]^{1/2} \\ \times \frac{2[J_{AB}(J_{AB}+1) - j_A(j_A+1) - j_B(j_B+1)]}{[2j_A(2j_A+1)(2j_A+2)2j_B(2j_B+1)(2j_B+2)]^{1/2}} \\ = (-1) [j_A(j_A+1)(2j_A+1)]^{1/2} [j_B(j_B+1)(2j_B+1)]^{1/2} \\ \times [(2J_{AB} + 1)/3]^{1/2} \\ \times \frac{2[J_{AB}(J_{AB}+1) - j_A(j_A+1) - j_B(j_B+1)]}{[2j_A(2j_A+1)(2j_A+2)2j_B(2j_B+1)(2j_B+2)]^{1/2}} [\hbar^2]$$

or

$$X_{11;0} = \delta_{J_{AB}, J'_{AB}} \frac{(-1)}{2\sqrt{3}} [(2J_{AB} + 1)]^{1/2} [J_{AB}(J_{AB} + 1) - j_A(j_A + 1) - j_B(j_B + 1)] [\hbar^2]$$

and the formula for the matrix element under consideration becomes

$$Z_{11;0} = \delta_{J_{AB}, J'_{AB}} \delta_{M_{AB}, M'_{AB}} (-1)^{J_{AB}-M_{AB}+1} \frac{1}{2\sqrt{3}} [J_{AB}(J_{AB} + 1) - j_A(j_A + 1) - j_B(j_B + 1)]$$

This result, however, can be obtained by more elementary approaches. The main goal of the procedure just followed lies in the fact that this can be easily

generalised for more complex problems where the matrix elements of a compound tensor operator consisting of the direct products of several angular momenta are considered.

Case 7. A vector product ($K = 1$) of two angular momenta (first-rank tensors) is

$$\begin{aligned} X_{11;1} &\equiv \langle j_A j_B J_{AB} \| \{J_1(A) \otimes J_1(B)\}_1 \| j_A j_B J'_{AB} \rangle \\ &= \langle j_A \| J_1(A) \| j_A \rangle \langle j_B \| J_1(B) \| j_B \rangle [(2J_{AB} + 1)(2J'_{AB} + 1)(2 \cdot 1 + 1)]^{1/2} \\ &\quad \times \begin{Bmatrix} j_A & j_A & 1 \\ j_B & j_B & 1 \\ J_{AB} & J'_{AB} & 1 \end{Bmatrix} \end{aligned}$$

The $9j$ -symbol adopts a special form and collapses to the $6j$ -symbol

$$\begin{aligned} \begin{Bmatrix} f & f & 1 \\ d & c & e \\ b & a & e \end{Bmatrix} &= \begin{Bmatrix} f & f & 0 \\ d & c & e \\ b & a & e \end{Bmatrix} \frac{d(d+1) + a(a+1) - b(b+1) - c(c+1)}{2[f(f+1)e(e+1)]^{1/2}} \\ &= \frac{(-1)^{b+c+e+f}}{[(2e+1)(2f+1)]^{1/2}} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} \\ &\quad \times \frac{d(d+1) + a(a+1) - b(b+1) - c(c+1)}{2[f(f+1)e(e+1)]^{1/2}} \end{aligned}$$

Case 8. A tensor product ($K = 2$) of two angular momenta (first-rank tensors) is

$$\begin{aligned} X_{11;2} &\equiv \langle j_A j_B J_{AB} \| \{J_1(A) \otimes J_1(B)\}_2 \| j_A j_B J'_{AB} \rangle \\ &= \langle j_A \| J_1(A) \| j_A \rangle \langle j_B \| J_1(B) \| j_B \rangle [(2J_{AB} + 1)(2J'_{AB} + 1)(2 \cdot 2 + 1)]^{1/2} \\ &\quad \times \begin{Bmatrix} j_A & j_A & 1 \\ j_B & j_B & 1 \\ J_{AB} & J'_{AB} & 2 \end{Bmatrix} \end{aligned}$$

The $9j$ -symbol after one permutation of rows has a sign factor

$$\{9j\} = \begin{Bmatrix} A & A & 1 \\ B & B & 1 \\ S & S & 2 \end{Bmatrix} = (-1)^{2A+2B+2S+4} \begin{Bmatrix} S & S & 2 \\ B & B & 1 \\ A & A & 1 \end{Bmatrix}$$

and with the help of the expansion formula [8] it adopts a special form of [18]

$$\{9j\} = \frac{(-1)^{2A+2B+2S+4}(-1)^{2S}}{5 \begin{Bmatrix} 2 & S & S \\ S & 1 & 1 \end{Bmatrix}} \left[\begin{Bmatrix} A & S & B \\ S & A & 1 \end{Bmatrix} \begin{Bmatrix} B & S & A \\ S & B & 1 \end{Bmatrix} \right. \\ \left. + \frac{(-1)^{A+B+S+1}}{3(2S+1)} \begin{Bmatrix} A & B & S \\ B & A & 1 \end{Bmatrix} \right]$$

The sign factor is ineffective when $S = A + B$ and then a closed formula is obtained

$$\{9j\} = \frac{-3[A(A+1) - B(B+1)]^2 + S(S+1)[S(S+1) + 2A(A+1) + 2B(B+1)]}{2[(2S+3)(2S-1)S(S+1)]^{1/2}[30(2S+1)]^{1/2}[A(A+1)(2A+1)B(B+1)(2B+1)]^{1/2}}$$

Results for some reduced matrix elements are compiled in Table 1.16.

For the coupling of three commuting angular momenta one can apply the following formula

$$\begin{aligned} & \left\langle j_1 j_2 j_3 J_{123} \left\| \left\{ \left\{ \hat{T}_{k_1} \otimes \hat{T}_{k_2} \right\}_{k_{12}} \otimes \hat{T}_{k_3} \right\}_{k_{123}} \right\| j'_1 j'_2 j'_3 J'_{123} \right\rangle \\ &= \langle j_1 \| \hat{T}_{k_1} \| j'_1 \rangle \langle j_2 \| \hat{T}_{k_2} \| j'_2 \rangle \langle j_3 \| \hat{T}_{k_3} \| j'_3 \rangle \\ & \times [(2j_{12} + 1)(2j'_{12} + 1)(2k_{12} + 1)]^{1/2} \begin{Bmatrix} j_1 & j'_1 & k_1 \\ j_2 & j'_2 & k_2 \\ j_{12} & j'_{12} & k_{12} \end{Bmatrix} \\ & \times [(2J_{123} + 1)(2J'_{123} + 1)(2k_{123} + 1)]^{1/2} \begin{Bmatrix} j_{12} & j'_{12} & k_{12} \\ j_3 & j'_3 & k_3 \\ J_{123} & J'_{123} & k_{123} \end{Bmatrix} \end{aligned}$$

and, analogously, for the coupling of four angular momenta one gets

$$R = \left\langle j_1 j_2 j_3 j_4 J_{1234} \left\| \left\{ \left\{ \left\{ \hat{T}_{k_1} \otimes \hat{T}_{k_2} \right\}_{k_{12}} \otimes \hat{T}_{k_3} \right\}_{k_{123}} \otimes \hat{T}_{k_4} \right\}_{k_{1234}} \right\| \right. \\ \left. j'_1 j'_2 j'_3 j'_4 J'_{1234} \right\rangle$$

TABLE 1.16
Some compound reduced matrix elements^a

Reduced matrix element	Expression
$\langle j_1 j_2 J_{12} \ \hat{1} \ j'_1 j'_2 J'_{12} \rangle$	$\delta_{j_1 j'_1} \delta_{j_2 j'_2} (2J_{12} + 1)^{1/2}$
$\langle j_1 j_2 J \ \hat{T}_k(j_1) \ j'_1 j'_2 J' \rangle$ for $\hat{T}_k(j_1)$ commuting with $\vec{j}_2$	$\delta_{j_2 j'_2} \langle j_1 \ \hat{T}_k(j_1) \ j'_1 \rangle [(2J + 1)(2J' + 1)]^{1/2} (-1)^{j_1 + j_2 + J' + k} \begin{Bmatrix} J' & J & k \\ j_1 & j'_1 & j_2 \end{Bmatrix}$
$\langle j_1 j_2 J \ \hat{T}_l(j_2) \ j'_1 j'_2 J' \rangle$ for $\hat{T}_l(j_2)$ commuting with $\vec{j}_1$	$\delta_{j_1 j'_1} \langle j_2 \ \hat{T}_l(j_2) \ j'_2 \rangle [(2J + 1)(2J' + 1)]^{1/2} (-1)^{j_1 + j'_2 + J + l} \begin{Bmatrix} J' & J & l \\ j_2 & j'_2 & j_1 \end{Bmatrix}$
$\frac{\langle j_1 j_2 J \ \vec{j}_1 \ j_1 j_2 J \rangle}{\langle J \ \vec{J} \ J \rangle}$	$[J(J + 1) + j_1(j_1 + 1) - j_2(j_2 + 1)]/[2J(J + 1)]$
$\frac{\langle j_1 j_2 J \ \vec{j}_2 \ j_1 j_2 J \rangle}{\langle J \ \vec{J} \ J \rangle}$	$[J(J + 1) + j_2(j_2 + 1) - j_1(j_1 + 1)]/[2J(J + 1)]$
$\langle j_1 j_2, J + 1 \ \vec{j}_1 \ j_1 j_2, J \rangle = -\langle j_1 j_2, J + 1 \ \vec{j}_2 \ j_1 j_2, J \rangle$	$(1/2)\{[(j_1 - j_2 + J + 1)(-j_1 + j_2 + J + 1)(j_1 + j_2 - J)(j_1 + j_2 + J + 2)]/(J + 1)\}^{1/2} [\hbar]$
$\langle j_1 j_2, J - 1 \ \vec{j}_1 \ j_1 j_2, J \rangle = -\langle j_1 j_2, J - 1 \ \vec{j}_2 \ j_1 j_2, J \rangle$	$-(1/2)\{[(j_1 - j_2 + J)(-j_1 + j_2 + J)(j_1 + j_2 - J + 1)(j_1 + j_2 + J + 1)]/J\}^{1/2} [\hbar]$
$\frac{\langle j_1 j_2 J \ (\vec{j}_1 \otimes \vec{j}_1)_2 \ j_1 j_2 J \rangle}{\langle J \ (\vec{J} \otimes \vec{J})_2 \ J \rangle}$	$\{3[j_2(j_2 + 1) - j_1(j_1 + 1) - J(J + 1)]^2 + 3[j_2(j_2 + 1) - j_1(j_1 + 1) - J(J + 1)] - 4J(J + 1)j_1(j_1 + 1)\}/\{2(2J + 3)(2J - 1)J(J + 1)\}$

TABLE 1.16
Some compound reduced matrix elements^a (*contd.*)

Reduced matrix element	Expression
$\frac{\langle j_1 j_2 J \ \vec{U}_2 \otimes \vec{J}_2 \ j_1 j_2 J \rangle}{\langle J \ \{\vec{J} \otimes \vec{J}\}_2 \ J \rangle}$	$\{3[j_1(j_1 + 1) - j_2(j_2 + 1) - J(J + 1)]^2 + 3[j_1(j_1 + 1) - j_2(j_2 + 1) - J(J + 1)] - 4J(J + 1)j_2(j_2 + 1)\} / \{2(2J + 3)(2J - 1)J(J + 1)\}$
$\langle j_1 j_2, J + 1 \ \vec{U}_1 \otimes \vec{J}_1 \ j_1 j_2, J \rangle$	$+ (1/2)\{[(j_1 + j_2 + J + 2)(j_1 + j_2 - J)(j_1 - j_2 + J + 1) \times (-j_1 + j_2 + J + 1)] / [2(J + 2)J(J + 1)]\}^{1/2} [J(J + 2) + j_1(j_1 + 1) - j_2(j_2 + 1)][\hbar^2]$
$\langle j_1 j_2, J - 1 \ \vec{U}_1 \otimes \vec{J}_1 \ j_1 j_2, J \rangle$	$- (1/2)\{[(j_1 - j_2 + J)(-j_1 + j_2 + J)(j_1 + j_2 - J + 1) \times (j_1 + j_2 + J + 1)] / [2(J + 1)(J - 1)J]\}^{1/2} [(J - 1)(J + 1) + j_1(j_1 + 1) - j_2(j_2 + 1)][\hbar^2]$
$\langle j_1 j_2, J + 1 \ \vec{U}_2 \otimes \vec{J}_2 \ j_1 j_2, J \rangle$	$- (1/2)\{[(j_1 + j_2 + J + 2)(j_1 + j_2 - J)(j_1 - j_2 + J + 1) \times (j_2 - j_1 + J + 1)] / [2(J + 2)J(J + 1)]\}^{1/2} [J(J + 2) - j_1(j_1 + 1) + j_2(j_2 + 1)][\hbar^2]$
$\langle j_1 j_2, J - 1 \ \vec{U}_2 \otimes \vec{J}_2 \ j_1 j_2, J \rangle$	$+ (1/2)\{[(j_1 - j_2 + J)(-j_1 + j_2 + J)(j_1 + j_2 - J + 1) \times (j_1 + j_2 + J + 1)] / [2(J + 1)(J - 1)J]\}^{1/2} [(J - 1)(J + 1) - j_1(j_1 + 1) + j_2(j_2 + 1)][\hbar^2]$
$\langle j_1 j_2, J + 2 \ \vec{U}_1 \otimes \vec{J}_1 \ j_1 j_2, J \rangle$ $= \langle j_1 j_2, J + 2 \ \vec{U}_2 \otimes \vec{J}_2 \ j_1 j_2, J \rangle$	$+ (1/4)\{[(j_1 + j_2 + J + 3)(j_1 + j_2 + J + 2) \times (j_1 - j_2 + J + 2)(-j_1 + j_2 + J + 2)(j_1 - j_2 + J + 1) \times (-j_1 + j_2 + J + 1)(j_1 + j_2 - J)(j_1 + j_2 - J - 1)] / [(J + 2)(2J + 3)(J + 1)]\}^{1/2} [\hbar^2]$

$$\begin{aligned}
& \langle j_1 j_2, J-2 \parallel \vec{U}_1 \otimes \vec{J}_1 \rangle_2 \parallel j_1 j_2, J \rangle \\
&= \langle j_1 j_2, J-2 \parallel \vec{U}_2 \otimes \vec{J}_2 \rangle_2 \parallel j_1 j_2, J \rangle \\
&\quad + (1/4) \{ [(j_1 + j_2 + J + 1)(j_1 + j_2 + J)(j_1 - j_2 + J)(-j_1 + j_2 + J)(j_1 - j_2 + J - 1) \\
&\quad \times (-j_1 + j_2 + J - 1)(j_1 + j_2 - J + 2)(j_1 + j_2 - J + 1)] / [J(2J - 1)(J - 1)] \}^{1/2} [\hbar^2]
\end{aligned}$$

^a If the substitution $J = 0$ makes a reduced matrix element indeterminate, the expression is equal to zero. In Rose's convention [4] the reduced matrix elements should be multiplied by $(2J + 1)^{-1/2}$. Notice that $\langle J \parallel \hat{T}_K \parallel J + 1 \rangle = -\langle J + 1 \parallel (\hat{T}_K)^+ \parallel J \rangle$.

$$\begin{aligned}
&= \langle j_1 \| \hat{T}_{k_1} \| j'_1 \rangle \langle j_2 \| \hat{T}_{k_2} \| j'_2 \rangle \langle j_3 \| \hat{T}_{k_3} \| j'_3 \rangle \langle j_4 \| \hat{T}_{k_4} \| j'_4 \rangle \\
&\quad \times [(2j_{12} + 1)(2j'_{12} + 1)(2k_{12} + 1)]^{1/2} \\
&\quad \times [(2j_{123} + 1)(2j'_{123} + 1)(2k_{123} + 1)]^{1/2} \\
&\quad \times [(2J_{1234} + 1)(2J'_{1234} + 1)(2k_{1234} + 1)]^{1/2} \\
&\quad \times \begin{Bmatrix} j_1 & j'_1 & k_1 \\ j_2 & j'_2 & k_2 \\ j_{12} & j'_{12} & k_{12} \end{Bmatrix} \begin{Bmatrix} j_{12} & j'_{12} & k_{12} \\ j_3 & j'_3 & k_3 \\ j_{123} & j'_{123} & k_{123} \end{Bmatrix} \begin{Bmatrix} j_{123} & j'_{123} & k_{123} \\ j_4 & j'_4 & k_4 \\ J_{1234} & J'_{1234} & k_{1234} \end{Bmatrix}
\end{aligned}$$

The order of the coupling can be changed, say

$$\begin{aligned}
R &= \left\langle j_1 j_2 j_{12} j_3 j_4 j_{34} J_{1234} \left\| \left\{ \left\{ \hat{T}_{k_1} \otimes \hat{T}_{k_2} \right\}_{k_{12}} \otimes \left\{ \hat{T}_{k_3} \otimes \hat{T}_{k_4} \right\}_{k_{34}} \right\}_{k_{1234}} \right\| \right. \\
&\quad \left. j'_1 j'_2 j'_{12} j'_3 j'_4 j'_{34} J'_{1234} \right\rangle \\
&= \langle j_1 \| \hat{T}_{k_1} \| j'_1 \rangle \langle j_2 \| \hat{T}_{k_2} \| j'_2 \rangle \langle j_3 \| \hat{T}_{k_3} \| j'_3 \rangle \langle j_4 \| \hat{T}_{k_4} \| j'_4 \rangle \\
&\quad \times [(2j_{12} + 1)(2j'_{12} + 1)(2k_{12} + 1)]^{1/2} \\
&\quad \times [(2j_{34} + 1)(2j'_{34} + 1)(2k_{34} + 1)]^{1/2} \\
&\quad \times [(2J_{1234} + 1)(2J'_{1234} + 1)(2k_{1234} + 1)]^{1/2} \\
&\quad \times \begin{Bmatrix} j_1 & j'_1 & k_1 \\ j_2 & j'_2 & k_2 \\ j_{12} & j'_{12} & k_{12} \end{Bmatrix} \begin{Bmatrix} j_3 & j'_3 & k_3 \\ j_4 & j'_4 & k_4 \\ j_{34} & j'_{34} & k_{34} \end{Bmatrix} \begin{Bmatrix} j_{12} & j'_{12} & k_{12} \\ j_{34} & j'_{34} & k_{34} \\ J_{1234} & J'_{1234} & k_{1234} \end{Bmatrix}
\end{aligned}$$

1.6 MOLECULAR SYMMETRY

Molecular symmetry originates in the fact that there exist symmetry operations (transformations of the nuclear coordinates) which transform the molecule into a nuclear configuration identical with an initial one. The symmetry elements (axis, plane, inversion centre) remain unchanged. Molecules belong to the point groups of symmetry as all the symmetry operations have at least one point in common (this point is not necessarily identified with any atom of the molecule) [5, 12, 19–38].

A brief summary of the properties of the symmetry point groups is presented in Table 1.17. Some more definitions follow:

- (1) a *subgroup* G' is a set of elements within a group G which, on their own, constitute a group;
- (2) two groups are *isomorphous* when there exists a one-to-one correspondence between their operations; they have the same defining relations and the same multiplication and character tables;
- (3) if there are two groups G_a and G_b , having only the identity in common and possessing elements $\hat{R}_a$ (for $a = 1, \dots, h_a$) and $\hat{R}_b$ (for $b = 1, \dots, h_b$), then the *direct product group* $G = G_a \otimes G_b$ is defined as the set of all distinct elements $\hat{R}_a \hat{R}_b = \hat{R}_b \hat{R}_a$ for all a and b .

The symmetry point groups, along with their important characteristics, are classified in Table 1.18.

A set of matrices $A(R_k)$, transforming coordinates in the same way as the symmetry operator $\hat{R}_k$, forms a *representation* Γ of the group G . The

TABLE 1.17
Elementary terms in symmetry point group theory

Term	Property	Note
Symmetry operation $\hat{R}_k$		Inverse operator $\hat{R}_k^{-1}$
$\hat{E}$, or $\hat{I}$	identity	$\hat{E}$
$\hat{C}_n$	rotation about angle $2\pi/n$	$\hat{C}_n^{n-k}$ for $\hat{C}_n^k$
$\hat{\sigma}(\hat{\sigma}_h, \hat{\sigma}_v, \hat{\sigma}_d)$	mirror plane (horizontal, vertical, diagonal)	$\hat{\sigma}$
$\hat{i}$ or $\hat{S}_2$	inverse centre	$\hat{i}$
$\hat{S}_n = \hat{\sigma}_h \hat{C}_n$	rotation followed by the mirror plane	$\hat{S}_n^{n-k}$ for $\hat{S}_n^k$
Properties of the symmetry group G of order h		
—existence of a product	$\hat{R}_i \hat{R}_j = \hat{R}_k$	$(\hat{R}_i, \hat{R}_j, \hat{R}_k) \in G$
—associative law	$\hat{R}_i(\hat{R}_j \hat{R}_k) = (\hat{R}_i \hat{R}_j) \hat{R}_k$	
—existence of identity	$\hat{R}_k \hat{E} = \hat{E} \hat{R}_k = \hat{R}_k$	
—existence of inversion	$\hat{R}_k \hat{R}_k^{-1} = \hat{R}_k^{-1} \hat{R}_k = \hat{E}$	$(\hat{R}_k, \hat{R}_k^{-1}) \in G$
Class T of the group G		
—a set of operators obeying	$\hat{R}_i = \hat{R}_s^{-1} \hat{R}_j \hat{R}_s$	$(\hat{R}_i, \hat{R}_j) \in T, \hat{R}_s \in G$
Representation Γ of the group G		
—existence of transformation matrices	$\hat{R}_k \Rightarrow A(R_k)$	for $k \in \langle 1, h \rangle$
—action on the basis $(f_1, \dots, f_l)$	$\hat{R}_k f_m = \sum_{n=1}^l [A(R_k)]_{nm} f_n$	for $k \in \langle 1, h \rangle$ and $m \in \langle 1, l \rangle$
—properties of matrices	$A(R_i)A(R_j) = A(R_k)$	when $\hat{R}_i \hat{R}_j = \hat{R}_k$, for $k \in \langle 1, h \rangle$
—dimension of the representation	$l = \text{dimension of } A$	
—equivalent representations	$B(R_k) = U^{-1} A(R_k) U$	$U = \text{unitary matrix, } k \in \langle 1, h \rangle$

TABLE 1.18
Symmetry point groups of molecules

Type, symbol	Symmetry operations	Order h	Number of IR	Notes
Nonaxial				
C_1	$\hat{E}$	1	1	$C_1 = C$
C_s	$\hat{E}, \hat{\sigma}_h$	2	2	$C_s = C_{1h} = C_{1v} = S_1$
C_i	$\hat{E}, \hat{i}$	2	2	$C_i = S_2$
Axial				
—cyclic				
C_n	$\hat{E}, \hat{C}_n$	n	n	$n = 2, 3, \dots$
S_{2n}	$\hat{E}, \hat{C}_n, \hat{S}_{2n}$	$2n$	$2n$	$S_6 = C_{3i}$
—noncyclic				
C_{nh}	$\hat{E}, \hat{C}_n, \hat{\sigma}_h, \hat{S}_n$	$2n$	$2n$	
C_{nv}	$\hat{E}, \hat{C}_n, n\hat{\sigma}_v$	$2n$	$(n+3)/2$ for odd n $(n+6)/2$ for even n	
—dihedral				
D_n	$\hat{E}, \hat{C}_n, n\hat{C}'_2$	$2n$	$(n+3)/2$ for odd n $(n+6)/2$ for even n ; $D_2 = V$	
D_{nh}	$\hat{E}, \hat{C}_n, n\hat{C}'_2, \hat{S}_n, \hat{\sigma}_h, n\hat{\sigma}_v$	$4n$	$n+3$ for odd n $n+6$ for even n ; $D_{2h} = V_h$	
D_{nd}	$\hat{E}, \hat{C}_n, n\hat{C}'_2, \hat{S}_{2n}, n\hat{\sigma}_d$	$4n$	$n+3$	$D_{nd} = S_{2nv}$; $D_{2d} = V_d$
—linear				
$C_{\infty v}$	$\hat{E}, \hat{C}_{\infty}, \infty\hat{\sigma}_v$	∞	∞	
$D_{\infty h}$	$\hat{E}, \hat{C}_{\infty}, \infty\hat{\sigma}_v, \hat{S}_{\infty}, \infty\hat{C}'_2$	∞	∞	
Cubic				
T	$\hat{E}, 4\hat{C}_3, 3\hat{C}_2$	12	4	
T_h	$\hat{E}, 4\hat{C}_3, 3\hat{C}_2, 4\hat{S}_6, 3\hat{\sigma}_v$	24	8	$T_h = C_i \otimes T$
T_d	$\hat{E}, 4\hat{C}_3, 3\hat{C}_2, 3\hat{S}_4, 6\hat{\sigma}_d$	24	5	regular tetrahedron
O	$\hat{E}, 4\hat{C}_3, 3\hat{C}_4, 6\hat{C}_2$	24	5	
O_h	$\hat{E}, 4\hat{C}_3, 3\hat{C}_4, 6\hat{C}_2, 3\hat{S}_4, 4\hat{S}_6, 3\hat{\sigma}_h, 6\hat{\sigma}_d$	48	10	$O_h = C_i \otimes O$ regular octahedron
Icosahedral				
I	$\hat{E}, 6\hat{C}_5, 10\hat{C}_3, 15\hat{C}_2$	60	5	
I_h	$\hat{E}, 6\hat{C}_5, 10\hat{C}_3, 15\hat{C}_2, 12\hat{S}_{10}, 10\hat{S}_6, 15\hat{\sigma}$	120	10	$I_h = C_i \otimes I$ regular icosahedron

representation is *reducible*, Γ_r , when by the same similarity transformation $\mathbf{U}$ a block-diagonal (bd) form of matrices $\mathbf{A}(R_k)$ is obtained

$$\mathbf{A}_{\text{bd}}(R_k) = \mathbf{U}^{-1} \mathbf{A}(R_k) \mathbf{U}$$

The reducible representation consists of *irreducible representations*. The decomposition of a reducible representation into its irreducible components may be written as follows

$$\Gamma_r = \sum_{\alpha} n_{\alpha} \Gamma_{\alpha}$$

where n_{α} is a multiplicity of unequivalent irreducible representations. Their orders obey the relationship

$$l_r = \sum_{\alpha} n_{\alpha} l_{\alpha}$$

where l_{α} is the dimension of the α th block $\mathbf{A}_{\alpha}$ in the reducible-representation matrix $\mathbf{A}_{\text{bd}}$. The matrix elements of irreducible representations (IR) satisfy the orthogonality relation

$$\sum_{k=1}^h [\mathbf{A}_{\alpha}(R_k)]_{\mu\nu} [\mathbf{B}_{\beta}(R_k)]_{\lambda\sigma} = h(l_{\alpha}l_{\beta})^{-1/2} \delta_{\alpha\beta} \delta_{\mu\lambda} \delta_{\nu\sigma}$$

The irreducible representations are fully characterised by their *characters*; these are formed by the traces of the transformation matrices

$$\chi_{\alpha}(R_k) = \text{Tr}\{\mathbf{A}_{\alpha}(R_k)\} = \sum_i^{l_{\alpha}} [A_{\alpha}(R_k)]_{ii} \quad [\text{for } k = 1, 2, \dots, h]$$

The characters are orthogonal one to another

$$\sum_{k=1}^h \chi_{\alpha}(R_k) \cdot \chi_{\beta}(R_k) = h \delta_{\alpha\beta}$$

The multiplicity n_{α} of the irreducible representation Γ_{α} in the reducible representation Γ_r is given by the formula

$$n_{\alpha} = \frac{1}{h} \sum_{k=1}^h \chi_{\alpha}(R_k) \cdot \chi_r(R_k)$$

The irreducible representations are denoted by two conventions: according to Mulliken (Table 1.19) or according to Bethe.

Of numerous applications of group theory the following theorem is of great importance: the matrix element

$$P_{ij} = \langle \Psi_i | \hat{P} | \Psi_j \rangle$$

is non-zero only when the double direct product of the irreducible representations involved

$$\Gamma(\Psi_i) \otimes \Gamma(\hat{P}) \otimes \Gamma(\Psi_j) = \Gamma_r = \Gamma_1 + \dots$$

(which is a reducible representation Γ_r) contains the totally symmetric representation Γ_1 of the relevant point group. Alternatively, the direct product of the irreducible representations of state vectors should contain a representation of the operator $\hat{P}$

$$\Gamma(\Psi_i) \otimes \Gamma(\Psi_j) = \Gamma_r = \sum_{\alpha} n_{\alpha} \Gamma_{\alpha} = \Gamma(\hat{P}) + \dots$$

The characters of the representations $\Gamma_{i \otimes j}$, spanned by a direct product $\Gamma_i \otimes \Gamma_j$, are obtained by multiplying corresponding characters of the contributing representations

$$\chi_{i \otimes j}(R_k) = \chi_i(R_k) \cdot \chi_j(R_k)$$

TABLE 1.19
Mulliken classification of irreducible representations

Representation	Name	Property: $\chi_{\alpha}(R_k) = m$	
		$\hat{R}_k$	m
<i>A</i>	one-dimensional	$\hat{C}_n$	+1
<i>B</i>	one-dimensional	$\hat{C}_n$	-1
<i>E</i>	two-dimensional		
<i>T</i> (or <i>F</i>)	three-dimensional		
<i>G</i> (or <i>U</i>)	four-dimensional		
<i>H</i> (or <i>V</i>)	five-dimensional		
<i>A'</i>	symmetric	$\hat{\sigma}_h$	+1
<i>A''</i>	antisymmetric	$\hat{\sigma}_h$	-1
<i>A_g</i>	even (gerade)		+1
<i>A_u</i>	odd (ungerade)		-1
<i>A₁</i> (or Σ^+), <i>E₁</i> (or Π)	symmetric	$\hat{\sigma}_v$	+1
<i>A₂</i> (or Σ^-), <i>E₂</i> (or Δ)	antisymmetric	$\hat{\sigma}_v$	-1
<i>A₃</i> , <i>E₃</i> (or Φ)		specific properties	

The reducible representation is then decomposed by using the formula

$$n_{\alpha} = \frac{1}{h} \sum_{k=1}^h \chi_{i \otimes j}(R_k) \cdot \chi_{\alpha}(R_k)$$

The direct product of irreducible representations follows the rules compiled in Table 1.20. For degenerate representations the rules are more complex and specific for the given group (Tables 1.21 and 1.22).

The direct product of a k -fold degenerate irreducible representation Γ_k with itself may be resolved into a symmetric component $[\Gamma_k^2]^+$ and an anti-symmetric component $[\Gamma_k^2]^-$

$$\Gamma_k \otimes \Gamma_k = [\Gamma_k^2]^+ + [\Gamma_k^2]^-$$

TABLE 1.20

Rules for the direct product of one-dimensional irreducible representations

Rule	Notes
(1) for representation A	
$A \otimes A = A$	
$A \otimes B = B$	
$A \otimes E_k = E_k$	
$A \otimes T = T$	
(2) for representation B	
$B \otimes B = A$	for all groups except D_2 and D_{2h}
$B \otimes B = B$	for groups D_2 and D_{2h} if their numerical indices are different
$B \otimes E = E$	
(3) for the lower indices	
$x_g \otimes x_g = x_g$	
$x_u \otimes x_g = x_u$	
$x_u \otimes x_u = x_g$	
(4) for the upper indices	
$x' \otimes x' = x'$	
$x'' \otimes x' = x''$	
$x'' \otimes x'' = x'$	
(5) for the numerical indices	
$x_1 \otimes x_1 = x_1$	
$x_1 \otimes x_2 = x_2$	
$x_2 \otimes x_2 = x_2$	for all groups except D_2 and D_{2h}
$x_1 \otimes x_2 = x_3$	for groups D_2 and D_{2h}
$x_2 \otimes x_3 = x_1$	for groups D_2 and D_{2h}
$x_1 \otimes x_3 = x_2$	for groups D_2 and D_{2h}

TABLE 1.21

Irreducible components of the direct product of multidimensional irreducible representations for axial groups $G_n = C_n, C_{nh}, C_{nv}, D_n, D_{nh}, D_{nd}, S_n^a$

Group	Irreducible representations				
$G_3 + S_6$	E				
E	$A_1, (A_2), E$				
$G_4 + D_{2d} - D_{4d}$	B	E			
B	A				
E	E	$A_1, (A_2), B_1, B_2$			
$G_5 + S_{10}$	E_1	E_2			
E_1	$A_1, (A_2), E_2$				
E_2	E_1, E_2	$A_1, (A_2), E_1$			
$G_6 - S_6 - D_{6d}$	B	E_1	E_2		
B	A				
E_1	E_2	$A_1, (A_2), E_2$			
E_2	E_1	B_1, B_2, E_1	$A_1, (A_2), E_2$		
G_7	E_1	E_2	E_3		
E_1	$A_1, (A_2), E_2$				
E_2	E_1, E_3	$A_1, (A_2), E_3$			
E_3	E_2, E_3	E_1, E_2	$A_1, (A_2), E_1$		
$G_8 + D_{4d} - D_{8d}$	B	E_1	E_2	E_3	
B	A				
E_1	E_3	$A_1, (A_2), E_2$			
E_2	E_2	E_1, E_3	$A_1, (A_2), B_1, B_2$		
E_3	E_1	B_1, B_2, E_2	E_1, E_3	$A_1, (A_2), E_2$	

^aThe antisymmetric component of the direct product is placed in parentheses.

In the relativistic theory, when the spin-orbit interaction is taken into account, the states of half-integral quantum number J are described by two-component spinors. In symmetry transformations these have doubled representations. *Double groups* are generated from the ordinary groups by adding an additional symmetry operation $\hat{Q}$; this means rotation by an angle 2π but differing from the identity operation ($\hat{Q} \neq \hat{E}$) which denotes rotation through an angle 4π . Every symmetry operation $\hat{R}_k$ in the ordinary group has its additional member $\hat{R}_k\hat{Q}$ within the double group. A symmetry operation consisting of a rotation through $\varphi = 2\pi + 2\pi k/n$ is written $\hat{C}_n^k\hat{Q}$.

For the characters of the irreducible representations common to a point group G and its corresponding double group G' (the single-valued representations of G) it holds true that

$$\chi_i(C_n^k Q) = \chi_i(C_n^k)$$

For the characters of the new irreducible representations of G' (the double-valued representations of G) it is

$$\chi_i(C_n^k Q) = -\chi_i(C_n^k)$$

TABLE 1.22

Irreducible components of the direct product of multidimensional irreducible representations for special groups

D_{6d} and S₁₂ groups

	<i>B</i>	<i>E</i> ₁	<i>E</i> ₂	<i>E</i> ₃	<i>E</i> ₄	<i>E</i> ₅
<i>B</i>	<i>A</i>					
<i>E</i> ₁	<i>E</i> ₅	<i>A</i> ₁ , <i>E</i> ₂ , (<i>A</i> ₂)				
<i>E</i> ₂	<i>E</i> ₄	<i>E</i> ₁ , <i>E</i> ₃	<i>A</i> ₁ , <i>E</i> ₄ , (<i>A</i> ₂)			
<i>E</i> ₃	<i>E</i> ₃	<i>E</i> ₂ , <i>E</i> ₄	<i>E</i> ₁ , <i>E</i> ₅	<i>A</i> ₁ , (<i>A</i> ₂), <i>B</i> ₁ , <i>B</i> ₂		
<i>E</i> ₄	<i>E</i> ₂	<i>E</i> ₃ , <i>E</i> ₅	<i>B</i> ₁ , <i>B</i> ₂ , <i>E</i> ₂	<i>E</i> ₁ , <i>E</i> ₅	<i>A</i> ₁ , <i>E</i> ₄ , (<i>A</i> ₂)	
<i>E</i> ₅	<i>E</i> ₁	<i>B</i> ₁ , <i>B</i> ₂ , <i>E</i> ₄	<i>E</i> ₃ , <i>E</i> ₅	<i>E</i> ₂ , <i>E</i> ₄	<i>E</i> ₁ , <i>E</i> ₃	<i>A</i> ₁ , <i>E</i> ₂ , (<i>A</i> ₂)

Linear groups (C_{∞v}, D_{∞h})

	Σ	Π	Δ
Σ	Σ		
Π	Π	Σ^+ , (Σ^-), Δ	
Δ	Δ	Π , Φ	Σ^+ , (Σ^-), Γ

Cubic groups (T, T_h, T_d, O, O_h)

	<i>E</i>	<i>T</i> ₁	<i>T</i> ₂
<i>E</i>	<i>A</i> ₁ , (<i>A</i> ₂), <i>E</i>		
<i>T</i> ₁	<i>T</i> ₁ , <i>T</i> ₂	<i>A</i> ₁ , <i>E</i> , (<i>T</i> ₁), <i>T</i> ₂	
<i>T</i> ₂	<i>T</i> ₁ , <i>T</i> ₂	<i>A</i> ₂ , <i>E</i> , <i>T</i> ₁ , <i>T</i> ₂	<i>A</i> ₂ , <i>E</i> , (<i>T</i> ₁), <i>T</i> ₂

Icosahedral groups (I, I_h)

	<i>T</i> ₁	<i>T</i> ₂	<i>G</i>	<i>H</i>
<i>T</i> ₁	<i>A</i> , <i>H</i> , (<i>T</i> ₁)			
<i>T</i> ₂	<i>G</i> , <i>H</i>	<i>A</i> , <i>H</i> , (<i>T</i> ₂)		
<i>G</i>	<i>T</i> ₂ , <i>G</i> , <i>H</i>	<i>T</i> ₁ , <i>G</i> , <i>H</i>	<i>A</i> , <i>G</i> , <i>H</i> , (<i>T</i> ₁ + <i>T</i> ₂)	
<i>H</i>	<i>T</i> ₁ , <i>T</i> ₂ , <i>G</i> , <i>H</i>	<i>T</i> ₁ , <i>T</i> ₂ , <i>G</i> , <i>H</i>	<i>T</i> ₁ , <i>T</i> ₂ , <i>G</i> , 2 <i>H</i>	<i>A</i> , <i>G</i> , 2 <i>H</i> , (<i>T</i> ₁ + <i>T</i> ₂ + <i>G</i>)

While the ordinary groups well describe the symmetry properties of (molecular) orbitals, the double groups are suitable in the description of spinorbitals. The irreducible representations of double groups have different degeneracy than those of the ordinary groups (Table 1.23). For example, the maximum multiplicity (degeneracy) of the irreducible representations in cubic double groups (like $\mathbf{O}'$) is four; hence only four spinorbitals can be degenerate.

The group $\mathbf{R}(3)$ comprises the infinite number of possible proper rotations about a point in three-dimensional space. It is the pure rotation subgroup of a sphere. The character $\chi_j(\vartheta)$ of the irreducible representation $D^{(j)}$ under pure rotation through an angle ϑ is

$$\chi_j(\vartheta) = \sum_{m=-j}^{+j} \exp(im\vartheta) = \frac{\sin[(2j+1)\vartheta/2]}{\sin(\vartheta/2)}$$

When $\vartheta = 0$ then

$$\chi_j(\vartheta) = 2j + 1$$

TABLE 1.23

Character tables for some isomorphous groups and their double groups

$\mathbf{T}_d$ ($h = 24$)	$\hat{E}$		$8\hat{C}_3$		$3\hat{C}_2$	$6\hat{S}_4$		$6\hat{\sigma}_d$
$\mathbf{O}$ ($h = 24$)	$\hat{E}$		$8\hat{C}_3$		$3\hat{C}_2$	$6\hat{C}_4$		$6\hat{C}_2'$
A_1	+1		+1		+1	+1		+1
A_2	+1		+1		+1	-1		-1
E	+2		-1		+2	0		0
T_1	+3		0		-1	+1		-1
T_2	+3		0		-1	-1		+1
$\mathbf{T}_d'$ ($h = 48$)	$\hat{E}$	$\hat{Q}$	$4\hat{C}_3$	$4\hat{C}_3^2$	$3\hat{C}_2$	$3\hat{S}_4$	$3\hat{S}_4^3$	$6\hat{\sigma}_d$
			$4\hat{C}_3\hat{Q}$	$4\hat{C}_3^2\hat{Q}$	$3\hat{C}_2\hat{Q}$	$3\hat{S}_4\hat{Q}$	$3\hat{S}_4^3\hat{Q}$	$6\hat{\sigma}_d\hat{Q}$
$\mathbf{O}'$ ($h = 48$)	$\hat{E}$	$\hat{Q}$	$4\hat{C}_3$	$4\hat{C}_3^2$	$3\hat{C}_2$	$3\hat{C}_4$	$3\hat{C}_4^3$	$6\hat{C}_2'$
			$4\hat{C}_3^2\hat{Q}$	$4\hat{C}_3\hat{Q}$	$3\hat{C}_2\hat{Q}$	$3\hat{C}_4^3\hat{Q}$	$3\hat{C}_4\hat{Q}$	$6\hat{C}_2'\hat{Q}$
$A_1 = \Gamma_1$	+1	+1	+1	+1	+1	+1	+1	+1
$A_2 = \Gamma_2$	+1	+1	+1	+1	+1	-1	-1	-1
$E_1 = \Gamma_3$	+2	+2	-1	-1	+2	0	0	0
$T_1 = \Gamma_4$	+3	+3	0	0	-1	+1	+1	-1
$T_2 = \Gamma_5$	+3	+3	0	0	-1	-1	-1	+1
$E_{1/2} = \Gamma_6$	+2	-2	+1	-1	0	$+\sqrt{2}$	$-\sqrt{2}$	0
$E_{5/2} = \Gamma_7$	+2	-2	+1	-1	0	$-\sqrt{2}$	$+\sqrt{2}$	0
$U_{3/2} = \Gamma_8$	+4	-4	-1	+1	0	0	0	0

When j is half-integral, the corresponding double group $\mathbf{R}(3)'$ is used. The full orthogonal group is

$$\mathbf{O}(3) = \mathbf{C}_i \otimes \mathbf{R}(3)$$

and has the full symmetry of the sphere.

SUMMARY

1. The proper description of a microobject (atom, molecule, cluster) is given by quantum mechanics: an operator is attributed to each observable; the operators act on the state vectors (kets); the state vectors bear all the physical information. The Schrödinger equation for stationary states is of key interest.
2. A many-electron wave function can be constructed from the set of occupied one-electron spinorbitals in the form of the Slater determinant. The molecular orbitals in the LCAO form are determined by solving the Roothaan equations. The MO method is improved by the configuration interaction. For evaluation of the matrix elements of operators over the determinantal functions, the Slater rules are helpful.
3. The linear variation method and the perturbation method for stationary states belong to the most important approximate methods of quantum mechanics. The latter exists in several variants.
4. The angular momentum vector can adopt only certain, quantised values and its orientation is limited to only certain, quantised projections. Its eigenfunctions are represented by spherical harmonics.
5. For a proper addition of angular momenta certain vector coupling coefficients are required: the Clebsch–Gordan coefficients, or alternatively the $3j$ -symbols, the $6j$ -symbols and $9j$ -symbols, for the coupling of two, three and four angular momenta, respectively. The $3j$ -symbols can be calculated through the Racah formula; the $6j$ -symbols can be expressed in terms of the $3j$ -symbols; and the $9j$ -symbols are evaluable with the help of either $3j$ -symbols or $6j$ -symbols. For some special cases closed-form formulae also exist.
6. The eigenvectors of the compound angular momentum can be generated by a recursion procedure: two angular momenta are coupled with the help of the Clebsch–Gordan coefficients, forming an intermediate coupling matrix. Then the next angular momentum is added: the next-generation coupling matrix is created from the previous-generation coupling matrix and a new set of the Clebsch–Gordan coefficients.
7. Any second-rank cartesian tensor with nine components is reducible into three parts: a scalar (the trace, one component), the polar vector (three

components) and a symmetric traceless tensor (five components). Such a tensor incorporates the isotropic, antisymmetric and anisotropic contributions. An irreducible spherical tensor transforms under the rotations like a spherical harmonic function. The tensor (direct) product of two irreducible tensor operators is, in general, reducible. An irreducible tensor product is formed through a proper linear combination by using the Clebsch–Gordan coefficients.

8. The Wigner–Eckart theorem allows the expression of the matrix element of a tensor operator through the reduced matrix elements (free of projections of angular momenta) and a coupling coefficient (the $3j$ -symbol). The reduced matrix elements of the compound angular momentum are evaluable according to the decoupling formula in which the reduced matrix elements of the uncoupled angular momenta and a $9j$ -symbol occur. Such an evaluation does not require an explicit form of the coupled wave functions. The replacement theorem allows one to express the matrix elements of any tensor operator using the matrix elements formed from the angular momentum operators and the ratio of the reduced matrix elements.
9. Group theory is an extremely useful tool for simplifying the relationships in systems possessing symmetry operations. All the information about the symmetry properties is carried by the characters of the irreducible representations within the given point group of symmetry. For theories dealing with the spin, including the magnetic energy levels, the double group concept is applicable.

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Macroscopic Magnetic Properties

2.1 MAGNETIC QUANTITIES

The external magnetic field is characterised by the vector of *magnetic induction* $\vec{B}(B_x, B_y, B_z)$ which is interrelated with the vector of *magnetic field strength* $\vec{H}(H_x, H_y, H_z)$ through a material constant—*permeability* μ , viz.

$$\vec{B} = \mu \vec{H}$$

Here we have assumed a homogeneous isotropic material but in general the permeability is a second-rank tensor $\bar{\mu}$ having 3×3 elements. The applied magnetic field is modified by the bulk magnetic properties of the substance and thus the magnetic field inside the sample becomes

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) = \mu_0 \vec{H} + \vec{J}$$

where the permeability of vacuum is $\mu_0 = 4\pi \times 10^{-7} \text{ kg m s}^{-2} \text{ A}^{-2}$. The vector quantity $\vec{M}$ just introduced is termed the *magnetisation*. Physically it represents a magnetic moment of the body or sample per volume element. The moving electrons present in any substance generate microscopic magnetic moments $\vec{m}_i$. The vector of *magnetic moment* is introduced through the intensity of a closed current I of charged particles and the corresponding surface vector $\vec{S}$ normal to the plane of the movement

$$\vec{m} = I \vec{S}$$

Hence

$$\vec{M} = \vec{m}/V = (1/V) \sum_i \vec{m}_i$$

More exactly, for a non-homogeneous material a differentiation should be applied

$$\vec{M} = d\vec{m}/dV$$

In a vacuum, the magnetisation vanishes and thus it holds true that

$$\vec{B}_{\text{vac}} = \mu_0 \vec{H}$$

By combining the above expressions we get

$$\vec{M} = \frac{\vec{B}}{\mu_0} - \vec{H} = \frac{\vec{B} - \vec{B}_{\text{vac}}}{\mu_0} = \left(\frac{\mu}{\mu_0} - 1 \right) \vec{H} = \bar{\chi} \vec{H}$$

Here a *mean volume magnetic susceptibility* has been introduced

$$\bar{\chi} = \vec{M} / \vec{H}$$

Its more general definition, valid for non-linear magnetics, is (Fig. 2.1)

$$\bar{\chi} = d\vec{M} / d\vec{H}$$

This is the *differential volume magnetic susceptibility*.

For anisotropic materials the susceptibility is a second-rank tensor $\bar{\bar{\chi}}$. The *mass susceptibility* and *molar susceptibility* are respectively

$$\chi_\rho = \chi / \rho$$

$$\chi_{\text{mol}} = M_r \chi_\rho = M_r \chi / \rho$$

where ρ is the density, M_r the molar mass.

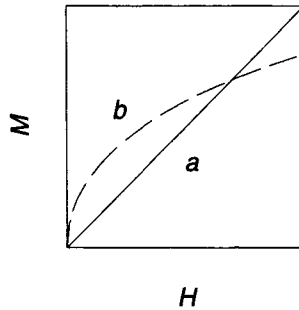


Fig. 2.1. Definition of the volume susceptibility: a—linear magnetics, $\bar{\chi} = \vec{M} / \vec{H} = \text{const.}$; b—non-linear magnetics, $\bar{\chi} = d\vec{M} / d\vec{H} = f(\vec{H})$.

Analogous relationships hold true among the (volume) magnetisation, mass magnetisation and molar magnetisation, hence

$$M_{\text{mol}} = M_r M_\rho = M_r M / \rho$$

The important relationships in magnetism are collected in Table 2.1. The corresponding expressions in the SI as well as the cgs & emu unit systems are compared since the latter is still more frequently used than the former. Table 2.2 contains units for magnetic properties [1].

The density of the energy of the magnetic field (volume energy density) is

$$W = \frac{1}{2} \vec{H} \cdot \vec{B}$$

and the magnetic energy E [J] of the sample with volume V is

$$E = \frac{1}{2} V \vec{H} \cdot \vec{B}$$

The magnetic induction, expressed through a volume susceptibility tensor, is

$$\vec{B} = \vec{\mu} \cdot \vec{H} = \mu_0 (\vec{1} + \vec{\chi}) \cdot \vec{H}$$

or, for individual components

$$B_a = \mu_0 \sum_b (\delta_{ab} + \chi_{ab}) H_b$$

TABLE 2.1
Basic relationships in magnetism

Quantity	SI units	cgs & emu units
magnetic induction	$\vec{B} = \mu_0 (\vec{H} + \vec{M})$ $\vec{B} = \mu \vec{H}$	$\vec{B} = \vec{H} + 4\pi \vec{M}$ $\vec{B} = \mu \vec{H}$
permeability	$\mu_r = \mu / \mu_0 = 1 + \chi$	$\mu = 1 + 4\pi \chi$
volume magnetisation	$\vec{M} = \vec{m} / V$	$\vec{M} = \vec{m} / V$
volume susceptibility	$\chi = d\vec{M} / d\vec{H}$	$\chi = d\vec{M} / d\vec{H}$
volume energy density	$W = (1/2) \vec{B} \cdot \vec{H}$	$W = (1/8\pi) \vec{B} \cdot \vec{H}$

TABLE 2.2
Units for magnetic properties

Quantity	Symbol	cgs & emu units	Conversion to SI	SI units ^a
magnetic flux	Φ	Mx (maxwell), G cm ²	10 ⁻⁸	Wb (weber), V s
magnetic flux density, magnetic induction	$\vec{B}$	G (gauss)	10 ⁻⁴	T (tesla), Wb m ⁻²
magnetic potential difference, magnetomotive force	U, F	Gb (gilbert)	10/4 π	A (ampere)
magnetic field strength, magnetising force	$\vec{H}$	Oe (oersted), Gb cm ⁻¹	10 ³ /4 π	A m ⁻¹
vector potential	$\vec{A}$	Oe cm	10 ⁻⁶	T m
volume magnetisation	$\vec{M}$	emu cm ⁻³	10 ³	A m ⁻¹
mass magnetisation	$\vec{\sigma}, \vec{M}_\rho$	emu g ⁻¹	1	A m ² kg ⁻¹
molar magnetisation	$\vec{M}_{\text{mol}}$	emu mol ⁻¹	10 ⁻³	A m ² mol ⁻¹
magnetic polarisation, intensity of magnetisation	$\vec{J}, I$	emu cm ⁻³	4 π 10 ⁻⁴	T, Wb m ⁻²
magnetic moment	$\vec{m}, \vec{\mu}$	emu, erg G ⁻¹	10 ⁻³	A m ² , J T ⁻¹
magnetic dipole moment	$\vec{j}$	emu, erg G ⁻¹	4 π 10 ⁻¹⁰	Wb m
volume susceptibility	χ, κ	dimensionless, emu cm ⁻³	4 π	dimensionless
mass susceptibility	χ_ρ, κ_ρ	cm ³ g ⁻¹ , emu g ⁻¹	4 π 10 ⁻³	m ³ kg ⁻¹
molar susceptibility	$\chi_{\text{mol}}, \kappa_{\text{mol}}$	cm ³ mol ⁻¹ , emu mol ⁻¹	4 π 10 ⁻⁶	m ³ mol ⁻¹
permeability	μ	dimensionless	4 π 10 ⁻⁷	H m ⁻¹ , Wb A ⁻¹ m ⁻¹
vacuum permeability	μ_0	1	4 π 10 ⁻⁷	H m ⁻¹
relative permeability	μ_r	not defined	—	dimensionless
volume energy density	W	erg cm ⁻³	10 ⁻¹	J m ⁻³
demagnetisation factor	D, N	dimensionless	1/4 π	dimensionless

^a 1 T = J A⁻¹ m⁻².

so that the energy becomes

$$\begin{aligned} E &= \frac{1}{2} V \sum_a H_a B_a = \frac{1}{2} V \mu_0 \sum_a \sum_b H_a (\delta_{ab} + \chi_{ab}) H_b \\ &= \frac{1}{2} V \mu_0 (H_x^2 + H_y^2 + H_z^2) + \frac{1}{2} V \mu_0 \sum_a \sum_b H_a \chi_{ab} H_b \end{aligned}$$

The first term, E_0 , is the energy of the magnetic field inside the sample. The second term, E_2 , represents the interaction energy of the sample with the applied field.

A common approach is to consider the energy of the system dependent somehow upon the magnetic induction

$$E = f(\dots, \vec{B}, \dots)$$

and in terms of a Taylor expansion it is

$$E = E_0 + \sum_a (\partial E / \partial B_a) B_a + (1/2) \sum_a \sum_b (\partial^2 E / \partial B_a \partial B_b) B_a B_b + \dots$$

The first derivatives define the (microscopic) *magnetic moment* vector $\vec{\mu}(\mu_x, \mu_y, \mu_z)$

$$\mu_a = -(\partial E / \partial B_a)$$

so that the interaction energy of the permanent magnetic moment of the system with the magnetic field is

$$E_1 = - \sum_a \mu_a B_a = -\vec{\mu} \cdot \vec{B}$$

The second derivatives form the *reduced magnetic susceptibility tensor* $\bar{\bar{\kappa}}$ with components

$$\kappa_{ab} = (\partial \mu_a / \partial B_b) = -(\partial^2 E / \partial B_a \partial B_b)$$

and thus the interaction energy of the system with the magnetic field becomes

$$E_2 = -(1/2) \sum_a \sum_b B_a \kappa_{ab} B_b = -(1/2) \vec{B} \cdot \bar{\bar{\kappa}} \cdot \vec{B}$$

The reduced susceptibility and volume (mass, molar) susceptibility are inter-related through

$$\chi_{ab} = (\mu_0/V)\kappa_{ab}$$

$$(\chi_\rho)_{ab} = (\mu_0/m)\kappa_{ab}$$

$$(\chi_{\text{mol}})_{ab} = (\mu_0/n)\kappa_{ab}$$

2.2 THERMODYNAMIC RELATIONSHIPS

2.2.1 State functions

The first law of thermodynamics postulates that the internal energy, which is a state function, consists of the heat (Q) and the work (w)

$$dU = dQ + dw$$

In the most common presentation the work embraces the volume work $dw = -p.dV$. However, other forms of work are possible (the surface work $dw = \vec{s} \cdot d\vec{\sigma}$, the mechanic work $dw = \vec{F} \cdot d\vec{r}$, the electric work $dw = q.dU$) and the *magnetic work*

$$dw = \mu_0 \vec{H} \cdot d\vec{M}$$

is one of them.

The individual constituents of the last expression have their dimensions as follows: μ_0 [$\text{J A}^{-2} \text{m}^{-1}$], H [A m^{-1}] and M [A m^{-1}]; then the expression has the dimension of [J m^{-3}] which refers to the volume energy. If M refers to the molar magnetisation, M_{mol} [$\text{A m}^2 \text{mol}^{-1}$], then the product $dw = \mu_0 \vec{H} \cdot d\vec{M}$ has the dimension of the molar energy [J mol^{-1}]. It is assumed hereafter that the other energy quantities (U, E, F, G, TS, CT) possess the same dimension.

Making use of $dQ = TdS$, we arrive at the expression for the internal energy

$$dU = TdS + \mu_0 H dM \quad [p = \text{const.}, V = \text{const.}, n_i = \text{const.}]$$

Since the internal energy U is an exact differential,

$$\left(\frac{\partial T}{\partial M}\right)_S = \mu_0 \left(\frac{\partial H}{\partial S}\right)_M$$

The other thermodynamic functions are introduced in a similar way (Table 2.3) [2, 3]. Of three observables (H, M, T) only two are independently variable, which is expressed by the constraint

$$\left(\frac{\partial H}{\partial T}\right)_M \left(\frac{\partial T}{\partial M}\right)_H \left(\frac{\partial M}{\partial H}\right)_T = -1$$

2.2.2 Heat capacities

In classical thermodynamics dealing with the volume work, two types of heat capacity are distinguished: C_V and C_p . The *specific heat* c_V [$\text{J g}^{-1} \text{K}^{-1}$] and the *molar heat capacity* C_V [$\text{J mol}^{-1} \text{K}^{-1}$] are interrelated through

$$C_V = c_V M_r$$

where M_r is the molar mass.

TABLE 2.3
Thermodynamic functions in magnetism

Function	Exact differential	Relationship
$X = X(A, B)$	$dX = \left(\frac{\partial X}{\partial A}\right)_B dA + \left(\frac{\partial X}{\partial B}\right)_A dB$	
internal energy $U = U(S, M)$	$dU = TdS + \mu_0 H dM$	$\left(\frac{\partial T}{\partial M}\right)_S = \mu_0 \left(\frac{\partial H}{\partial S}\right)_M$
enthalpy (E instead of H) $E = E(S, H)$	$dE = TdS - \mu_0 M dH$	$\left(\frac{\partial T}{\partial H}\right)_S = -\mu_0 \left(\frac{\partial M}{\partial S}\right)_H$
Helmholtz free energy $F = F(T, M)$	$dF = -SdT + \mu_0 H dM$	$\left(\frac{\partial S}{\partial M}\right)_T = -\mu_0 \left(\frac{\partial H}{\partial T}\right)_M$
Gibbs energy $G = G(T, H)$	$dG = -SdT - \mu_0 M dH$	$\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 \left(\frac{\partial M}{\partial T}\right)_H$
entropy		
$S = S(T, M)$	$dS = \frac{C_M}{T} dT + \left(\frac{\partial S}{\partial M}\right)_T dM$	
$S = S(T, H)$	$dS = \frac{C_H}{T} dT + \left(\frac{\partial S}{\partial H}\right)_T dH$	

The difference between C_V and C_p for solids is

$$C_p - C_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p$$

Making use of the relationship among state variables $p = p(V, T)$ in the differential form

$$dp = \left(\frac{\partial p}{\partial V} \right)_T dV + \left(\frac{\partial p}{\partial T} \right)_V dT$$

at constant pressure, $dp = 0$, and thus we get

$$\left(\frac{\partial p}{\partial T} \right)_V = - \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p$$

Then the difference between the molar heat capacities becomes

$$C_p - C_V = -T \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p^2 = \frac{TV_m \beta^2}{K_T}$$

where V_m is the molar volume. The *isothermal compressibility*, measured at constant temperature, is introduced through the formula

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

and the *coefficient of volumetric expansion* is

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

For isotropic solids, β is related to the coefficient of linear thermal expansion α by

$$\beta = \frac{1}{l^3} \left(\frac{\partial l^3}{\partial T} \right)_p = \frac{3}{l} \left(\frac{\partial l}{\partial T} \right)_p = 3\alpha$$

where l is the dimension of a cube of the solid. The mechanical stability of a solid requires $K_T > 0$ and consequently $C_p \geq C_V$. Although data on linear thermal expansion are available for many solids over a broad interval of

temperature, experimental values of compressibility are often known around room temperature only.

By introducing the *adiabatic compressibility* measured at constant entropy

$$K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$$

one can derive an expression

$$C_p/C_V = K_T/K_S$$

In thermodynamics dealing with the magnetic work the following types of heat capacity are defined

$$C_M = \left(\frac{\partial Q}{\partial T} \right)_M = T \left(\frac{\partial S}{\partial T} \right)_M$$

$$C_H = \left(\frac{\partial Q}{\partial T} \right)_H = T \left(\frac{\partial S}{\partial T} \right)_H$$

It is of interest to express $C_H - C_M$ and C_H/C_M in terms of observables (H, M, T). Making use of expressions for entropy

$$dS = \frac{C_M}{T} dT + \left(\frac{\partial S}{\partial M} \right)_T dM = \frac{C_H}{T} dT + \left(\frac{\partial S}{\partial H} \right)_T dH$$

and taking into account the relationships listed in Table 2.3, we get

$$\frac{C_M}{T} dT - \mu_0 \left(\frac{\partial H}{\partial T} \right)_M dM = \frac{C_H}{T} dT + \mu_0 \left(\frac{\partial M}{\partial T} \right)_H dH$$

This equation can be rewritten as

$$\frac{C_H - C_M}{T} dT = -\mu_0 \left(\frac{\partial H}{\partial T} \right)_M dM - \mu_0 \left(\frac{\partial M}{\partial T} \right)_H dH$$

or

$$dT = -\frac{T}{C_H - C_M} \mu_0 \left(\frac{\partial H}{\partial T} \right)_M dM - \frac{T}{C_H - C_M} \mu_0 \left(\frac{\partial M}{\partial T} \right)_H dH$$

and compared with the identity

$$dT = \left(\frac{\partial T}{\partial M} \right)_H dM + \left(\frac{\partial T}{\partial H} \right)_M dH$$

The same coefficients of dM require the validity of

$$-\frac{T}{C_H - C_M} \mu_0 \left(\frac{\partial H}{\partial T} \right)_M = \left(\frac{\partial T}{\partial M} \right)_H$$

The boundary between observables allows us to eliminate

$$\left(\frac{\partial H}{\partial T} \right)_M = - \left(\frac{\partial M}{\partial T} \right)_H \left(\frac{\partial H}{\partial M} \right)_T$$

and finally we arrive at the formula

$$C_H - C_M = \mu_0 T \left(\frac{\partial M}{\partial T} \right)_H^2 \left(\frac{\partial H}{\partial M} \right)_T$$

The second expression for entropy can also be written in the form of

$$dT = \frac{T}{C_H} dS - \frac{T}{C_H} \mu_0 \left(\frac{\partial M}{\partial T} \right)_H dH$$

and compared with the identity

$$dT = \left(\frac{\partial T}{\partial S} \right)_H dS + \left(\frac{\partial T}{\partial H} \right)_S dH$$

yielding the same coefficient at dH , i.e.

$$-\frac{T}{C_H} \mu_0 \left(\frac{\partial M}{\partial T} \right)_H = \left(\frac{\partial T}{\partial H} \right)_S$$

The first expression for entropy can be rearranged as

$$dT = \frac{T}{C_M} dS + \frac{T}{C_M} \mu_0 \left(\frac{\partial H}{\partial T} \right)_M dM$$

and again compared with the identity

$$dT = \left(\frac{\partial T}{\partial S}\right)_M dS + \left(\frac{\partial T}{\partial M}\right)_S dM$$

giving the same coefficient at dM , viz.

$$\frac{T}{C_M} \mu_0 \left(\frac{\partial H}{\partial T}\right)_M = \left(\frac{\partial T}{\partial M}\right)_S$$

The ratio of the magnetic heat capacities stands

$$\frac{C_H}{C_M} = -\frac{\left(\frac{\partial M}{\partial T}\right)_H \left(\frac{\partial H}{\partial T}\right)_S}{\left(\frac{\partial M}{\partial T}\right)_S \left(\frac{\partial H}{\partial T}\right)_M} = -\frac{\left(\frac{\partial T}{\partial M}\right)_S \left(\frac{\partial H}{\partial T}\right)_S}{\left(\frac{\partial T}{\partial M}\right)_H \left(\frac{\partial H}{\partial T}\right)_M} = \frac{\left(\frac{\partial M}{\partial H}\right)_T}{\left(\frac{\partial M}{\partial H}\right)_S}$$

Now we introduce the *isothermal susceptibility* (measured at constant temperature)

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T$$

and the *adiabatic susceptibility* (measured at constant entropy)

$$\chi_S = \left(\frac{\partial M}{\partial H}\right)_S$$

The ratio of the magnetic heat capacities is just the ratio of the magnetic susceptibilities

$$C_H/C_M = \chi_T/\chi_S$$

Important relationships among heat capacities are collected in Table 2.4. It is worth noting that the relations between heat capacities and compressibilities in classical thermodynamics have an analogy in the relations between magnetic heat capacities and magnetic susceptibilities.

TABLE 2.4
Relationships for heat capacities

Function ^a	Heat capacity	Expression
<i>(a) Volume work</i>		
$U(S, V)$	$C_V = \left(\frac{\partial U}{\partial T}\right)_V$	$C_V = N_A \frac{\partial}{\partial T} \left[kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \right]_V$
$E(S, p)$	$C_p = \left(\frac{\partial E}{\partial T}\right)_p$	$C_p = N_A \frac{\partial}{\partial T} \left[kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V + kT \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T \right]_p$
	$C_p - C_V$	$T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p = -T \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p^2$
	C_p/C_V	$\left(\frac{\partial V}{\partial p} \right)_T / \left(\frac{\partial V}{\partial p} \right)_S = K_T/K_S$
$S(T, V)$		$dS = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV$
$S(T, p)$		$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_p dp$
<i>(b) Magnetic work</i>		
$U(S, M)$	$C_M = \left(\frac{\partial U}{\partial T}\right)_M$	$C_M = N_A \frac{\partial}{\partial T} \left[kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_M \right]_M$
$E(S, H)$	$C_H = \left(\frac{\partial E}{\partial T}\right)_H$	$C_H = N_A \frac{\partial}{\partial T} \left[kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_M + kT \left(\frac{\partial \ln Z}{\partial \ln M} \right)_T \right]_H$
	$C_H - C_M$	$-\mu_0 T \left(\frac{\partial H}{\partial T} \right)_M \left(\frac{\partial M}{\partial T} \right)_H = \mu_0 T \left(\frac{\partial H}{\partial M} \right)_T \left(\frac{\partial M}{\partial T} \right)_H^2$
	C_H/C_M	$\left(\frac{\partial M}{\partial H} \right)_T / \left(\frac{\partial M}{\partial H} \right)_S = \chi_T/\chi_S$
$S(T, M)$		$dS = \frac{C_M}{T} dT - \mu_0 \left(\frac{\partial H}{\partial T} \right)_M dM$
$S(T, H)$		$dS = \frac{C_H}{T} dT + \mu_0 \left(\frac{\partial M}{\partial T} \right)_H dH$

^a Enthalpy is denoted as E ; H is the magnetic field strength.

2.3 ALTERNATING FIELDS

2.3.1 AC susceptibility

When the magnetic field is switched on the magnetisation needs some time to achieve thermodynamic equilibrium. The magnetic susceptibility, measured at thermal equilibrium, is the isothermal susceptibility χ_T .

In an alternating field, however, the situation is different. The alternating current (AC) is used to generate the alternating magnetic field (Fig. 2.2). The time evolution of the magnetic field strength is

$$H_{AC} = H_0 \cos(\omega t)$$

where H_0 is the amplitude of the field, ω is the angular frequency of the AC field ($\omega = 2\pi\nu$).

The magnetisation M_{AC} cannot follow the incident field immediately and is shifted by a phase angle θ , so that

$$M_{AC} = M_0 \cos(\omega t - \theta)$$

This formula can be rewritten using the relationship

$$\cos(\alpha - \beta) = \cos \alpha \cos \beta + \sin \alpha \sin \beta$$

Then the time evolution of the magnetisation is

$$\begin{aligned} M_{AC} &= M_0 \cos \theta \cos(\omega t) + M_0 \sin \theta \sin(\omega t) \\ &= \chi' H_0 \cos(\omega t) + \chi'' H_0 \sin(\omega t) \end{aligned}$$

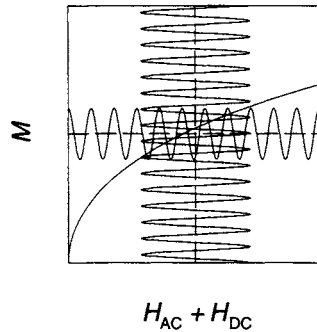


Fig. 2.2. AC measurement in conjunction with an applied DC field.

with

$$\chi' = (M_0/H_0) \cos \theta$$

$$\chi'' = (M_0/H_0) \sin \theta$$

The quantity just introduced is the magnetic susceptibility, having two components. The in-phase (real) component is χ' and it corresponds to the dispersive magnetic response; therefore it is termed the *dispersion*. The out-of-phase (imaginary) component is χ'' and it corresponds to the energy dissipation (i.e. the energy absorbed by the material from the applied AC field); it is termed the *absorption*. Normally the out-of-phase component χ'' is small and varies around zero (being lower by orders than χ'). It adopts significance (positive values) when the sample, owing to processes inside the material, absorbs magnetic energy.

Thus the magnetic susceptibility in an alternating field, the *AC susceptibility*, can be viewed as a complex quantity

$$\chi = \chi' - i\chi''$$

The components of the AC susceptibility depend upon the frequency of the applied field. When the frequency of the field is low, the magnetisation can readily follow the applied field so that the low-frequency limit corresponds to the isothermal susceptibility

$$\lim_{\omega \rightarrow 0} \chi = \left(\frac{\partial M_{AC}}{\partial H} \right)_T = \chi_T$$

This is comparable with the susceptibility measured in static fields. The greater the frequency, the lower the AC susceptibility, which in the opposite limit approaches the adiabatic value

$$\lim_{\omega \rightarrow \infty} \chi = \left(\frac{\partial M_{AC}}{\partial H} \right)_S = \chi_S$$

The recovery of a perturbed system to a new equilibrium is described by introducing the *relaxation time* τ

$$\frac{dM}{dt} = \frac{M(\infty) - M(t)}{\tau}$$

where $M(\infty)$ is the equilibrium magnetisation and $M(t)$ is the magnetisation at time t .

An example of such a relaxation process is represented by the transfer of energy between the magnetic spin entity and the lattice vibrations (spin-lattice relaxation). The isothermal, adiabatic and AC susceptibilities are interrelated through (Fig. 2.3)

$$\chi_{AC} = \frac{\chi_T - \chi_S}{1 + i\omega\tau} + \chi_S$$

and for individual components it holds that

$$\chi'(\omega) = \frac{\chi_T - \chi_S}{1 + \omega^2\tau^2} + \chi_S$$

$$\chi''(\omega) = \frac{\omega\tau(\chi_T - \chi_S)}{1 + \omega^2\tau^2}$$

Now for $\omega \ll \tau^{-1}$ the in-phase component becomes the isothermal susceptibility $\chi' = \chi_T$ and the out-of-phase component approaches zero. On the other hand, for $\omega \gg \tau^{-1}$ the in-phase component equals the adiabatic susceptibility, $\chi' = \chi_S$, and χ'' vanishes again. Just for $\omega = \tau^{-1}$ the out-of-phase component adopts a maximum value of

$$\chi'' = (\chi_T - \chi_S)/2$$

The alternating magnetic field can be combined with an admixture of the constant field generated by a DC current. The magnetic moment is induced in a sample through the application of the DC bias field, produced either by the primary coil or by a superconducting magnet.

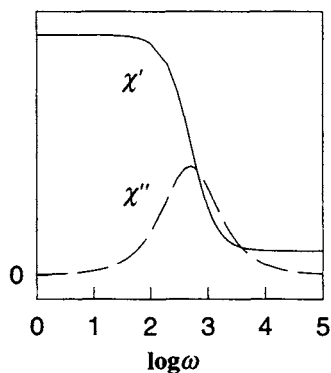


Fig. 2.3. Frequency dependence of AC susceptibility.

2.3.2 Harmonic susceptibilities

If the material response in AC magnetisation measurements is nonlinear, the magnetisation oscillations do not follow the *fundamental susceptibility* perfectly. The perfect sinusoidal AC field induces non-sinusoidal oscillations of the magnetisation which can be described as a sum of several sinusoidal components oscillating at the harmonics of the driving frequency [4] (Fig. 2.4)

$$M_{AC}(t) = H_0 \sum_n [\chi'_n \cos(n\omega t) + \chi''_n \sin(n\omega t)]$$

Here χ'_n and χ''_n define the in-phase and out-of-phase components of the *harmonic susceptibilities*

$$\chi_n = \chi'_n - i\chi''_n$$

for the harmonic degree $n = 1, 2, 3, \dots$

Full characterisation of a magnetic material with nonlinear response requires measurements of harmonic susceptibilities beyond the fundamental susceptibility χ_1 . These are useful, for example, in the identification of multiple phase transitions in high T_C superconductors and in the determination of magnetic phase diagrams.

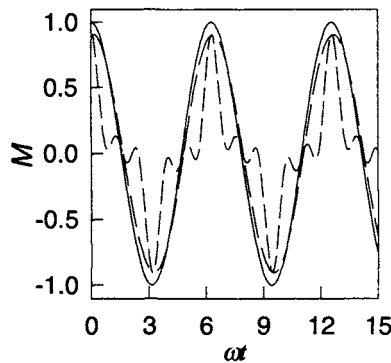


Fig. 2.4. AC magnetisation response to harmonic susceptibilities: solid line—a perfect first harmonic; long dashed—a shift due to the complex susceptibility; short dashed—warping due to the third and fifth harmonics.

2.4 DEMAGNETISATION CORRECTION

The magnetic field H actually acting on a sample of definite geometrical shape consists of two contributions: the applied external field H_a and the demagnetising field H_d

$$H = H_a + H_d$$

The origin of the demagnetising field lies in the magnetic poles on the surface of a magnetised specimen; the sample behaves like a magnet of opposite polarisation to that of the applied field. The greater the magnetisation, the greater the demagnetising field with the opposite sign

$$H_d = -NM$$

The proportionality constant N is termed the *demagnetisation factor* (dimensionless in SI) and is evaluable from the sample shape. Then the internal magnetic field becomes

$$H = H_a - NM$$

As $0 < N < 1$, the internal field is lower than the applied field: $H < H_a$.

The susceptibility which is measured experimentally refers to the *external susceptibility* which is characteristic of the sample

$$\chi_{\text{ext}} = dM/dH_a$$

On the other hand, the *internal susceptibility*, which is characteristic of the material, is

$$\chi_{\text{int}} = dM/dH$$

These quantities are interrelated through

$$\chi_{\text{int}} = \chi_{\text{ext}}/(1 - N\chi_{\text{ext}})$$

For AC susceptibility both χ_{ext} and χ_{int} are complex. The individual components are related

$$\chi'_{\text{int}} = [\chi'_{\text{ext}} - N(\chi_{\text{ext}}^2 + \chi_{\text{ext}}''^2)]/[N^2(\chi_{\text{ext}}^2 + \chi_{\text{ext}}''^2) - 2N\chi'_{\text{ext}} + 1]$$

$$\chi''_{\text{int}} = \chi''_{\text{ext}}/[N^2(\chi_{\text{ext}}^2 + \chi_{\text{ext}}''^2) - 2N\chi'_{\text{ext}} + 1]$$

For many magnetic materials the demagnetisation correction for susceptibility is not important since $\chi \ll 1$ which implies $\chi_{\text{int}} \approx \chi_{\text{ext}}$. When the susceptibility is high, the demagnetisation correction adopts its significance.

In general, the demagnetisation is a second rank tensor $\overline{\overline{N}}$ entering the vector equation

$$\vec{H} = \vec{H}_a + \vec{H}_d = \vec{H}_a - \overline{\overline{N}} \cdot \vec{M}$$

The demagnetisation correction is applicable only to the volume susceptibility. This requires an accurate determination of the sample volume, which may not be trivial. Normally the amount of the sample is determined by weighing and it refers to the sample mass. The determination of the volume is less accurate and more complex for powders.

Demagnetisation factors have been derived for several important bodies: a spheroid, a cylinder and a thin film (Fig. 2.5) [1].

- (a) For ellipsoids the magnetic poles are distributed in such a way that the demagnetising field H_d is uniform (also H_a , H and M are uniform). If $\vec{H}_a$ is along a principal axis of the ellipsoid, N is a scalar quantity. If $\vec{H}_a$ is not along a principal axis and $\chi \neq 0$, $\vec{M}$ is uniform but not coaxial with $\vec{H}_a$. The direction and magnitude of $\vec{M}$ depend on χ .
- (b) For spheroids N does not depend on susceptibility and is a function of the aspect ratio $\gamma = l_z/l_x$ (a ratio of the polar axis l_z to the equatorial axis l_x) [5,6]
 - (b1) for $\gamma < 1$: $N = [1 - \gamma(1 - \gamma^2)^{-1/2} \cos^{-1} \gamma]/(1 - \gamma^2)$
 - (b2) for $\gamma = 1$: $N = 1/3$
 - (b3) for $\gamma > 1$: $N = [\gamma(\gamma^2 - 1)^{-1/2} \cosh^{-1} \gamma - 1]/(\gamma^2 - 1)$
- (c) For cylinders $N = f(\chi, \gamma)$ where $\gamma = l/d$ is the ratio of the length to the diameter of the cylinder
 - (c1) for $\chi \rightarrow 0$: M is uniform,
 - (c2) for $\chi \rightarrow \infty$: $H_d = -H_a$ are uniform,
 - (c3) for $\chi \rightarrow -1$: $(M + H_d) = -H_a$ are uniform.

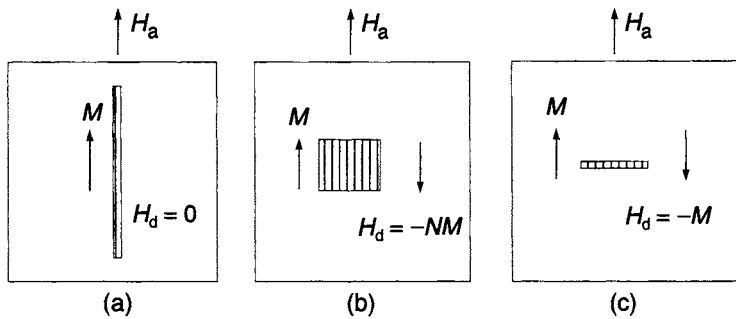


Fig. 2.5. Demagnetising field: (a) in a bar (long needle); (b) in a cylinder; (c) in a slab (thin film).

The *magnetometric demagnetisation factor*, when the response of the full volume is detected, for cylinders is defined as

$$N^{(m)} = -\langle H_d \rangle_V / \langle M \rangle_V$$

where an average over the volume of the cylinder is applied. This is a function $N^{(m)} = f(\chi, \gamma)$ so that values for $\chi \rightarrow 0$ (Table 2.5) are different from those for $\chi \rightarrow -1$.

Note that the sum of the transverse and longitudinal magnetometric demagnetisation factors for cylinders obeys

$$\text{for } \chi \rightarrow 0: \eta = 2N_{\perp}^{(m)} + N_{\parallel}^{(m)} = 1$$

$$\text{for } \chi \rightarrow -1: \eta \geq 1$$

as exemplified by Table 2.6.

- (d) When the applied magnetic field is perpendicular to the plane of a thin film ($\gamma \rightarrow 0$) the longitudinal demagnetisation factor approaches the

TABLE 2.5

Longitudinal magnetometric demagnetisation factor for cylinders with $\chi \rightarrow 0^a$

$\gamma = l/d$	$N^{(m)}$	$\gamma = l/d$	$N^{(m)}$	$\gamma = l/d$	$N^{(m)}$
0.0	1.000	2.0	0.181	4.0	0.0978
0.1	0.796	2.1	0.174	4.1	0.0956
0.2	0.680	2.2	0.167	4.2	0.0935
0.3	0.594	2.3	0.161	4.3	0.0914
0.4	0.528	2.4	0.155	4.4	0.0895
0.5	0.474	2.5	0.149	4.5	0.0876
0.6	0.430	2.6	0.144	4.6	0.0858
0.7	0.393	2.7	0.140	4.7	0.0841
0.8	0.361	2.8	0.135	4.8	0.0824
0.9	0.334	2.9	0.131	4.9	0.0808
1.0	0.311	3.0	0.127	5.0	0.0793
1.1	0.291	3.1	0.123	5.5	0.0723
1.2	0.273	3.2	0.120	6.0	0.0666
1.3	0.257	3.3	0.116	6.5	0.0616
1.4	0.242	3.4	0.113	7.0	0.0573
1.5	0.230	3.5	0.110	7.5	0.0536
1.6	0.218	3.6	0.107	8.0	0.0503
1.7	0.207	3.7	0.105	8.5	0.0473
1.8	0.198	3.8	0.102	9.0	0.0447
1.9	0.189	3.9	0.100	10.0	0.0403

^aAccording to Ref. [7].

TABLE 2.6
Magnetometric demagnetisation factors^a

Cylinders $\gamma = l/d$	$\chi \rightarrow -1$		$\chi \rightarrow 0$	
	$N_{\parallel}^{(m)}$	$N_{\perp}^{(m)}$	$N_{\parallel}^{(m)}$	$N_{\perp}^{(m)}$
0	1	0	1	0
0.25	0.6764	0.2136		
0.5	0.5258	0.2928	0.474	0.263
1	0.3692	0.3669	0.311	0.344
2	0.2341	0.4237	0.181	0.409
4	0.1361	0.4596	0.0978	0.451
∞	0	0.5	0	0.5
long needle			0	1/2
sphere			1/3	1/3
thin film			1	0

^a According to Ref. [8].

value of 1. For a substance with $\chi \rightarrow -1$ (a perfectly shielding superconductor) there is

$$\lim_{\substack{\chi \rightarrow -1 \\ N \rightarrow 1}} \chi_{\text{ext}} = \lim_{\substack{\chi \rightarrow -1 \\ N \rightarrow 1}} \chi_{\text{int}} / (1 + N\chi_{\text{int}}) = \lim_{N \rightarrow 1} [-1/(1 - N)] = -\infty$$

and thus the measured external susceptibility adopts very highly negative values.

2.5 OVERVIEW OF MAGNETIC SUSCEPTIBILITIES

A list of the different types of magnetic susceptibility including some useful relationships among them, is given in Table 2.7. The most important message from this overview is that one should be careful when speaking about the magnetic susceptibility to give its proper definition.

The popular experimental techniques involve Faraday or Gouy balance measurements where the quantity being measured is the force acting on a body when it is in the magnetic field

$$\vec{F} = -\vec{\nabla} w$$

The work done in bringing the body of volume V with a uniform magnetisation $\vec{M}$ into a magnetic field is

$$dw = -\mu_0 V \vec{H} \cdot d\vec{M}$$

TABLE 2.7

Various types of magnetic susceptibility

Susceptibility	Relationship
reduced	$\kappa_{ab} = -(\partial^2 E / \partial B_a \partial B_b)$
volume	$\chi_{ab} = (\partial M_a / \partial H_b) = \mu_0 (\partial M_a / \partial B_b) = (\mu_0 / V) \kappa_{ab}$
mass	$\chi_\rho = \chi / \rho$
molar	$\chi_{\text{mol}} = \chi_\rho M_r = \chi M_r / \rho$
mean	$\bar{\chi} = M / H = \mu_0 M / B$
differential	$\tilde{\chi} = (\partial M / \partial H) = \mu_0 (\partial M / \partial B)$
isothermal	$\chi_T = (\partial M / \partial H)_T$
adiabatic	$\chi_S = (\partial M / \partial H)_S$
alternating current	$\chi = \chi' - i\chi''$
dispersion	$\chi' = (M_0 / H_0) \cos \theta$
absorption	$\chi'' = (M_0 / H_0) \sin \theta$
harmonic	$\chi_n = \chi'_n - i\chi''_n$
external	$\chi_{\text{ext}} = dM / dH_a$
internal	$\chi_{\text{int}} = dM / dH = \chi_{\text{ext}} / (1 - N\chi_{\text{ext}})$
averaged	$\chi_{\text{av}} = (2\chi_\perp + \chi_\parallel) / 3$

For isotropic non-ferromagnetic materials with volume susceptibility χ it is

$$d\vec{M} = \chi d\vec{H}$$

and thus

$$w = -\mu_0 V \int \chi \vec{H} \cdot d\vec{H}$$

For susceptibility independent of the field, $\bar{\chi} = \text{const.}$, there is

$$w = -\frac{1}{2} \mu_0 V \bar{\chi} \vec{H}^2$$

and the force becomes expressed as

$$\vec{F} = \frac{1}{2} \mu_0 \chi V (\vec{\nabla} H^2)$$

When the sample is allowed to move in one direction (z) only, then one gets

$$F_z = \mu_0 \chi V H_z \frac{\partial H}{\partial z} = \mu_0 \chi_\rho m H_z \frac{\partial H}{\partial z}$$

Evidently, the susceptibility subduced from such experiments is the mean mass susceptibility. This quantity, for linear magnetics, is close to the isothermal susceptibility. However, deviations from linear behaviour increase with

- (a) increasing magnetic field,
- (b) temperature lowering,
- (c) sample magnetisation,

and then dealing with the mean magnetic susceptibility becomes incorrect.

As already mentioned, induction methods, such as AC susceptibility measurements, yield the value of the differential adiabatic susceptibility. This can be scanned either in the single mode (giving rise to $|\chi|$) or, alternatively, in the dual mode (when the dispersion χ' and the absorption χ'' are distinguished). The adiabatic susceptibility approaches the isothermal susceptibility only when the frequency of the alternating field is small.

When there is a necessity to distinguish clearly between the differential and mean susceptibilities, the symbol $\tilde{\chi}$ is used hereafter for the differential susceptibility.

2.6 STATISTICAL THERMODYNAMICS

2.6.1 Introduction to statistical treatment

Let us consider a simple model with only two attainable energy states. A good representation could be an assembly of N similar spins, each independent of the others. We are interested in the properties of the average, in the *thermodynamic limit*, when $N \rightarrow \infty$. The energy of the spins in an applied magnetic field is

$$e = -\mu_e \cdot B = -\left(\pm \frac{1}{2} g \mu_B\right) B = \mp \frac{1}{2} g \mu_B B = \mp \varepsilon$$

where the minus sign is valid for the n spins pointing parallel to the field direction (lower energy) and the plus sign for the $(N - n)$ spins pointing antiparallel. Then the average energy $\bar{E}$ of each spin is expressed through the total energy as follows [9]

$$\bar{E} = \frac{E}{N} = \frac{(N - n)\varepsilon - n\varepsilon}{N} = (1 - 2p)\varepsilon$$

with the fraction of spins pointing parallel to the field direction

$$p = \frac{n}{N}$$

The probability $Q(n)$ of attaining the configuration of the average energy is a product of two probabilities: the statistical probability $S(n)$ and the thermal probability $P(E)$

$$Q(n) = S(n)P(E)$$

The statistical probability contains in the numerator a binomial coefficient which counts the number of distinct arrangements of N spins which exactly have the energy $E = (N - 2n)\epsilon$, and in the denominator the total number of distinct configurations 2^N

$$S(n) = \frac{N!}{n!(N - n)!} \frac{1}{2^N}$$

An application of the Stirling formula (well valid for large N) yields

$$\ln(N!) \approx N \ln N - N + \dots$$

and thus we get

$$\begin{aligned} \ln S(n) = N \ln N - N - [n \ln n - n + (N - n) \ln(N - n) - (N - n) \\ + N \ln 2] \end{aligned}$$

which can be rewritten as

$$\ln S(n) = -N[\ln 2 + p \ln p + (1 - p) \ln(1 - p)]$$

Because of an explicit dependence on the number of particles, the $\ln(S)$ is an extensive quantity.

The thermal probability of the system having energy E is given by the Maxwell–Boltzmann factor

$$P(E) = \exp(-\beta E) = \exp(-E/kT)$$

with

$$\beta \equiv 1/kT$$

Such a function accommodates the following requirements:

- (1) $\ln(P)$ is an extensive quantity;
 - (2) $\ln(P)$ is dimensionless;
 - (3) P and hence $\ln(P)$ favours low energies (it must be maximal in the ground state);
 - (4) Q should be maximised to receive the most probable values of p and $\bar{E}$.
- We introduce the *free energy* F through the relationship

$$2^N Q = \exp(-\beta F) = \exp(-F/kT)$$

so that

$$\begin{aligned} -F/kT &= \ln(2^N Q) \\ &= N \ln 2 + \ln Q \\ &= \ln P(E) - N[p \ln p + (1-p) \ln(1-p)] \\ &= -E/kT - N[p \ln p + (1-p) \ln(1-p)] \end{aligned}$$

Then the free energy per spin becomes

$$\begin{aligned} f &= F/N \\ &= E/N + kT[p \ln p + (1-p) \ln(1-p)] \\ &= (1-2p)\varepsilon + kT[p \ln p + (1-p) \ln(1-p)] \end{aligned}$$

The last expression contains only a single undetermined parameter p which can be determined from the requirement of Q attaining a maximum, equivalent to f being a minimum

$$0 = \frac{df}{dp} = -2\varepsilon + kT \left[\ln p + p \frac{1}{p} + -1 \cdot \ln(1-p) + (1-p) \frac{1}{1-p} (-1) \right]$$

or

$$\ln\left(\frac{1-p}{p}\right) = -2\varepsilon/kT$$

yielding the result for the thermal equilibrium value of p

$$p = \frac{1}{1 + \exp(-2\varepsilon/kT)}$$

Now, having determined the fraction of spins aligned parallel to the field direction, the evaluation of the thermodynamic functions is straightforward: the free energy per spin is

$$f = -kT \ln[2 \cosh(\varepsilon/kT)]$$

and the internal energy per spin is

$$u = \bar{E} = -\varepsilon \tanh(\varepsilon/kT)$$

2.6.2 Partition function

For a more complex situation the set of non-interacting particles is separated into a number of subsets, each having energy $\varepsilon_i n_i$. The free energy is written as

$$F = \sum_i f_i = \sum_i [\varepsilon_i p_i + kT p_i \ln p_i]$$

Such a function is to be minimised with the constraint that all fractions are summed up to unity, i.e.

$$\sum_i p_i = 1$$

The actual functional to be minimised contains the Lagrange multiplier λ in front of the constraint

$$\tilde{F} = \sum_i [\varepsilon_i p_i + kT p_i \ln p_i] + \lambda \sum_i p_i = \min$$

which yields

$$0 = \frac{\partial \tilde{F}}{\partial p_i} = \varepsilon_i + kT \left[\ln p_i + p_i \frac{1}{p_i} \right] + \lambda$$

or

$$p_i = \left[\exp\left(-\frac{\lambda + kT}{kT}\right) \right] \exp(-\varepsilon_i/kT)$$

Hence we have

$$\sum_i p_i = \left[\exp\left(-\frac{\lambda + kT}{kT}\right) \right] \sum_i \exp(-\varepsilon_i/kT) = 1$$

and

$$\left[\exp\left(-\frac{\lambda + kT}{kT}\right) \right] = \frac{1}{\sum_i \exp(-\varepsilon_i/kT)}$$

Making use of

$$Z = \sum_i \exp(-\varepsilon_i/kT)$$

for the definition of the *partition function* Z (for “Zustandsumme”) the individual fractions become

$$p_i = \frac{\exp(-\varepsilon_i/kT)}{Z}$$

All the thermodynamic functions (U, H, S, F, G, C_p, C_v but also $M, C_H, C_M, \chi_T, \chi_S$) can be expressed with the help of the partition function. For example, the mean energy per particle is

$$\bar{E} = \sum_i p_i \varepsilon_i = \frac{\sum_i \varepsilon_i \exp(-\varepsilon_i/kT)}{Z}$$

and since

$$\sum_i \varepsilon_i \exp(-\beta \varepsilon_i) = - \sum_i \frac{\partial}{\partial \beta} \exp(-\beta \varepsilon_i) = - \frac{\partial Z}{\partial \beta}$$

it results in

$$\bar{E} = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial \beta}$$

For N particles the internal energy becomes

$$U = N\bar{E}$$

The entropy can be expressed as

$$S = k(\ln Z + \beta \bar{E}) = k \ln Z + \frac{\bar{E}}{T}$$

and the free energy as

$$F = U - TS = -NkT \ln Z$$

The valuable expressions in terms of the partition function of a canonical system are presented in Table 2.8.

TABLE 2.8

Thermodynamic functions in terms of the canonical partition function

Function	General expression (per particle)	Standard state of a perfect gas (1 mol) ^a
$U(S, V)$	$kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{V,N}$	
$F(T, V)$	$-kT \ln Z$	
$p = -\left(\frac{\partial F}{\partial V} \right)_{T,N}$	$kT \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N}$	$\frac{RT}{V}$
pV	$kT \left(\frac{\partial \ln Z}{\partial \ln V} \right)_{T,N}$	RT
$H(S, p)$	$kT \left(\frac{\partial \ln Z}{\partial \ln T} \right)_{V,N} + kT \left(\frac{\partial \ln Z}{\partial \ln V} \right)_{T,N}$	$H_T^\circ = H_0^\circ + RT \left(\frac{\partial \ln Z}{\partial \ln T} \right)_p$
$\left. \begin{matrix} S(U, V) \\ S(H, p) \end{matrix} \right\}$	$k \ln Z + k \left(\frac{\partial \ln Z}{\partial \ln T} \right)_{V,N}$	$S_T^\circ = R \ln \left(\frac{Z}{N_A^*} \right) + R \left(\frac{\partial \ln Z}{\partial \ln T} \right)_p$
$G(T, p)$	$-kT \ln Z + kT \left(\frac{\partial \ln Z}{\partial \ln V} \right)_{T,N}$	$G_T^\circ = H_0^\circ - RT \ln \left(\frac{Z}{N_A^*} \right)$
$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N}$	$k \left(\frac{\partial \ln Z}{\partial \ln T} \right)_{V,N} + k \left(\frac{\partial^2 \ln Z}{\partial (\ln T)^2} \right)_{V,N}$	
$C_p = \left(\frac{\partial H}{\partial T} \right)_{p,N}$		$C_p^\circ = R \left(\frac{\partial \ln Z}{\partial \ln T} \right)_p + R \left(\frac{\partial^2 \ln Z}{\partial (\ln T)^2} \right)_p$

^a $U_0^\circ = H_0^\circ = F_0^\circ = G_0^\circ = N_A(E_0^{\text{el}} + \epsilon_0^{\text{vib}})$; N_A^* is the numerical value of the Avogadro constant (number of particles per mole).

The partition function for a molecule is formed of the partition functions for individual types of energy increments (motions), i.e. from the translational, rotational, internal rotational (free rotation, hindered rotation), vibrational, electronic and nuclear spin partition functions

$$z^{\text{mol}} = z^{\text{t}} z^{\text{r}} z^{\text{ir}} \dots z^{\text{v}} z^{\text{e}} z^{\text{n}}$$

These increments have been expressed for certain model cases, as exemplified by Table 2.9.

For a system of N identical, non-interacting particles the total partition function is

(a) distinguishable particles (as in a solid state)

$$Z = (z)^N$$

(b) non-distinguishable particles (as in a perfect gas)

$$Z = \frac{(z)^N}{N!}$$

Using the Stirling formula

$$\ln N! \approx N \ln N - N$$

the last expression can be rewritten as

$$\ln Z = N \ln z - \ln N! = N[\ln(z/N) + 1]$$

All energies entering the partition function should be related to the same reference state E_0 . Usually this is a state of free, independent molecules in the ground nuclear and electronic configuration with the lowest values of quantum numbers for other motions. This means that E_0 includes the zero-point vibration energy, $\varepsilon_0^{\text{vib}}$, as well. Then, for a system of N molecules

$$U_0 = NE_0 = N(E_0^{\text{el}} + \varepsilon_0^{\text{vib}})$$

represents the internal energy of a perfect gas.

A unimolecular reaction $A \rightleftharpoons B$ in the gas phase is characterised by the equilibrium constant

$$K_p = \exp[-(G_{T,B}^0 - G_{T,A}^0)/RT] = \left(\frac{z_B}{z_A}\right) \exp[-(H_{0,B}^0 - H_{0,A}^0)/RT]$$

TABLE 2.9
Partition functions for a molecule

Type	Typical value	Model	Expression ^a
Translational, z^t	$10^{25} V$	particle in a rectangular box $V = abc$	$(2\pi mkT)^{3/2} h^{-3} V$
Rotational, z^r	10^3	solid rotator	$8\pi^2 (8\pi^3 I_A I_B I_C)^{1/2} (kT)^{3/2} h^{-3} / \sigma$
—linear molecule	10^2		$8\pi^2 I k T h^{-2} / \sigma$
Internal rotation—free, z^{fr}	10	symmetric rotator	$(8\pi^3 I_r k T)^{1/2} h^{-1} / \sigma_m$
—hindered, z^{hr}	10	periodical potential	$z^{fr} \int_0^{2\pi} \exp[-(1 - \cos n\alpha) V_0] d\alpha$
Vibrational, z^v	10	harmonic oscillator	$\prod_{i=1}^{3n-6} \frac{1}{1 - \exp(-h\nu_i/kT)}$
—zero-point	1		$\sum_{i=1}^{3n-6} \exp(-h\nu_i/2kT)$
—anharmonic corrections, z^a	1	anharmonic oscillator	$\prod_i^{3n-6} \left(1 - \frac{g_i^v (g_i^v + 1) h x_{ii} / kT}{[\exp(h\nu_i/kT) - 1]^2} \right)$
Electronic, z^e	1	adiabatic potential minima	$\sum_i g_i^e \exp[-(E_i - E_0)/kT]$
Nuclear, z^n	1	nuclear spins	$\prod_N (2I_N + 1)$

^aSymbols used: m —mass of the molecule, I_A —moments of inertia, I_r —reduced moment of inertia, σ —symmetry number, α —angle of hindered rotation, V_0 —barrier to internal rotation, ν_i —frequencies of the fundamental vibrations, x_{ii} —anharmonicity constants, g_i^e —degeneracy of electronic states, E_i —energies of electronic states, E_0 —reference energy level (origin), I_N —nuclear spin number, g_i^v —degeneracy of vibrational states.

For the general type of chemical reaction

$$\sum_i \nu_i A_i = 0$$

(the stoichiometric coefficients ν_i are negative for reactants and positive for products) the equilibrium constant becomes expressed through

$$-RT \ln K_p = \sum_i \nu_i G_{T,i}^\circ$$

and since

$$G_{T,i}^\circ = H_{T,i}^\circ - RT \ln \left(\frac{z_i}{N_A^*} \right)$$

this implies the validity of

$$K_p = \prod_i \left(\frac{z_i}{N_A^*} \right)^{\nu_i} \exp \left(- \sum_i \nu_i H_{T,i}^\circ / RT \right)$$

2.6.3 Partition function in magnetism

When the individual particles of the system have magnetic moments μ_i , then their energies in the presence of a field B are

$$\varepsilon_i = -\mu_i B$$

The thermal average of the macroscopic magnetic moment is

$$\bar{\mu} = \sum_i p_i \mu_i = \frac{\sum_i \mu_i \exp(\beta \mu_i B)}{Z}$$

and since

$$\sum_i \mu_i \exp(\beta \mu_i B) = \frac{1}{\beta} \sum_i \frac{\partial}{\partial B} \exp(\beta \mu_i B) = \frac{1}{\beta} \frac{\partial Z}{\partial B}$$

it follows that

$$\bar{\mu} = \frac{1}{\beta Z} \frac{\partial Z}{\partial B} = kT \frac{\partial \ln Z}{\partial B}$$

If N is the number of magnetic moments per unit volume, the magnetisation becomes expressed as

$$M = NkT \frac{\partial \ln Z}{\partial B} = - \frac{\partial F}{\partial B}$$

The magnetic susceptibility adopts the form of

$$\chi = \mu_0 \frac{\partial M}{\partial B} = -\mu_0 \frac{\partial^2 F}{\partial B^2}$$

However, the magnetic moment is a vector and the magnetic susceptibility a second-rank tensor so that the rigorous transcription is

$$\chi_{ab} = \mu_0 \frac{\partial}{\partial B_a} \left[\frac{\sum_i (\mu_i)_b \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} \right]$$

with

$$(\mu_i)_b = - \frac{\partial \varepsilon_i}{\partial B_b}$$

Important expressions of statistical thermodynamics in magnetism are collected in Table 2.10.

2.6.4 Density matrix

The density matrix (the thermal average density matrix operator) is introduced through

$$\rho = \frac{\exp(-\beta \hat{H})}{Z}$$

The partition function Z is the trace (sum of diagonal elements) of a matrix for which the diagonal elements are

$$A_{ii} = \exp(-\beta \varepsilon_i)$$

TABLE 2.10

Thermodynamic functions of magnetism in terms of the canonical partition function

Function ^a	General expression (per particle)
$U(S, M)$	$kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_M$
$F(T, M)$	$-kT \ln Z$
$M = - \left(\frac{\partial F}{\partial B} \right)_T$	$kT \left(\frac{\partial \ln Z}{\partial B} \right)_T$
$\mu_0 HM$	$kT \left(\frac{\partial \ln Z}{\partial \ln B} \right)_T$
$E(S, H) = U(S, M) - \mu_0 HM$	$kT \left(\frac{\partial \ln Z}{\partial \ln T} \right)_M - kT \left(\frac{\partial \ln Z}{\partial \ln B} \right)_T$
$\left. \begin{aligned} S(U, M) &= (U - F)/T \\ S(E, H) &= (E - G)/T \end{aligned} \right\}$	$k \ln Z + k \left(\frac{\partial \ln Z}{\partial \ln T} \right)_M$
$G(T, H) = F(T, M) - \mu_0 HM$	$-kT \ln Z - kT \left(\frac{\partial \ln Z}{\partial \ln B} \right)_T$
$C_M = \left(\frac{\partial U}{\partial T} \right)_M$	$k \left(\frac{\partial \ln Z}{\partial \ln T} \right)_M + k \left(\frac{\partial^2 \ln Z}{\partial (\ln T)^2} \right)_M$
$C_H = \left(\frac{\partial E}{\partial T} \right)_H$	
$\chi_T = \left(\frac{\partial M}{\partial H} \right)_T$	$-\mu_0 \left(\frac{\partial^2 F}{\partial B^2} \right)_T$
$\chi_S = \left(\frac{\partial M}{\partial H} \right)_S$	

^aSymbol E is used for enthalpy instead of H which is the magnetic field strength.

Such a matrix would be obtained as the representation in the orthogonal eigenstates of a Hamiltonian $\hat{H}$. Thus Z is no longer an operator; it is a number serving as the normalisation constant. The above density matrix is normalised

$$\text{Tr}\{\rho\} = 1$$

and can be used to compute the thermal average of any observable or operator

$$\langle A \rangle_T = \text{Tr}\{A\rho\} = \text{Tr}\{\rho A\}$$

Thus the thermal average energy is the internal energy

$$U = \bar{E} = N_A \langle \hat{H} \rangle_T = N_A \text{Tr}\{\hat{H}\rho\} = N_A \frac{\text{Tr}\{\hat{H} \exp(-\beta\hat{H})\}}{\text{Tr}\{\exp(-\beta\hat{H})\}}$$

and since it holds true that

$$Z = \exp(-\beta F) = \text{Tr}\{\exp(-\beta\hat{H})\}$$

a well known thermodynamic identity is also obeyed

$$U = \frac{\partial(\beta F)}{\partial\beta}$$

The normalised density matrix satisfies

$$-\frac{\partial\rho}{\partial\beta} = \left(\hat{H} - \langle \hat{H} \rangle_T\right)\rho$$

The molar heat capacity can be expressed through the formula

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} = \frac{\partial U}{\partial\beta} \frac{\partial\beta}{\partial T} = \frac{\partial U}{\partial\beta} \frac{\partial}{\partial T} \left(\frac{1}{kT} \right) = -\frac{1}{kT^2} \frac{\partial U}{\partial\beta} \\ &= -N_A k\beta^2 \frac{\partial}{\partial\beta} \left[\frac{\text{Tr}\{\hat{H} \exp(-\beta\hat{H})\}}{\text{Tr}\{\exp(-\beta\hat{H})\}} \right] \end{aligned}$$

After the derivatives are accomplished, the following form appears

$$\begin{aligned}
 C_V &= -N_A k \beta^2 \frac{\partial}{\partial \beta} \frac{\sum_i \hat{H} \exp(-\beta \hat{H})}{\sum_i \exp(-\beta \hat{H})} \\
 &= -N_A k \beta^2 \frac{1}{\left[\sum_i \exp(-\beta \hat{H}) \right]^2} \left\{ \left[\sum_i (-\hat{H}^2) \exp(-\beta \hat{H}) \right] \left[\sum_i \exp(-\beta \hat{H}) \right] \right. \\
 &\quad \left. - \left[\sum_i \hat{H} \exp(-\beta \hat{H}) \right] \left[\sum_i (-\hat{H}) \exp(-\beta \hat{H}) \right] \right\} \\
 &= N_A k \beta^2 \left\{ \frac{\sum_i (\hat{H}^2) \exp(-\beta \hat{H})}{\sum_i \exp(-\beta \hat{H})} - \left[\frac{\sum_i \hat{H} \exp(-\beta \hat{H})}{\sum_i \exp(-\beta \hat{H})} \right]^2 \right\} = N_A k \beta^2 \left\{ \langle \hat{H}^2 \rangle_T - \langle \hat{H} \rangle_T^2 \right\}
 \end{aligned}$$

which can be rewritten through a statistical variance as follows

$$C_V = N_A k \beta^2 \langle (\hat{H} - U)^2 \rangle_T$$

This result can be interpreted that the heat capacity (measured at constant volume) is a thermal fluctuation in the internal energy.

As soon as the magnetic field is applied, the Hamiltonian relaxes to

$$\hat{H} = \hat{H}_0 - B \hat{M}$$

where $\hat{M}$ [$\text{A m}^2 = \text{J T}^{-1}$] is the *magnetisation operator* (magnetic moment operator). The thermal average magnetisation is

$$\overline{M} = \langle M \rangle_T = N_A \text{Tr}\{\hat{M} \rho\} = -\frac{\partial F}{\partial B}$$

The molar isothermal magnetic susceptibility becomes expressed as follows

$$\chi_T = N_A \mu_0 \frac{\partial}{\partial B} \langle M \rangle_T = N_A \mu_0 \frac{\partial}{\partial B} \left[\frac{\text{Tr}\{\hat{M} \exp(-\beta \hat{H})\}}{\text{Tr}\{\exp(-\beta \hat{H})\}} \right]$$

An analogous procedure of the differentiation as above yields the final result

$$\chi_T = N_A \mu_0 \beta \langle (\hat{M} - \overline{M})^2 \rangle_T$$

which can be interpreted that the isothermal magnetic susceptibility is, in fact, a thermal fluctuation of the magnetisation.

SUMMARY

1. The magnetic susceptibility is introduced as a thermodynamic quantity which requires a partial differentiation of the magnetisation according to the applied field. This differential (isothermal) magnetic susceptibility differs from the frequent definition of mean magnetic susceptibility if the behaviour of the magnetic material is nonlinear.
2. Different experimental techniques, depending on whether they register the magnetic response in static or alternating fields, yield different types of magnetic susceptibility. In certain situations a correction to the demagnetisation effects is necessary.
3. A linkage between quantum theory (Hamiltonian, energy levels) and the macroscopic thermodynamical quantities (magnetisation, magnetic heat capacity, magnetic susceptibility) is given by statistical thermodynamics, in which the partition function adopts a key role.

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Microscopic Magnetic Properties

3.1 MAGNETIC PARAMETERS

Magnetoactive components of a molecule comprise:

- (a) the electronic orbital angular momentum $\vec{L} = \sum_i \vec{l}_i$ with quantum numbers L, M_L (present in any molecule),
- (b) the magnetic moment of the molecule $\vec{\mu}_e$ owing to the electron spin angular momentum $\vec{S} = \sum_i \vec{s}_i$ (present in open shell molecules),
- (c) permanent magnetic moments of the nuclei $\vec{\mu}_N$ owing to their non-zero nuclear spin I_N ,
- (d) the rotational angular momentum of a (gaseous) molecule with the quantum number J .

Normally only some of them are considered in the energy expression up to the second order of the Taylor expansion [1–4].

Let us consider a simple case where the energy depends upon two parameters, $E = f(\vec{B}, \vec{\mu}_e)$. The wave function $\Psi(\vec{B}, \vec{\mu}_e)$ of the system is expanded around the zero-field values of $\vec{B}$ and $\vec{\mu}_e$

$$\Psi(\vec{B}, \vec{\mu}_e) = \Psi^{(0,0)} + \vec{\Psi}^{(1,0)} \cdot \vec{B} + \vec{\Psi}^{(0,1)} \cdot \vec{\mu}_e + \dots$$

and truncated after linear terms; the vector quantities $\vec{\Psi}^{(m,n)}$ are the expansion coefficients, m -linear in $\vec{B}$ and n -linear in $\vec{\mu}_e$. We will see later that these coefficients can be expressed by means of perturbation theory. Also, the Hamiltonian of the system can be expressed in the form of an expansion

$$\begin{aligned} \hat{H} = & H^{(0,0)} + \vec{H}^{(1,0)} \cdot \vec{B} + \frac{1}{2} \vec{B} \cdot \vec{\overline{H}}^{(2,0)} \cdot \vec{B} \\ & + \vec{H}^{(0,1)} \cdot \vec{\mu}_e + \vec{\mu}_e \cdot \vec{\overline{H}}^{(1,1)} \cdot \vec{B} + \frac{1}{2} \vec{\mu}_e \cdot \vec{\overline{H}}^{(0,2)} \cdot \vec{\mu}_e \end{aligned}$$

truncated after quadratic terms. The expression for the total energy of the system is possible in the form

$$E(\vec{B}, \vec{\mu}_e) = \left\langle \Psi(\vec{B}, \vec{\mu}_e) \left| \hat{H}(\vec{B}, \vec{\mu}_e) \right| \Psi(\vec{B}, \vec{\mu}_e) \right\rangle$$

but when the wave function is treated by means of perturbation theory the following expression holds true

$$E(\vec{B}, \vec{\mu}_e) = \left\langle \Psi^{(0,0)} \left| \hat{H}(\vec{B}, \vec{\mu}_e) \right| \Psi(\vec{B}, \vec{\mu}_e) \right\rangle$$

Then

$$\begin{aligned} E(\vec{B}, \vec{\mu}_e) = & \left\langle \Psi^{(0,0)} \left| \left[H^{(0,0)} + \vec{H}^{(1,0)} \cdot \vec{B} + \frac{1}{2} \vec{B} \cdot \overline{\overline{H}}^{(2,0)} \cdot \vec{B} \right. \right. \right. \\ & \left. \left. + \vec{H}^{(0,1)} \cdot \vec{\mu}_e + \vec{\mu}_e \cdot \overline{\overline{H}}^{(1,1)} \cdot \vec{B} + \frac{1}{2} \vec{\mu}_e \cdot \overline{\overline{H}}^{(0,2)} \cdot \vec{\mu}_e \right] \right. \\ & \left. \left| \Psi^{(0,0)} + \vec{\Psi}^{(1,0)} \cdot \vec{B} + \vec{\Psi}^{(0,1)} \cdot \vec{\mu}_e \right| \right\rangle \end{aligned}$$

The last expression contains 6×3 terms but these can be collected according to the same power of $\vec{B}$ and $\vec{\mu}_e$. Hence we arrive at

$$\begin{aligned} E(\vec{B}, \vec{\mu}_e) = & E_0 - \vec{\gamma} \cdot \vec{B} - \frac{1}{2} \vec{B} \cdot \overline{\overline{\kappa}} \cdot \vec{B} - \vec{\mu}_e \cdot \vec{B} \\ & + \vec{\mu}_e \cdot \overline{\overline{\Delta g}} \cdot \vec{B} - \frac{1}{2} \vec{\mu}_e \cdot \overline{\overline{D}} \cdot \vec{\mu}_e + \dots \end{aligned}$$

(notice the assignment of the signs and factors of $1/2$). In this expression: $\vec{\gamma}$ is the permanent magnetic moment of the system, $\overline{\overline{\kappa}}$ is the (reduced) magnetic susceptibility tensor, $\overline{\overline{\Delta g}}$ is the electron spin induced (differential) magneto-gyric-ratio tensor, and $\overline{\overline{D}}$ is the electron spin-spin coupling tensor.

The susceptibility tensor results from

$$-\frac{1}{2} \vec{B} \cdot \overline{\overline{\kappa}} \cdot \vec{B} = \left\langle \Psi^{(0,0)} \left| \frac{1}{2} \vec{B} \cdot \overline{\overline{H}}^{(2,0)} \cdot \vec{B} \right| \Psi^{(0,0)} \right\rangle + \left\langle \Psi^{(0,0)} \left| \vec{H}^{(1,0)} \cdot \vec{B} \right| \vec{\Psi}^{(1,0)} \cdot \vec{B} \right\rangle$$

The g -tensor is evaluable through

$$\begin{aligned} \vec{\mu}_e \cdot \overline{\overline{\Delta g}} \cdot \vec{B} = & \left\langle \Psi^{(0,0)} \left| \vec{\mu}_e \cdot \overline{\overline{H}}^{(1,1)} \cdot \vec{B} \right| \Psi^{(0,0)} \right\rangle \\ & + \left\langle \Psi^{(0,0)} \left| \vec{H}^{(1,0)} \cdot \vec{B} \right| \vec{\Psi}^{(0,1)} \cdot \vec{\mu}_e \right\rangle + \left\langle \Psi^{(0,0)} \left| \vec{H}^{(0,1)} \cdot \vec{\mu}_e \right| \vec{\Psi}^{(1,0)} \cdot \vec{B} \right\rangle \end{aligned}$$

Finally, the D -tensor is determined via

$$-\frac{1}{2}\vec{\mu}_e \cdot \vec{\bar{D}} \cdot \vec{\mu}_e = \left\langle \Psi^{(0,0)} \left| \frac{1}{2}\vec{\mu}_e \cdot \vec{\bar{H}}^{(0,2)} \cdot \vec{\mu}_e \right| \Psi^{(0,0)} \right\rangle \\ + \left\langle \Psi^{(0,0)} \left| \vec{\bar{H}}^{(0,1)} \cdot \vec{\mu}_e \right| \bar{\Psi}^{(0,1)} \cdot \vec{\mu}_e \right\rangle$$

Now it is possible to generalise the above expression taking into account different energy dependences upon the magnetoactive components in molecules from which different sets of magnetic parameters result (Table 3.1). The additional tensor quantities are: $\vec{\bar{\sigma}}_N$ is the magnetic shielding tensor of the N th nucleus, $\vec{\bar{K}}_{MN}$ is the nuclear spin-spin coupling tensor of nuclei M and N , $\vec{\bar{T}}_N$ is the electron-nuclear hyperfine coupling tensor for the N th nucleus (often denoted as $\vec{\bar{A}}_N$), $\vec{\bar{g}}_J$ is the rotationally induced molecular magnetogyric-ratio tensor, and $\vec{\bar{M}}_N$ is the spin-rotation coupling tensor for the N th nucleus.

Each magnetic parameter can be expressed as an appropriate second derivative of the energy, i.e.

$$\kappa_{ab} = -[\partial^2 E(\vec{B})/\partial B_a \partial B_b]_0$$

$$\Delta g_{ab} = [\partial^2 E(\vec{B}, \vec{\mu}_e)/\partial B_a \partial \mu_{e,b}]_0$$

$$D_{ab} = [\partial^2 E(\vec{\mu}_e)/\partial \mu_{e,a} \partial \mu_{e,b}]_0$$

$$\sigma_{N,ab} = [\partial^2 E(\vec{B}, \vec{\mu}_N)/\partial B_a \partial \mu_{N,b}]_0$$

TABLE 3.1

A survey of magnetic parameters

Energy dependence	Magnetic parameters $\vec{P}^{(m,n,k)}$
$E(A, B, C)$	m —linear in A , n —linear in B and k —linear in C
$E(\vec{B})$	$\vec{\bar{\kappa}}^{(2)}$
$E(\vec{B}, \vec{\mu}_e)$	$\vec{\bar{\kappa}}^{(2,0)}, \vec{\bar{\Delta g}}^{(1,1)}, \vec{\bar{D}}^{(0,2)}$
$E(\vec{B}, \vec{\mu}_N)$	$\vec{\bar{\kappa}}^{(2,0)}, \vec{\bar{\sigma}}_N^{(1,1)}, \vec{\bar{K}}_{M,N}^{(0,2)}$
$E(\vec{B}, \vec{\mu}_N, \vec{\mu}_e)$	$\vec{\bar{\kappa}}^{(2,0,0)}, \vec{\bar{\sigma}}_N^{(1,1,0)}, \vec{\bar{K}}_{M,N}^{(0,2,0)}, \vec{\bar{\Delta g}}^{(1,0,1)}, \vec{\bar{T}}_N^{(0,1,1)}, \vec{\bar{D}}^{(0,0,2)}$
$E(\vec{B}, \vec{\mu}_N, \vec{J})$	$\vec{\bar{\kappa}}^{(2,0,0)}, \vec{\bar{\sigma}}_N^{(1,1,0)}, \vec{\bar{K}}_{M,N}^{(0,2,0)}, \vec{\bar{g}}_J^{(1,0,1)}, \vec{\bar{M}}_N^{(0,1,1)}, \vec{\bar{D}}_J^{(0,0,2)}$

$$K_{MN,ab} = [\partial^2 E(\vec{\mu}_M, \vec{\mu}_N) / \partial \mu_{M,a} \partial \mu_{N,b}]_0$$

$$T_{N,ab} = [\partial^2 E(\vec{\mu}_N, \vec{\mu}_e) / \partial \mu_{N,a} \partial \mu_{e,b}]_0$$

The derivatives are evaluated at the point $\vec{B} = \vec{\mu}_M = \vec{\mu}_N = \vec{\mu}_e = 0$. These reduced magnetic parameters may require a transformation when compared with experimental data (unit homogeneity). Note that $\bar{k}$ is a symmetric tensor whereas $\bar{\sigma}_N$ is not.

The expressions for individual magnetic parameters depend upon the form of the Hamiltonian terms $H^{(m,n,k)}$. These result from the inclusion of the magnetic field into the Schrödinger equation and/or Dirac equation.

3.2 ELECTROMAGNETIC POTENTIAL

The electromagnetic field is characterised by the scalar potential $\Phi(\vec{r}, t)$ and the vector potential $\vec{A}(\vec{r}, t)$. The scalar potential contributes to the potential energy

$$V_i = q_i \Phi_i$$

and the vector potential to the linear momentum

$$\vec{\pi}_i = \vec{p}_i - q_i \vec{A}_i$$

where q_i are charges of particles (SI units are used). Within the cgs & emu unit system the contribution to the linear momentum reads $(q_i/c)\vec{A}_i$.

The vector potential should be fixed somehow and the most frequently used condition is the *Coulomb gauge*

$$\text{div} \vec{A} = \vec{\nabla} \cdot \vec{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z} = 0$$

The magnetic induction is introduced as

$$\vec{B} = \text{rot} \vec{A} = \vec{\nabla} \times \vec{A}$$

For a homogeneous magnetic field the expression of $\vec{A}$ in terms of $\vec{B}$ is possible

$$\vec{A}(\vec{r}) = \frac{1}{2} \vec{B} \times (\vec{r} - \vec{G})$$

where $\vec{G}$ is an arbitrary point in space called the *gauge origin*. A change of the origin of $\vec{G}$ is only one type of possible gauge transformation. The exact quantum-mechanical expressions are invariant with respect to any choice of the gauge origin; however, the approximate expressions are not.

The internal vector potential due to the non-zero nuclear magnetic moment $\vec{\mu}_N$ (nuclear spin) is

$$\vec{A}_N(\vec{r}) = \frac{\mu_0 \vec{\mu}_N \times (\vec{r} - \vec{r}_N)}{4\pi |\vec{r} - \vec{r}_N|^3}$$

where $\vec{r}_N$ is the position of the N th nucleus. This is also a natural gauge origin for the nucleus.

Analogously, the internal vector potential due to the non-zero electronic magnetic moment $\vec{\mu}_i$ (electron spin) is

$$\vec{A}_i(\vec{r}) = \frac{\mu_0 \vec{\mu}_i \times (\vec{r} - \vec{r}_i)}{4\pi |\vec{r} - \vec{r}_i|^3}$$

The total vector potential is the sum of the external, electronic and nuclear contributions

$$\vec{A}_{\text{tot}}(\vec{r}) = \vec{A}_{\text{ext}}(\vec{r}) + \sum_i \vec{A}_i(\vec{r}) + \sum_N \vec{A}_N(\vec{r})$$

The magnetic induction due to the internal source (electron or a magnetoactive nucleus) is

$$\vec{B}_i(\vec{r}) = \vec{\nabla} \times \vec{A}_i(\vec{r}) = -\frac{\mu_0}{4\pi} \left\{ \frac{\vec{\mu}_i}{|\vec{r} - \vec{r}_i|^3} - 3 \frac{[\vec{\mu}_i \cdot (\vec{r} - \vec{r}_i)]}{|\vec{r} - \vec{r}_i|^5} (\vec{r} - \vec{r}_i) \right\}$$

$$\vec{B}_N(\vec{r}) = \vec{\nabla} \times \vec{A}_N(\vec{r}) = -\frac{\mu_0}{4\pi} \left\{ \frac{\vec{\mu}_N}{|\vec{r} - \vec{r}_N|^3} - 3 \frac{[\vec{\mu}_N \cdot (\vec{r} - \vec{r}_N)]}{|\vec{r} - \vec{r}_N|^5} (\vec{r} - \vec{r}_N) \right\}$$

In the above formulae the permeability of the vacuum can be replaced by the permittivity of the vacuum since $\epsilon_0 \mu_0 c^2 = 1$.

3.3 THE SCHRÖDINGER EQUATION IN A MAGNETIC FIELD

The spin-less non-relativistic Hamiltonian of interacting particles consists of the kinetic energy and the potential energy

$$\hat{H} = \hat{T} + \hat{V} = \sum_{\alpha} \left[\frac{1}{2m_{\alpha}} (\vec{\pi}_{\alpha})^2 \right] + \sum_{\alpha} \hat{V}_{\alpha} + \sum_{\alpha < \beta} \hat{V}_{\alpha\beta}$$

For a molecule consisting of N nuclei and n electrons exposed to the external electromagnetic field it adopts the form of

$$\hat{H}_{\text{elmg}} = \sum_{\alpha}^{N+n} \left[\frac{1}{2m_{\alpha}} (\vec{p}_{\alpha} - q_{\alpha} \vec{A}_{\alpha})^2 + q_{\alpha} \Phi_{\alpha} \right] + \sum_{\alpha < \beta}^{N+n} \frac{q_{\alpha} q_{\beta}}{4\pi\epsilon_0 r_{\alpha\beta}}$$

For the electromagnetic field switched off, the Hamiltonian of a free molecule is

$$\hat{H}_0 = \sum_{\alpha}^{N+n} \left[\frac{1}{2m_{\alpha}} (\vec{p}_{\alpha})^2 \right] + \sum_{\alpha < \beta}^{N+n} \frac{q_{\alpha} q_{\beta}}{4\pi\epsilon_0 r_{\alpha\beta}}$$

Then we can write

$$\hat{H}_{\text{elmg}} = \hat{H}_0 + \sum_{\alpha}^{N+n} \left[q_{\alpha} \Phi_{\alpha} - \frac{q_{\alpha}}{2m_{\alpha}} \vec{A}_{\alpha} \cdot \vec{p}_{\alpha} - \frac{q_{\alpha}}{2m_{\alpha}} \vec{p}_{\alpha} \cdot \vec{A}_{\alpha} + \frac{q_{\alpha}^2}{2m_{\alpha}} (\vec{A}^2)_{\alpha} \right]$$

Since $\vec{p} = -i\hbar\vec{\nabla}$ is a differential operator, the product $\vec{p} \cdot \vec{A}$ should be analysed in more detail, i.e.

$$\vec{p} \cdot \vec{A} \Psi = \vec{A} \cdot (\vec{p} \Psi) + \Psi (\vec{p} \cdot \vec{A})$$

Because it is

$$\vec{p} \cdot \vec{A} = -i\hbar\vec{\nabla} \cdot \vec{A} = -i\hbar \text{div} \vec{A}$$

and under the Coulomb gauge ($\text{div} \vec{A} = 0$) we receive

$$\hat{H}_{\text{elmg}} = \hat{H}_0 + \sum_{\alpha}^{N+n} \left[q_{\alpha} \Phi_{\alpha} - \frac{q_{\alpha}}{m_{\alpha}} \vec{A}_{\alpha} \cdot \vec{p}_{\alpha} + \frac{q_{\alpha}^2}{2m_{\alpha}} (\vec{A}^2)_{\alpha} \right]$$

For a magnetostatic field only, making use of the expression of $\vec{A}$ in terms of $\vec{B}$, we get for electrons ($q = -e$)

$$\hat{H}_{\text{mg}} = \hat{H}_0 + \frac{e}{2m_e} \sum_i^n \vec{B} \times (\vec{r}_i - \vec{G}) \cdot \vec{p}_i + \frac{e^2}{8m_e} \sum_i^n \left[\vec{B} \times (\vec{r}_i - \vec{G}) \right]^2$$

The second term contains the product which can be rewritten as

$$\vec{B} \times (\vec{r}_i - \vec{G}) \cdot \vec{p}_i = \vec{B} \cdot (\vec{r}_i - \vec{G}) \times \vec{p}_i = \vec{B} \cdot \vec{l}_{Gi} = \vec{l}_{Gi} \cdot \vec{B}$$

where the vector product

$$\vec{l}_{Gi} = (\vec{r}_i - \vec{G}) \times \vec{p}_i$$

is the (orbital) angular momentum operator referring to the gauge origin $\vec{G}$. The last term contains the product which can be manipulated as

$$(\vec{d} \times \vec{B}) \cdot (\vec{d} \times \vec{B}) = (\vec{d}^2)(\vec{B}^2) - (\vec{d} \cdot \vec{B})(\vec{B} \cdot \vec{d})$$

where

$$\vec{d} = \vec{r}_{Gi} = \vec{r}_i - \vec{G}$$

Then the magnetic Hamiltonian becomes

$$\hat{H}_{\text{mg}} = \hat{H}_0 + \frac{e}{2m_e} \sum_i^n \vec{B} \cdot \vec{l}_{Gi} + \frac{e^2}{8m_e} \sum_i^n \left[B^2 (\vec{r}_{Gi})^2 - (\vec{B} \cdot \vec{r}_{Gi})^2 \right]$$

This operator has the form of

$$\hat{H} = H^{(0)} + \vec{H}^{(1)} \cdot \vec{B} + \frac{1}{2} \vec{B} \cdot \overline{\vec{H}}^{(2)} \cdot \vec{B}$$

and thus it is suitable for generating the magnetic parameters—at least the susceptibility tensor $\bar{\kappa}$. However, the above magnetic Hamiltonian is far from being satisfactorily complete: the spin-orbit coupling and other fine interactions are missing in the non-relativistic case. Therefore it has only a limited validity. It can be unambiguously seen that the reduced magnetic susceptibility for the zero-order wave function $\Psi^{(0)}$ is

$$\begin{aligned}\kappa_{ab} &= - \left(\frac{\partial^2 \langle \Psi^{(0)} | \hat{H}_{\text{mg}} | \Psi^{(0)} \rangle}{\partial B_a \partial B_b} \right)_0 \\ &= - \frac{e^2}{8m_e} \left(\frac{\partial^2 \langle \Psi^{(0)} | \sum_i^n [B^2(\vec{r}_{Gi})^2 - (\vec{B} \cdot \vec{r}_{Gi})^2] | \Psi^{(0)} \rangle}{\partial B_a \partial B_b} \right)_0\end{aligned}$$

The derivatives can be worked out as follows

$$\frac{\partial^2 [B^2 \vec{d} \cdot \vec{d} - (\vec{B} \cdot \vec{d})(\vec{B} \cdot \vec{d})]}{\partial B_a \partial B_b} = 2[(d_x^2 + d_y^2 + d_z^2)\delta_{ab} - d_a d_b]$$

so that we arrive at a negative contribution describing the underlying *diamagnetism* of any substance

$$\kappa_{ab} = - \frac{e^2}{4m_e} \left\langle \Psi^{(0)} \left| \sum_i^n \{(\vec{r}_{Gi})^2 \delta_{ab} - (\vec{r}_{Gi})_a (\vec{r}_{Gi})_b\} \right| \Psi^{(0)} \right\rangle$$

On proceeding to the molar magnetic susceptibility the necessary transformation to SI units is

$$(\chi_{\text{mol}})_{ab} = N_A \mu_0 \kappa_{ab}$$

3.4 INCLUSION OF THE ELECTRON SPIN

3.4.1 Properties of the spin

The own angular momentum of an electron—the spin $\vec{s}(s_x, s_y, s_z)$ —is a degree of freedom which obeys the general properties of angular momentum, i.e.

(a) non-commutation of individual components, viz.

$$\hat{s}_x \hat{s}_y - \hat{s}_y \hat{s}_x = i\hbar \hat{s}_z$$

(b) commutation of each component with the Hamiltonian $\hat{H}_0$

$$\hat{s}_\alpha \hat{H}_0 - \hat{H}_0 \hat{s}_\alpha = 0$$

(c) commutation of each component with the square $\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$

$$\hat{s}_\alpha \hat{s}^2 - \hat{s}^2 \hat{s}_\alpha = 0$$

(d) commutation of the square of the spin with the Hamiltonian

$$\hat{s}^2 \hat{H}_0 - \hat{H}_0 \hat{s}^2 = 0$$

Of those five operators only three can each commute with the others (say $\hat{s}^2, \hat{s}_z, \hat{H}_0$) and thus only these operators may have the same set of wave functions $|s, m_s, E\rangle$. Unlike the orbital angular momentum, neither is the differential form of the spin operators presented, nor is the functional form of the spin functions known.

The spin number for electrons is $s = 1/2$ and thus the spin projections are

$$\hat{s}_z |s, m_s\rangle = m_s \hbar |s, m_s\rangle$$

where the quantum number m_s is restricted by $-s \leq m_s \leq +s$. Alternatively, one can write

$$\hat{s}_z |s, m_s\rangle = (\hbar/2) \hat{\sigma}_z |s, m_s\rangle$$

where $\hat{\sigma}_z$ is the z -component of the *Pauli operator*. The wave function, which is the eigenfunction of the $\hat{s}_z$ operator, is doubly valued and denoted as

$$|s, m_s\rangle = \begin{cases} |1/2, 1/2\rangle = |\alpha\rangle \\ |1/2, -1/2\rangle = |\beta\rangle \end{cases}$$

In this notation it holds true that

$$\hat{s}_z |\alpha\rangle = (\hbar/2) |\alpha\rangle, \text{ or } \hat{\sigma}_z |\alpha\rangle = |\alpha\rangle$$

$$\hat{s}_z |\beta\rangle = -(\hbar/2) |\beta\rangle, \text{ or } \hat{\sigma}_z |\beta\rangle = -|\beta\rangle$$

Such rules are satisfied for the Pauli operator in the matrix form

$$\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

acting on the basis set of column vectors

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The eigenvalues of the operator $\hat{s}_x$ can be evaluated using known expressions for the shift operators

$$\begin{aligned}\hat{s}_x|s, m_s\rangle &= (1/2)(\hat{s}_+ + \hat{s}_-)|s, m_s\rangle \\ &= (1/2)[(s - m_s)(s + m_s + 1)]^{1/2}\hbar|s, m_s + 1\rangle \\ &\quad + (1/2)[(s - m_s + 1)(s + m_s)]^{1/2}\hbar|s, m_s - 1\rangle\end{aligned}$$

which is equivalent to a couple of equations

$$\hat{s}_x|\alpha\rangle = (\hbar/2)|\beta\rangle, \text{ or } \hat{\sigma}_x|\alpha\rangle = |\beta\rangle$$

$$\hat{s}_x|\beta\rangle = (\hbar/2)|\alpha\rangle, \text{ or } \hat{\sigma}_x|\beta\rangle = |\alpha\rangle$$

and the x -component of the Pauli operator becomes

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Analogously, the eigenvalues of the operator $\hat{s}_y$ are evaluated as

$$\begin{aligned}\hat{s}_y|s, m_s\rangle &= (1/2i)(\hat{s}_+ - \hat{s}_-)|s, m_s\rangle \\ &= (1/2i)[(s - m_s)(s + m_s + 1)]^{1/2}\hbar|s, m_s + 1\rangle \\ &\quad - (1/2i)[(s - m_s + 1)(s + m_s)]^{1/2}\hbar|s, m_s - 1\rangle\end{aligned}$$

which is equivalent to a couple of equations

$$\hat{s}_y|\alpha\rangle = i(\hbar/2)|\beta\rangle, \text{ or } \hat{\sigma}_y|\alpha\rangle = i|\beta\rangle$$

$$\hat{s}_y|\beta\rangle = i(\hbar/2)|\alpha\rangle, \text{ or } \hat{\sigma}_y|\beta\rangle = i|\alpha\rangle$$

and the y -component of the Pauli operator is

$$\hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

The spin operators obey the anticommutation relationships

$$\hat{s}_x\hat{s}_y + \hat{s}_y\hat{s}_x = 0$$

$$\hat{s}_y\hat{s}_z + \hat{s}_z\hat{s}_y = 0$$

$$\hat{s}_z\hat{s}_x + \hat{s}_x\hat{s}_z = 0$$

which can be easily proven by matrix multiplication of the Pauli matrices.

3.4.2 Spin-magnetic field interaction

The electron spin generates a magnetic moment $\vec{\mu}_e$ which contributes to the energy in the presence of the magnetic field through the operator

$$\hat{H}_1^{(s-B)} = -\vec{\mu}_e \cdot \vec{B}$$

The magnetic moment of a charged particle associated with some angular momentum $\vec{l}$ is

$$\vec{\mu} = \frac{q}{2m} \vec{l}$$

For electrons ($q = -e$) it is

$$\vec{\mu}_e = -g_e \frac{e}{2m_e} \vec{s} = -g_e \frac{e}{2m_e} \frac{\hbar}{2} \vec{\sigma} = -\frac{1}{2} g_e \mu_B \vec{\sigma} \approx -\mu_B \vec{\sigma}$$

where g_e is the magnetogyric ratio for electrons (experimentally, $g_e = 2.0023$), $\mu_B = e\hbar/2m_e$ is the elementary magnetic quantum (Bohr magneton), and $\vec{\sigma}$ is the vector of Pauli spin matrix operators, $\vec{\sigma} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$.

The above expression can be rewritten as

$$\hat{H}_1^{(s-B)} = \mu_B (\hat{\sigma}_x B_x + \hat{\sigma}_y B_y + \hat{\sigma}_z B_z) = \mu_B \begin{pmatrix} B_z; & B_x - iB_y \\ B_x + iB_y; & -B_z \end{pmatrix}$$

The characteristic equation

$$(\hat{H}_0 + \hat{H}_1^{(s-B)})\Psi = E\Psi$$

adopts the form of

$$\left[\begin{pmatrix} \hat{H}_0 & 0 \\ 0 & \hat{H}_0 \end{pmatrix} + \mu_B \begin{pmatrix} B_z; & B_x - iB_y \\ B_x + iB_y; & -B_z \end{pmatrix} \right] \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} = \begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$$

and the satisfaction

$$\hat{H}_0 \Psi_1 = E_0 \Psi_1$$

$$\hat{H}_0 \Psi_2 = E_0 \Psi_2$$

is assumed. The wave function has two components

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$$

and is termed the *spinor*.

The solutions of the above homogeneous system of linear equations exist only when the determinant of the system equals zero, i.e.

$$\det \begin{pmatrix} E_0 + \mu_B B_z - E; & \mu_B(B_x - iB_y) \\ \mu_B(B_x + iB_y); & E_0 - \mu_B B_z - E \end{pmatrix} = 0$$

The evaluation of the determinant yields the quadratic equation

$$(E_0 - E)^2 - \mu_B^2(B_x^2 + B_y^2 + B_z^2) = 0$$

having two energy solutions

$$E_{\pm} = E_0 \pm \mu_B |B|$$

Exactly,

$$E_{\pm} = E_0 \pm (1/2)g_e\mu_B |B|$$

or

$$E = E_0 + m_s g_e \mu_B |B|$$

The energy shift due to the electron spin interacting with the magnetic field is named the *Zeeman term*.

Having determined the eigenvalues, the evaluation of the wave functions will continue. Making use of interrelations between the cartesian and polar coordinates, viz.

$$B_x = |B| \sin \vartheta \cos \varphi$$

$$B_y = |B| \sin \vartheta \sin \varphi$$

$$B_z = |B| \cos \vartheta$$

the electron spin-magnetic field interaction operator can be rewritten as

$$\hat{H}_1^{(s-B)} = \mu_B |B| \begin{pmatrix} \cos \vartheta & \sin \vartheta \exp(-i\varphi) \\ \sin \vartheta \exp(i\varphi) & -\cos \vartheta \end{pmatrix}$$

For the energy solution $E_+ = E_0 + \mu_B|B|$ the characteristic equation becomes

$$\begin{pmatrix} E_0 - E_+ + \mu_B|B| \cos \vartheta; & \mu_B|B| \sin \vartheta \exp(-i\varphi) \\ \mu_B|B| \sin \vartheta \exp(i\varphi); & E_0 - E_+ - \mu_B|B| \cos \vartheta \end{pmatrix} \begin{pmatrix} \Psi_1^{(+)} \\ \Psi_2^{(+)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

which implies the condition

$$(\cos \vartheta - 1)\Psi_1^{(+)} + \sin \vartheta \exp(-i\varphi)\Psi_2^{(+)} = 0$$

At the same time the normalisation condition should be obeyed

$$\left(\Psi_1^{(+)}\right)^* \left(\Psi_1^{(+)}\right) + \left(\Psi_2^{(+)}\right)^* \left(\Psi_2^{(+)}\right) = 1$$

These two requirements are fulfilled for

$$\begin{pmatrix} \Psi_1^{(+)} \\ \Psi_2^{(+)} \end{pmatrix} = \begin{pmatrix} \cos(\vartheta/2) \exp(-i\varphi/2) \\ \sin(\vartheta/2) \exp(+i\varphi/2) \end{pmatrix}$$

as can easily be proven by elementary trigonometry. This spinor describes a spinning particle in the external field defined by polar coordinates (ϑ, φ) . Analogously, for $E_- = E_0 - \mu_B|B|$ one can find

$$\begin{pmatrix} \Psi_1^{(-)} \\ \Psi_2^{(-)} \end{pmatrix} = \begin{pmatrix} -\sin(\vartheta/2) \exp(-i\varphi/2) \\ \cos(\vartheta/2) \exp(+i\varphi/2) \end{pmatrix}$$

Let the magnetic field be parallel with the z -axis (the polar angle $\vartheta = 0$). Then

$$\begin{pmatrix} \Psi_1^{(+)} \\ \Psi_2^{(+)} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

and

$$\begin{pmatrix} \Psi_1^{(-)} \\ \Psi_2^{(-)} \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The time evolution of the wave function follows from the time-dependent Schrödinger equation; thus

$$\Psi(t) = \begin{pmatrix} \Psi_1^{(+)}(t) \\ \Psi_2^{(+)}(t) \end{pmatrix} = \begin{pmatrix} \Psi_1^{(+)}(0) \cdot \exp(-iE_+t/\hbar) \\ \Psi_2^{(+)}(0) \cdot \exp(-iE_+t/\hbar) \end{pmatrix}$$

The expressions $P_+ = |\Psi_1^{(+)}(t)|^2 = 1$ and $P_- = |\Psi_2^{(-)}(t)|^2 = 1$ are equal to the probabilities that the spin is oriented parallel and antiparallel with the z -direction, respectively. Since these are independent of time, the z -projection of the spin is a constant of motion.

For the general orientation of the magnetic field in the direction (ϑ, φ) the angle ϑ remains constant but the angle φ varies with time as

$$\varphi = \frac{eB}{m_e} t$$

so that in the external magnetic field the spin rotates with angular velocity

$$\omega = eB/m_e = -2\mu_e B/\hbar$$

around the direction of the applied field. The angular velocity of precession of any angular momentum is termed the *Larmor frequency* (Larmor angular velocity).

The Hamiltonian term, including the electron spin–magnetic field interaction, is envisaged as

$$\hat{H}_1^{(s-B)} = \frac{eg_e}{2m_e} \vec{B} \cdot \vec{s} = \frac{g_e\mu_B}{2} \vec{B} \cdot \vec{\sigma}$$

and for more electrons it can be generalised as

$$\hat{H}_1^{(s-B)} = \frac{eg_e}{2m_e} \sum_i \vec{B} \cdot \vec{s}_i$$

3.4.3 Spin–orbit interaction

There is, however, one more interaction which should be (at least phenomenologically) included into the magnetic Hamiltonian: the *spin–orbit interaction*.

Let us consider an electron moving with the velocity $\vec{v}_e$ around a nucleus. The electric field strength $\vec{E}_N$ acting on the electron originates from the nuclear charge screened by other electrons. For the moving electron and fixed nucleus and/or fixed electron and moving nucleus the magnetic induction is the same and it reads

$$\vec{B}_N = (-1/c^2)\vec{v}_e \times \vec{E}_N = (1/c^2)\vec{E}_N \times \vec{v}_e$$

If we apply a central field (which is exactly true for a free atom and a good approximation for an atom in a ligand field), the $\Phi_N(r)$ is a scalar function. The electric field strength becomes

$$\vec{E}_N = -\text{grad}\Phi_N(r) = -\vec{\nabla}\Phi_N(r) = -\left(\frac{\partial\Phi_N(r)}{\partial r}\right)\left(\frac{\vec{r}}{r}\right)$$

and the magnetic induction is

$$\vec{B}_N = -\frac{1}{c^2 r} \left(\frac{\partial\Phi_N(r)}{\partial r} \right) \vec{r} \times \vec{v}_e$$

The interaction energy of the electron spin–internal magnetic field $\vec{B}_N$ is given by the operator

$$\begin{aligned} \hat{H}_1^{(s-l)} &= -\mu_e \cdot \vec{B}_N = -\left(-\frac{eg_e}{2m_e} \vec{s}\right) \cdot \left[-\frac{1}{c^2 r} \left(\frac{\partial\Phi_N(r)}{\partial r}\right) \vec{r} \times \vec{v}_e\right] \\ &= -\frac{eg_e}{2m_e^2 c^2} \frac{1}{r} \left(\frac{\partial\Phi_N(r)}{\partial r}\right) \vec{s} \cdot \vec{r} \times \vec{p}_e = \xi_N(r) \vec{s} \cdot \vec{l} \end{aligned}$$

This equation defines the *spin–orbit coupling constant* $\xi_N(r)$ as a function of the electron–nuclear distance, for which the approximate expression is

$$\xi_N(r) = -\frac{eg_e}{2m_e^2 c^2} \left(\frac{1}{r} \frac{\partial\Phi_N(r)}{\partial r} \right), \quad [\text{incomplete}]$$

We have abstracted so far from the so-called *Thomas precession*. This originates in the relativistic transformations which account for the fact that the electron is moving in a curved path around a fixed nucleus. If an axis of the gyroscope obeys an own dynamical precession with the Larmor angular velocity $\omega_L = (e/m)B$, then the corrected precession in the inertial system associated with the fixed nucleus is $\omega = \omega_L + \omega_T$, the Thomas precession being

$$\vec{\omega}_T = -(1/2c^2) \vec{v} \times \vec{a}$$

where $\vec{v}$ is the velocity, $\vec{a}$ is the acceleration. Since

$$m\vec{a} = -e\vec{E}$$

we get that the Thomas precession is

$$\vec{\omega}_T = \frac{e}{2c^2 m} \vec{v} \times \vec{E} = -\frac{e}{2m} B = -\frac{1}{2} \omega_L$$

The Thomas correction is substantial and leads to an added factor of 1/2 in the formula for the spin-orbit coupling constant

$$\xi_N(r) = -\frac{eg_e}{4m_e^2c^2} \left(\frac{1}{r} \frac{\partial \Phi_N(r)}{\partial r} \right), \quad [\text{true}]$$

There is no need to deal with this subject in more detail since in the relativistic Dirac approach the above result is natural.

For the Coulomb potential due to the nuclear charge

$$\Phi_N(r) = \frac{eZ_N}{4\pi\epsilon_0 r}$$

(Z_N is the proton number of the nucleus or the charge number of the atomic core) we obtain

$$\xi_N(r) = \frac{e^2 g_e}{16\pi\epsilon_0 m_e^2 c^2} \frac{Z_N}{r^3} = \frac{\mu_0 \mu_B^2 g_e}{4\pi \hbar^2} \frac{Z_N}{r^3}$$

For many-electron systems the electrostatic potential acting on a given electron is a superposition of Coulomb potentials of individual nuclei and remaining electrons. Such a potential, however, is non-local and its partial derivative is not defined. In this case an approximate expression is accepted

$$\hat{H}_1^{(s-l)} = \frac{e^2 g_e}{16\pi\epsilon_0 m_e^2 c^2} \sum_i \sum_N \frac{Z_N}{r_{Ni}^3} \vec{s}_i \cdot \vec{l}_{Ni} = \frac{\mu_0 \mu_B^2}{4\pi \hbar^2} g_e \sum_i \sum_N \frac{Z_N}{r_{Ni}^3} \vec{s}_i \cdot \vec{l}_{Ni}$$

or

$$\hat{H}_1^{(s-l)} = \sum_i \sum_N \xi_N(r_{Ni}) \vec{s}_i \cdot \vec{l}_{Ni}$$

where the electron-nuclear distance is r_{Ni} .

3.4.4 Magnetic Hamiltonian with electron spin

We have obtained so far that the magnetic Hamiltonian $\hat{H}_{\text{mg}}(\vec{B}, \vec{\mu}_e)$ contains the following terms

$$\begin{aligned}\hat{H}_{\text{mg}}(\vec{B}, \vec{\mu}_e) &= \hat{H}_0 + \hat{H}_1^{(s-l)} + \hat{H}_1^{(l-B)} + \hat{H}_1^{(s-B)} + \hat{H}_1^{(B-B)} \\ &= \hat{H}_0 + \sum_i \sum_N \xi_N(r_{Ni}) \vec{s}_i \cdot \vec{l}_{Ni} + \frac{\mu_B}{\hbar} \sum_i \vec{B} \cdot (\vec{l}_{Gi} + g_e \vec{s}_i) \\ &\quad + \frac{e^2}{8m_e} \sum_i^n [B^2(\vec{r}_{Gi})^2 - (\vec{B} \cdot \vec{r}_{Gi})^2]\end{aligned}$$

This can be compared with the expansion in powers of $\vec{B}$ and $\vec{\mu}_e$

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}_{10} + \hat{H}_{20} + \hat{H}_{01} + \hat{H}_{11} + \hat{H}_{02} \\ &= \hat{H}^{(0,0)} + \vec{H}^{(1,0)} \cdot \vec{B} + \frac{1}{2} \vec{B} \cdot \overline{\overline{H}}^{(2,0)} \cdot \vec{B} \\ &\quad + \vec{H}^{(0,1)} \cdot \vec{\mu}_e + \vec{\mu}_e \cdot \overline{\overline{H}}^{(1,1)} \cdot \vec{B} + \frac{1}{2} \vec{\mu}_e \cdot \overline{\overline{H}}^{(0,2)} \cdot \vec{\mu}_e\end{aligned}$$

Then the individual Hamiltonian terms are

- (a) operator of the *orbital Zeeman interaction*
—for the whole system

$$\hat{H}_{10} = \vec{H}^{(1,0)} \cdot \vec{B} = \frac{\mu_B}{\hbar} \sum_i \vec{l}_{Gi} \cdot \vec{B}$$

—for one (*ath*) vector component

$$\hat{H}_a^{(1,0)} B_a = \frac{\mu_B}{\hbar} \sum_i \hat{l}_{Gia} B_a$$

- (b) operator of the *spin-(own) orbit interaction*
—for the whole system

$$\begin{aligned}\hat{H}_{01} &= \vec{H}^{(0,1)} \cdot \vec{\mu}_e = -\frac{g_e \mu_B}{\hbar} \vec{H}^{(0,1)} \cdot \vec{S} = -\frac{g_e \mu_B}{\hbar} \sum_i \vec{H}_i^{(0,1)} \cdot \vec{s}_i \\ &= \left(\frac{\mu_0}{4\pi}\right) \frac{\mu_B^2}{\hbar^2} g_e \sum_i \sum_N Z_N r_{Ni}^{-3} \vec{l}_{Ni} \cdot \vec{s}_i = \sum_i \sum_N \xi_N(r_{Ni}) \vec{l}_{Ni} \cdot \vec{s}_i \\ \vec{H}^{(0,1)} \cdot \vec{S} &= \sum_i \vec{H}_i^{(0,1)} \cdot \vec{s}_i\end{aligned}$$

—for one electron

$$\vec{H}_i^{(0,1)} \cdot \vec{s}_i = -\left(\frac{\mu_0}{4\pi}\right) \frac{\mu_B}{\hbar} \sum_N Z_N r_{Ni}^{-3} \vec{l}_{Ni} \cdot \vec{s}_i = \sum_N \xi_N(r_{Ni}) \vec{l}_{Ni} \cdot \vec{s}_i$$

—for one electron and one vector component

$$\hat{H}_{ia}^{(0,1)} \hat{s}_{ia} = -\left(\frac{\mu_0}{4\pi}\right) \frac{\mu_B}{\hbar} \sum_N Z_N r_{Ni}^{-3} \hat{l}_{Nia} \hat{s}_{ia} = \sum_N \xi_N(r_{Ni}) \hat{l}_{Nia} \hat{s}_{ia}$$

(c) the operator of the *diamagnetic term*

—for the whole system

$$\hat{H}_{20} = \frac{1}{2} \vec{B} \cdot \overline{\overline{H}}^{(2,0)} \cdot \vec{B} = \frac{e^2}{8m_e} \sum_i [B^2(\vec{r}_{Gi})^2 - (\vec{B} \cdot \vec{r}_{Gi})^2]$$

—for individual tensor components

$$\hat{H}_{ab}^{(2,0)} = \frac{e^2}{8m_e} \sum_i (r_{Gi}^2 \delta_{ab} - r_{Gia} r_{Gib})$$

(d) the operator of the *spin-magnetic field interaction* is, at the moment, trivial

$$\overline{\overline{H}}^{(1,1)} = -1$$

(e) the operator of the *spin-spin interaction* $\overline{\overline{H}}^{(0,2)}$ is, at this stage, blank. These operators will be considered in deriving the formulae for the *D*-tensor, *g*-tensor and κ -tensor contributing to the energy $E(\vec{B}, \vec{\mu}_e)$.

3.4.5 Electron magnetic parameters

The *D*-tensor formula is reduced to the following form

$$E_1 = -\frac{1}{2} \vec{\mu}_e \cdot \overline{\overline{D}} \cdot \vec{\mu}_e = \left\langle \Psi^{(0,0)} \left| \vec{H}^{(0,1)} \cdot \vec{\mu}_e \right| \tilde{\Psi}^{(0,1)} \cdot \vec{\mu}_e \right\rangle$$

By substituting for

$$\vec{\mu}_e = -\frac{\mu_B}{\hbar} g_e \vec{S} = -\frac{\mu_B}{\hbar} g_e \sum_i \vec{s}_i$$

the left side can be written as

$$E_1 = -\frac{\mu_B^2}{2\hbar^2} g_e^2 \vec{S} \cdot \vec{D} \cdot \vec{S} = -\frac{\mu_B^2}{2\hbar^2} g_e^2 \sum_a \sum_b S_a D_{ab} S_b$$

and the right side is

$$\begin{aligned} E_1 &= \frac{g_e^2 \mu_B^2}{\hbar^2} \left\langle \Psi^{(0,0)} \left| \vec{H}^{(0,1)} \cdot \vec{S} \right| \tilde{\Psi}^{(0,1)} \cdot \vec{S} \right\rangle \\ &= \frac{g_e^2 \mu_B^2}{\hbar^2} \left\langle \Psi^{(0,0)} \left| \sum_i \vec{H}_i^{(0,1)} \cdot \vec{s}_i \right| \sum_j \tilde{\Psi}^{(0,1)} \cdot \vec{s}_j \right\rangle \\ &= \frac{g_e^2 \mu_B^2}{\hbar^2} \sum_a \sum_b \sum_i \sum_j \left\langle \Psi^{(0,0)} \left| \hat{H}_{ia}^{(0,1)} \hat{s}_{ia} \right| \Psi_b^{(0,1)} \hat{s}_{jb} \right\rangle \end{aligned}$$

so that their comparison yields

$$-\frac{1}{2} S_a D_{ab} S_b = \sum_i \sum_j \hat{s}_{ia} \hat{s}_{jb} \left\langle \Psi^{(0,0)} \left| \hat{H}_{ia}^{(0,1)} \right| \Psi_{jb}^{(0,1)} \right\rangle$$

Since the operator $\hat{H}_{ia}^{(0,1)}$ refers to spin-orbit coupling, it can be concluded that the D -tensor appears as an effect of the spin-orbit coupling.

The g -tensor formula, with the omission of $\vec{H}^{(1,1)}$, adopts the following form

$$\begin{aligned} E_1 &= \vec{\mu}_e \cdot \vec{\Delta g} \cdot \vec{B} = \vec{B} \cdot \vec{\Delta g} \cdot \vec{\mu}_e \\ &= \left\langle \Psi^{(0,0)} \left| \vec{H}^{(0,1)} \cdot \vec{\mu}_e \right| \tilde{\Psi}^{(1,0)} \cdot \vec{B} \right\rangle + \left\langle \Psi^{(0,0)} \left| \vec{H}^{(1,0)} \cdot \vec{B} \right| \tilde{\Psi}^{(0,1)} \cdot \vec{\mu}_e \right\rangle \end{aligned}$$

The left side equals

$$E_1 = -\frac{g_e \mu_B}{\hbar} \vec{S} \cdot \vec{\Delta g} \cdot \vec{B} = -\frac{g_e \mu_B}{\hbar} \sum_a \sum_b S_a \Delta g_{ab} B_b$$

while the right side becomes

$$\begin{aligned}
 E_1 &= -\frac{g_e \mu_B}{\hbar} \left[\left\langle \Psi^{(0,0)} \left| \vec{H}^{(0,1)} \cdot \vec{S} \right| \vec{\Psi}^{(1,0)} \cdot \vec{B} \right\rangle + \left\langle \Psi^{(0,0)} \left| \vec{H}^{(1,0)} \cdot \vec{B} \right| \vec{\Psi}^{(0,1)} \cdot \vec{S} \right\rangle \right] \\
 &= -\frac{g_e \mu_B}{\hbar} \left[\left\langle \Psi^{(0,0)} \left| \sum_i \vec{H}_i^{(0,1)} \cdot \vec{s}_i \right| \vec{\Psi}^{(1,0)} \cdot \vec{B} \right\rangle \right. \\
 &\quad \left. + \left\langle \Psi^{(0,0)} \left| \vec{H}^{(1,0)} \cdot \vec{B} \right| \sum_i \Psi_i^{(0,1)} \cdot \vec{s}_i \right\rangle \right] \\
 &= -\frac{g_e \mu_B}{\hbar} \sum_a \sum_b \left[\left\langle \Psi^{(0,0)} \left| \sum_i \hat{H}_{ia}^{(0,1)} \hat{s}_{ia} \right| \Psi_b^{(1,0)} B_b \right\rangle \right. \\
 &\quad \left. + \left\langle \Psi^{(0,0)} \left| \hat{H}_a^{(1,0)} B_a \right| \sum_i \Psi_{ib}^{(0,1)} \hat{s}_{ib} \right\rangle \right]
 \end{aligned}$$

Their comparison gives

$$S_a \Delta g_{ab} = \left\langle \Psi^{(0,0)} \left| \sum_i \hat{H}_{ia}^{(0,1)} \hat{s}_{ia} \right| \Psi_b^{(1,0)} \right\rangle + \text{second term}$$

A similar derivation when the field and magnetic moment are interchanged yields

$$\Delta g_{ab} S_b = \text{first term} + \left\langle \Psi^{(0,0)} \left| \hat{H}_a^{(1,0)} \right| \sum_i \Psi_{ib}^{(0,1)} \hat{s}_{ib} \right\rangle$$

Therefore the final formula becomes

$$\Delta g_{ab} = S_a^{-1} \left\langle \Psi^{(0,0)} \left| \sum_i \hat{H}_{ia}^{(0,1)} \hat{s}_{ia} \right| \Psi_b^{(1,0)} \right\rangle + S_b^{-1} \left\langle \Psi^{(0,0)} \left| \hat{H}_a^{(1,0)} \right| \sum_i \Psi_{ib}^{(0,1)} \hat{s}_{ib} \right\rangle$$

Because the operators do not vanish for an unquenched angular momentum and the spin-orbit coupling, this result can be interpreted that the differential g -tensor originates in the combined effect of the angular momentum and the spin-orbit coupling.

The formula for the κ -tensor, with omission of $\overline{\overline{H}}^{(2,0)}$ which has already been found as a net diamagnetic contribution, is

$$\begin{aligned}
 E_1 &= -\frac{1}{2} \vec{B} \cdot \vec{\kappa} \cdot \vec{B} = \left\langle \Psi^{(0,0)} \left| \vec{H}^{(1,0)} \cdot \vec{B} \right| \tilde{\Psi}^{(1,0)} \cdot \vec{B} \right\rangle \\
 &= \sum_a \sum_b B_a \left\langle \Psi^{(0,0)} \left| \hat{H}_a^{(1,0)} \right| \Psi_b^{(1,0)} \right\rangle B_b
 \end{aligned}$$

which implies that the *paramagnetic susceptibility* (the van Vleck term) is

$$-\frac{1}{2} \kappa_{ab}^{\text{para}} = \left\langle \Psi^{(0,0)} \left| \hat{H}_a^{(1,0)} \right| \Psi_b^{(1,0)} \right\rangle$$

The only operator acting in this formula, $\hat{H}_a^{(1,0)}$, refers to the angular momentum, so that one can say that the additional contribution to the magnetic susceptibility has roots in the unquenched angular momentum.

The above derivations were rather formal since we have not specified (because there has been no necessity so far) the form of the perturbed wave functions $\tilde{\Psi}^{(1,0)}$ and $\tilde{\Psi}^{(0,1)}$, respectively. However, this easy step follows from the (sum over the states) perturbation theory, hence

$$\tilde{\Psi}^{(1,0)} = - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left\langle \Psi_K \left| \vec{H}^{(1,0)} \right| \Psi_0 \right\rangle \Psi_K$$

$$\tilde{\Psi}^{(0,1)} = - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left\langle \Psi_K \left| \vec{H}^{(0,1)} \right| \Psi_0 \right\rangle \Psi_K$$

$$\tilde{\Psi}^{(0,1)} \cdot \vec{S} = - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left\langle \Psi_K \left| \sum_i \vec{H}_i^{(0,1)} \cdot \vec{s}_i \right| \Psi_0 \right\rangle \Psi_K$$

Here $\Psi_K \equiv \Psi_K^{(0,0)}$ denotes the zero-order wave function for the K th excited state with associated energy E_K . Under this assumption the magnetic parameters adopt the form of

$$\begin{aligned}
 -\frac{1}{2} S_a D_{ab} S_b &= - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left\langle \Psi_0 \left| \sum_i \hat{H}_{ia}^{(0,1)} \hat{s}_{ia} \right| \Psi_K \right\rangle \\
 &\quad \times \left\langle \Psi_K \left| \sum_j \hat{H}_{jb}^{(1,0)} \hat{s}_{jb} \right| \Psi_0 \right\rangle
 \end{aligned}$$

$$\Delta g_{ab} = - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left[S_a^{-1} \left\langle \Psi_0 \left| \sum_i \hat{H}_{ia}^{(0,1)} \hat{s}_{ia} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \hat{H}_b^{(1,0)} \right| \Psi_0 \right\rangle \right. \\ \left. + S_b^{-1} \left\langle \Psi_0 \left| \hat{H}_a^{(1,0)} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \sum_i \hat{H}_{ib}^{(0,1)} \hat{s}_{ib} \right| \Psi_0 \right\rangle \right] \\ - \frac{1}{2} \kappa_{ab} = - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left\langle \Psi_0 \left| \hat{H}_a^{(1,0)} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \hat{H}_b^{(1,0)} \right| \Psi_0 \right\rangle$$

Having introduced the following matrix elements

$$X_a^{AB} = \left\langle \Psi_A \left| \hat{H}_a^{(1,0)} \right| \Psi_B \right\rangle = (\mu_B / \hbar) \left\langle \Psi_A \left| \sum_i \hat{l}_{Gia} \right| \Psi_B \right\rangle$$

and

$$Y_a^{AB} = \left\langle \Psi_A \left| \sum_i \hat{H}_{ia}^{(0,1)} \right| \Psi_B \right\rangle = \left\langle \Psi_A \left| \sum_i \sum_N \xi_N(r_{Ni}) \hat{l}_{Nia} \hat{s}_{ia} \right| \Psi_B \right\rangle$$

the magnetic parameters occurring in $E(\vec{B}, \vec{\mu}_e)$ can be expressed in a more compressed form

$$-\frac{1}{2} S_a D_{ab} S_b = - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} Y_a^{0K} Y_b^{K0} \\ \Delta g_{ab} = - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} (S_a^{-1} Y_a^{0K} X_b^{K0} + S_b^{-1} X_a^{0K} Y_b^{K0}) \\ - \frac{1}{2} \kappa_{ab} = - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} X_a^{0K} X_b^{K0}$$

3.5 INCLUSION OF THE NUCLEAR SPIN

3.5.1 Magnetic Hamiltonian with nuclear spin

Let us consider the second important case when the energy of the system $E(\vec{B}, \vec{\mu}_N)$ depends upon the external magnetic field and the magnetic moments of nuclei due to their spin. The total electromagnetic potential consists of two terms

$$\vec{A}_{\text{tot}}(\vec{r}) = \vec{A}(\vec{r}) + \vec{A}_{\text{nuc}}(\vec{r})$$

While the first term is due to the external magnetic field, the second one arises from the contribution of nuclei. The external electromagnetic potential is expressed through the magnetic induction and the position vector measured relative to the gauge origin

$$\vec{A}(\vec{r}) = \frac{1}{2} \vec{B} \times (\vec{r} - \vec{G})$$

whereas the nuclear electromagnetic potential

$$\vec{A}_{\text{nuc}}(\vec{r}) = \sum_N \vec{A}_N(\vec{r}) = \sum_N \frac{\mu_0}{4\pi} \frac{\vec{\mu}_N \times (\vec{r} - \vec{r}_N)}{|\vec{r} - \vec{r}_N|^3}$$

refers to the position of the nucleus. The magnetic induction due to the nucleus is

$$\vec{B}_N(\vec{r}) = \vec{\nabla} \times \vec{A}_N = -\frac{\mu_0}{4\pi} \left\{ \frac{\vec{\mu}_N}{|\vec{r} - \vec{r}_N|^3} - 3 \frac{[\vec{\mu}_N \cdot (\vec{r} - \vec{r}_N)]}{|\vec{r} - \vec{r}_N|^5} (\vec{r} - \vec{r}_N) \right\}$$

When several contributions to the vector potential are simultaneously present, then squares and cross-terms exist

$$\vec{A}_{\text{tot}}^2 = \left(\vec{A} + \sum_N \vec{A}_N \right)^2 = \vec{A}^2 + 2 \sum_N \vec{A} \cdot \vec{A}_N + \sum_N \sum_M \vec{A}_N \cdot \vec{A}_M$$

which can be written as

$$\begin{aligned} \vec{A}_{\text{tot}}^2 &= \frac{1}{4} [B^2 r_{Ge}^2 - (\vec{B} \cdot \vec{r}_{Ge})^2] \\ &+ \frac{\mu_0}{4\pi} \sum_N \frac{1}{r_{Ne}^3} [(\vec{\mu}_N \cdot \vec{B})(\vec{r}_{Ge} \cdot \vec{r}_{Ne}) - (\vec{B} \cdot \vec{r}_{Ne})(\vec{r}_{Ge} \cdot \vec{\mu}_N)] \\ &+ \frac{\mu_0^2}{16\pi^2} \sum_N \sum_M \frac{1}{r_{Ne}^3} \frac{1}{r_{Me}^3} [(\vec{\mu}_N \cdot \vec{\mu}_M)(\vec{r}_{Ne} \cdot \vec{r}_{Me}) - (\vec{\mu}_N \cdot \vec{r}_{Me})(\vec{\mu}_M \cdot \vec{r}_{Ne})] \end{aligned}$$

The position vectors are

$$\vec{r}_{Ge} = \vec{r} - \vec{G}$$

and

$$\vec{r}_{Ne} = \vec{r} - \vec{r}_N$$

The linear momentum adopts the form of

$$\vec{\pi}_i = \vec{p}_i - q_i \vec{A}_i = \vec{p}_i - q_i \vec{A}(\vec{r}) - q_i \vec{A}_{\text{nuc}}(\vec{r})$$

Let us deal, for clarity, with a single electron and a single magnetoactive nucleus first. Then the kinetic energy operator for one electron ($q_i = -e$, $\vec{A}_{\text{nuc}} = \vec{A}_N$) is

$$\begin{aligned} \hat{T} &= \frac{1}{2m_e} \vec{\pi}^2 = \frac{1}{2m_e} (\vec{p} + e\vec{A} + e\vec{A}_N)^2 \\ &= \frac{1}{2m_e} \vec{p}^2 + \frac{e}{m_e} (\vec{A} \cdot \vec{p} + \vec{A}_N \cdot \vec{p} + \vec{p} \cdot \vec{A} + \vec{p} \cdot \vec{A}_N) \\ &\quad + \frac{e^2}{2m_e} (\vec{A}^2 + \vec{A}_N^2 + \vec{A} \cdot \vec{A}_N + \vec{A}_N \cdot \vec{A}) \end{aligned}$$

Since within the Coulomb gauge the following manipulations hold true

$$\vec{p} \cdot \vec{A} \Psi = \vec{A} \cdot (\vec{p} \Psi) + \Psi (\vec{p} \cdot \vec{A}) = \vec{A} \cdot (\vec{p} \Psi) - i\hbar \Psi \vec{\nabla} \cdot \vec{A} = \vec{A} \cdot (\vec{p} \Psi)$$

the kinetic energy operator is simplified to

$$\hat{T} = \frac{1}{2m_e} \vec{p}^2 + \frac{e}{m_e} (\vec{A} \cdot \vec{p} + \vec{A}_N \cdot \vec{p}) + \frac{e^2}{2m_e} (\vec{A}^2 + 2\vec{A} \cdot \vec{A}_N + \vec{A}_N^2)$$

For the magnetostatic field the Hamiltonian is

$$\begin{aligned} \hat{H}_{\text{mg}} &= \hat{T} + \hat{V} = \frac{1}{2m_e} \vec{p}^2 + \frac{e}{m_e} (\vec{A} \cdot \vec{p} + \vec{A}_N \cdot \vec{p}) \\ &\quad + \frac{e^2}{2m_e} (\vec{A}^2 + 2\vec{A} \cdot \vec{A}_N + \vec{A}_N^2) + \hat{V} \\ &= \hat{H}_0 + \frac{e}{m_e} (\vec{A} \cdot \vec{p} + \vec{A}_N \cdot \vec{p}) + \frac{e^2}{2m_e} (\vec{A}^2 + 2\vec{A} \cdot \vec{A}_N + \vec{A}_N^2) \end{aligned}$$

This can be viewed in the form

$$\hat{H}_{\text{mg}} = \hat{H}_0 + \hat{H}_{10} + \hat{H}_{01} + \hat{H}_{20} + \hat{H}_{11} + \hat{H}_{02}$$

with

- (a) operator of the *orbital Zeeman interaction* (magnetic field–electronic orbital angular momentum interaction)

$$\begin{aligned}\hat{H}_{10} &= \frac{e}{m_e} \vec{A} \cdot \vec{p} = \frac{e}{2m_e} \vec{B} \times (\vec{r} - \vec{G}) \cdot \vec{p} \\ &= \frac{e}{2m_e} \vec{B} \cdot (\vec{r} - \vec{G}) \times \vec{p} = \frac{e}{2m_e} \vec{B} \cdot \vec{l}_{Ge}\end{aligned}$$

where the angular momentum refers to the gauge origin;

- (b) operator of the *orbital hyperfine interaction* (nuclear spin–electronic orbital angular momentum interaction)

$$\begin{aligned}\hat{H}_{01} &= \frac{e}{m_e} \vec{A}_N \cdot \vec{p} = \frac{\mu_0}{4\pi} \frac{e}{m_e} \frac{\vec{\mu}_N \times (\vec{r} - \vec{r}_N)}{|\vec{r} - \vec{r}_N|^3} \cdot \vec{p} \\ &= \frac{\mu_0}{4\pi} \frac{e}{m_e} |\vec{r} - \vec{r}_N|^{-3} \vec{\mu}_N \cdot (\vec{r} - \vec{r}_N) \times \vec{p} \\ &= \frac{\mu_0}{4\pi} \frac{e}{m_e} r_{Ne}^{-3} \vec{\mu}_N \cdot \vec{l}_{Ne}\end{aligned}$$

where the angular momentum refers to the nuclear position;

- (c) operator of the *diamagnetic term*

$$\begin{aligned}\hat{H}_{20} &= \frac{e^2}{2m_e} \vec{A}^2 = \frac{e^2}{8m_e} [\vec{B} \times (\vec{r} - \vec{G})]^2 = \frac{e^2}{8m_e} \{B^2(\vec{r} - \vec{G})^2 - [\vec{B} \cdot (\vec{r} - \vec{G})]^2\} \\ &= \frac{e^2}{8m_e} [B^2 r_{Ge}^2 - (\vec{B} \cdot \vec{r}_{Ge})^2]\end{aligned}$$

referring to the gauge origin;

- (d) operator of the *electron–nuclear Zeeman correction* (electronic orbital angular momentum–nuclear spin interaction)

$$\begin{aligned}\hat{H}_{11} &= \frac{e^2}{m_e} (\vec{A} \cdot \vec{A}_N) = \frac{e^2}{m_e} \left[\frac{1}{2} \vec{B} \times (\vec{r} - \vec{G}) \right] \cdot \left[\frac{\mu_0}{4\pi} \frac{\vec{\mu}_N \times (\vec{r} - \vec{r}_N)}{|\vec{r} - \vec{r}_N|^3} \right] \\ &= \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} |\vec{r} - \vec{r}_N|^{-3} \{ (\vec{B} \cdot \vec{\mu}_N) [(\vec{r} - \vec{G}) \cdot (\vec{r} - \vec{r}_N)] \\ &\quad - [\vec{B} \cdot (\vec{r} - \vec{r}_N)] [(\vec{r} - \vec{G}) \cdot \vec{\mu}_N] \} \\ &= \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} r_{Ne}^{-3} [(\vec{B} \cdot \vec{\mu}_N)(\vec{r}_{Ge} \cdot \vec{r}_{Ne}) - (\vec{B} \cdot \vec{r}_{Ne})(\vec{r}_{Ge} \cdot \vec{\mu}_N)]\end{aligned}$$

- (e) operator of the *electron coupled nuclear spin-spin interaction* written for two interacting nuclei

$$\begin{aligned}
 \hat{H}_{02}(1; N, M) &= \frac{e^2}{2m_e} \vec{A}_N \cdot \vec{A}_M = \frac{e^2}{2m_e} \left[\frac{\mu_0 \vec{\mu}_N \times (\vec{r} - \vec{r}_N)}{4\pi |\vec{r} - \vec{r}_N|^3} \right] \\
 &\quad \cdot \left[\frac{\mu_0 \vec{\mu}_M \times (\vec{r} - \vec{r}_M)}{4\pi |\vec{r} - \vec{r}_M|^3} \right] \\
 &= \left(\frac{\mu_0}{4\pi} \right)^2 \frac{e^2}{2m_e} |\vec{r} - \vec{r}_N|^{-3} |\vec{r} - \vec{r}_M|^{-3} [\vec{\mu}_N \times (\vec{r} - \vec{r}_N)] \\
 &\quad \cdot [\vec{\mu}_M \times (\vec{r} - \vec{r}_M)] \\
 &= \left(\frac{\mu_0}{4\pi} \right)^2 \frac{e^2}{2m_e} r_{Ne}^{-3} r_{Me}^{-3} [(\vec{\mu}_N \cdot \vec{\mu}_M)(\vec{r}_{Ne} \cdot \vec{r}_{Me}) \\
 &\quad - (\vec{\mu}_N \cdot \vec{r}_{Me})(\vec{\mu}_M \cdot \vec{r}_{Ne})]
 \end{aligned}$$

All these terms can be easily generalised for more electrons and more nuclei.

There are two more interactions independent of electronic variables:

- (f) operator of the *nuclear Zeeman interaction*

$$\hat{H}_{01}(2) = \vec{\mu}_N \cdot \vec{B}$$

- (g) operator of the direct *nuclear dipolar interaction*

$$\begin{aligned}
 \hat{H}_{02}(2; N, M) &= -\vec{B}_N(\vec{r}_M) \cdot \vec{\mu}_M \\
 &= \frac{\mu_0}{4\pi} \left\{ \frac{\vec{\mu}_N}{|\vec{r}_M - \vec{r}_N|^3} - 3 \frac{[\vec{\mu}_N \cdot (\vec{r}_M - \vec{r}_N)]}{|\vec{r}_M - \vec{r}_N|^5} (\vec{r}_M - \vec{r}_N) \right\} \cdot \vec{\mu}_M \\
 &= \frac{\mu_0}{4\pi} r_{NM}^{-5} [r_{NM}^2 \vec{\mu}_N \cdot \vec{\mu}_M - 3(\vec{\mu}_N \cdot \vec{r}_{NM})(\vec{r}_{NM} \cdot \vec{\mu}_M)]
 \end{aligned}$$

When the explicit expansion of the magnetic Hamiltonian is considered

$$\begin{aligned}
 \vec{H}_{\text{mg}}(\vec{B}, \vec{\mu}_N) &= \hat{H}^{(0,0)} + \vec{H}^{(1,0)} \cdot \vec{B} + \sum_N \vec{H}_N^{(0,1)} \cdot \vec{\mu}_N \\
 &\quad + \frac{1}{2} \vec{B} \cdot \vec{H}^{(2,0)} \cdot \vec{B} + \sum_N \vec{B} \cdot \vec{H}_N^{(1,1)} \cdot \vec{\mu}_N \\
 &\quad + \frac{1}{2} \sum_N \sum_M \vec{\mu}_N \cdot \vec{H}_{NM}^{(0,2)} \cdot \vec{\mu}_M
 \end{aligned}$$

then its individual vector and/or tensor components are

$$\hat{H}_a^{(1,0)} = \frac{e}{2m_e} \sum_i \hat{l}_{Gia} = \frac{\mu_B}{\hbar} \sum_i \hat{l}_{Gia}$$

$$\hat{H}_{Na}^{(0,1)} = \frac{\mu_0}{4\pi} \frac{e}{m_e} \sum_i r_{Ni}^{-3} \hat{l}_{Nia}$$

$$\hat{H}_{ab}^{(2,0)} = \frac{e^2}{8m_e} \sum_i (r_{Gi}^2 \delta_{ab} - r_{Gia} r_{Gib})$$

$$\hat{H}_{Nab}^{(1,1)} = \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} \sum_i r_{Ni}^{-3} (r_{Gi} r_{Ni} \delta_{ab} - r_{Gia} r_{Nib})$$

$$\begin{aligned} \hat{H}_{NMab}^{(0,2)} &= \left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^2}{2m_e} \sum_i r_{Ni}^{-3} r_{Mi}^{-3} [(\vec{r}_{Ni} \cdot \vec{r}_{Mi}) \delta_{ab} - r_{Nia} r_{Mib}] \\ &\quad + \frac{\mu_0}{4\pi} r_{NM}^{-5} [r_{NM}^2 \delta_{ab} - 3r_{NMa} r_{NMb}] \end{aligned}$$

The nuclear magnetic moment and its spin are interrelated through

$$\vec{\mu}_N = \frac{g_N \mu_p}{\hbar} \vec{I}_N$$

where g_N is the nuclear magnetogyric factor and $\mu_p = e\hbar/2m_p$ is the nuclear magneton.

3.5.2 Nuclear magnetic parameters

The derivation of the nuclear magnetic parameters, i.e. $\bar{\bar{\sigma}}_N^{(1,1)}$, $\bar{\bar{K}}_{NM}^{(0,2)}$ and $\bar{\bar{\kappa}}^{(2,0)}$, is similar to the case of the electron magnetic parameters. The magnetic susceptibility tensor is identical with the derivation done before and, in the absence of electron spin (spin-orbit interaction), only the diamagnetic term survives.

The dependence of energy upon the magnetic field and nuclear spins is assumed to be

$$\begin{aligned} E(\vec{B}, \vec{\mu}_N) &= E_0 - \vec{\gamma} \cdot \vec{B} - \sum_N \vec{\mu}_N \cdot \vec{B} - \frac{1}{2} \vec{B} \cdot \bar{\bar{\kappa}} \cdot \vec{B} \\ &\quad + \sum_N \vec{\mu}_N \cdot \bar{\bar{\sigma}}_N \cdot \vec{B} + \frac{1}{2} \sum_N \sum_M \vec{\mu}_N \cdot \bar{\bar{K}}_{NM} \cdot \vec{\mu}_M + \dots \end{aligned}$$

The wave function is expanded as

$$\Psi(\vec{B}, \vec{\mu}_N) = \Psi^{(0,0)} + \vec{\Psi}^{(1,0)} \cdot \vec{B} + \sum_N \vec{\Psi}_N^{(0,1)} \cdot \vec{\mu}_N + \dots$$

and the perturbation theory yields the energy expectation value

$$\begin{aligned} E(\vec{B}, \vec{\mu}_N) = & \left\langle \Psi^{(0,0)} \left| \left[\hat{H}^{(0,0)} + \vec{H}^{(1,0)} \cdot \vec{B} + \sum_N \vec{H}_N^{(0,1)} \cdot \vec{\mu}_N \right. \right. \right. \\ & + \frac{1}{2} \vec{B} \cdot \vec{\bar{H}}^{(2,0)} \cdot \vec{B} + \sum_N \vec{B} \cdot \vec{\bar{H}}_N^{(1,1)} \cdot \vec{\mu}_N \\ & \left. \left. + \frac{1}{2} \sum_N \sum_M \vec{\mu}_N \cdot \vec{\bar{H}}_{NM}^{(0,2)} \cdot \vec{\mu}_M \right] \right. \\ & \left. \left| \Psi^{(0,0)} + \vec{\Psi}^{(1,0)} \cdot \vec{B} + \sum_N \vec{\Psi}_N^{(0,1)} \cdot \vec{\mu}_N \right| \right\rangle \end{aligned}$$

containing 6×3 terms. Their collection according to the same power of $\vec{B}$ and $\vec{\mu}_N$ gives the expressions

$$\begin{aligned} E_1 = & \sum_N \vec{\mu}_N \cdot \vec{\bar{\sigma}}_N \cdot \vec{B} = \left\langle \Psi^{(0,0)} \left| \sum_N \vec{\mu}_N \cdot \vec{\bar{H}}_N^{(1,1)} \cdot \vec{B} \right| \Psi^{(0,0)} \right\rangle \\ & + \left\langle \Psi^{(0,0)} \left| \vec{H}^{(1,0)} \cdot \vec{B} \right| \sum_N \vec{\Psi}_N^{(0,1)} \cdot \vec{\mu}_N \right\rangle \\ & + \left\langle \Psi^{(0,0)} \left| \sum_N \vec{H}_N^{(0,1)} \cdot \vec{\mu}_N \right| \vec{\Psi}^{(1,0)} \cdot \vec{B} \right\rangle \end{aligned}$$

and

$$\begin{aligned} E_1 = & \frac{1}{2} \sum_N \sum_M \vec{\mu}_N \cdot \vec{\bar{K}}_{NM} \cdot \vec{\mu}_M \\ = & \left\langle \Psi^{(0,0)} \left| \sum_N \sum_M \vec{\mu}_N \cdot \vec{\bar{H}}_{NM}^{(0,2)} \cdot \vec{\mu}_M \right| \Psi^{(0,0)} \right\rangle \\ & + \left\langle \Psi^{(0,0)} \left| \sum_N \vec{H}_N^{(0,1)} \cdot \vec{\mu}_N \right| \sum_M \vec{\Psi}_M^{(0,1)} \cdot \vec{\mu}_M \right\rangle \end{aligned}$$

Then the nuclear shielding tensor becomes

$$\begin{aligned}\sigma_{Nab} &= \left\langle \Psi^{(0,0)} \left| \hat{H}_{Nab}^{(1,1)} \right| \Psi^{(0,0)} \right\rangle + \left\langle \Psi^{(0,0)} \left| \hat{H}_a^{(1,0)} \right| \Psi_{Nb}^{(0,1)} \right\rangle + \left\langle \Psi^{(0,0)} \left| \hat{H}_{Na}^{(0,1)} \right| \Psi_b^{(1,0)} \right\rangle \\ &= \sigma_{Nab}^{\text{dia}} + \sigma_{Nab}^{\text{para}}\end{aligned}$$

which can be written as the sum of a *diamagnetic contribution*

$$\sigma_{Nab}^{\text{dia}} = \left\langle \Psi^{(0,0)} \left| \hat{H}_{Nab}^{(1,1)} \right| \Psi^{(0,0)} \right\rangle$$

and a *paramagnetic contribution*

$$\sigma_{Nab}^{\text{para}} = \left\langle \Psi^{(0,0)} \left| \hat{H}_a^{(1,0)} \right| \Psi_{Nb}^{(0,1)} \right\rangle + \left\langle \Psi^{(0,0)} \left| \hat{H}_{Na}^{(0,1)} \right| \Psi_b^{(1,0)} \right\rangle$$

Analogously, the nuclear spin–spin coupling tensor is

$$\begin{aligned}K_{NMab} &= \left\langle \Psi^{(0,0)} \left| \hat{H}_{NMab}^{(0,2)} \right| \Psi^{(0,0)} \right\rangle + \left\langle \Psi^{(0,0)} \left| \hat{H}_{Na}^{(0,1)} \right| \Psi_{Mb}^{(0,1)} \right\rangle \\ &= K_{NMab}^{\text{dia}} + K_{NMab}^{\text{para}}\end{aligned}$$

and, again, a partitioning to the diamagnetic and paramagnetic contributions is possible

$$K_{NMab}^{\text{dia}} = \left\langle \Psi^{(0,0)} \left| \hat{H}_{NMab}^{(0,2)} \right| \Psi^{(0,0)} \right\rangle$$

$$K_{NMab}^{\text{para}} = \left\langle \Psi^{(0,0)} \left| \hat{H}_{Na}^{(0,1)} \right| \Psi_{Mb}^{(0,1)} \right\rangle, \quad [\text{incomplete}]$$

(There is another important term contributing to K_{NMab}^{para} when the electron–nuclear dipolar interaction is on.)

The diamagnetic part of the susceptibility tensor is

$$-\frac{1}{2}\kappa_{ab}^{\text{dia}} = \left\langle \Psi^{(0,0)} \left| \hat{H}_{ab}^{(2,0)} \right| \Psi^{(0,0)} \right\rangle$$

The paramagnetic part vanishes when the angular momentum is quenched.

Now the application of the (sum over the states) perturbation theory

$$\tilde{\Psi}^{(1,0)} = - \sum_K (E_K - E_0)^{-1} \langle \Psi_K | \tilde{H}^{(1,0)} | \Psi_0 \rangle \Psi_K$$

$$\tilde{\Psi}_N^{(0,1)} = - \sum_K (E_K - E_0)^{-1} \langle \Psi_K | \tilde{H}_N^{(0,1)} | \Psi_0 \rangle \Psi_K$$

leads to the expressions

$$\sigma_{Nab}^{\text{para}} = - \sum_K (E_K - E_0)^{-1} \left[\langle \Psi_0 | \hat{H}_a^{(1,0)} | \Psi_K \rangle \langle \Psi_K | \hat{H}_{Nb}^{(0,1)} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H}_{Na}^{(0,1)} | \Psi_K \rangle \langle \Psi_K | \hat{H}_b^{(1,0)} | \Psi_0 \rangle \right]$$

and

$$K_{NMab}^{\text{para}} = - \sum_K (E_K - E_0)^{-1} \left[\langle \Psi_0 | \hat{H}_{Ma}^{(0,1)} | \Psi_K \rangle \langle \Psi_K | \hat{H}_{Nb}^{(0,1)} | \Psi_0 \rangle \right], \text{ [incomplete]}$$

When the following matrix elements are introduced

$$Z_{Na}^{AB} = \langle \Psi_A | \hat{H}_{Na}^{(0,1)} | \Psi_B \rangle = \frac{\mu_0 e}{4\pi m_e} \left\langle \Psi_A \left| \sum_i r_{Ni}^{-3} \hat{l}_{Nia} \right| \Psi_B \right\rangle$$

$$X_a^{AB} = \langle \Psi_A | \hat{H}_a^{(1,0)} | \Psi_B \rangle = \frac{\mu_B}{\hbar} \left\langle \Psi_A \left| \sum_i \hat{l}_{Gia} \right| \Psi_B \right\rangle$$

the above contributions to the magnetic parameters can be written in a more compressed form

$$\sigma_{Nab}^{\text{para}} = - \sum_K (E_K - E_0)^{-1} (X_a^{0K} Z_{Nb}^{K0} + Z_{Na}^{0K} X_b^{K0})$$

$$K_{NMab}^{\text{para}} = - \sum_K (E_K - E_0)^{-1} (Z_{Na}^{0K} Z_{Mb}^{K0}), \text{ [incomplete]}$$

3.6 INCLUSION OF THE ELECTRON AND NUCLEAR SPINS

3.6.1 Magnetic Hamiltonian with electron and nuclear spins

In the third, the most general case the energy of the system depends upon the external magnetic field, the magnetic moments of nuclei and the electronic magnetic moment. The following expansion of the magnetic Hamiltonian is assumed

$$\begin{aligned}
 \vec{H}_{mg}(\vec{B}, \vec{\mu}_N, \vec{\mu}_e) = & \hat{H}^{(0,0,0)} + \vec{H}^{(1,0,0)} \cdot \vec{B} + \frac{1}{2} \vec{B} \cdot \vec{\overline{H}}^{(2,0,0)} \cdot \vec{B} \\
 & + \sum_N \vec{H}_N^{(0,1,0)} \cdot \vec{\mu}_N + \sum_N \vec{B} \cdot \vec{\overline{H}}_N^{(1,1,0)} \cdot \vec{\mu}_N \\
 & + \frac{1}{2} \sum_N \sum_{M \neq N} \vec{\mu}_N \cdot \vec{\overline{H}}_{NM}^{(0,2,0)} \cdot \vec{\mu}_M + \sum_i \vec{\mu}_{ei} \cdot \vec{H}_i^{(0,0,1)} \\
 & + \sum_i \vec{\mu}_{ei} \cdot \vec{\overline{H}}_i^{(1,0,1)} \cdot \vec{B} + \frac{1}{2} \sum_i \sum_{j \neq i} \vec{\mu}_{ei} \cdot \vec{\overline{H}}_{ij}^{(0,0,2)} \cdot \vec{\mu}_{ej} \\
 & + \sum_i \sum_N \vec{\mu}_{ei} \cdot \vec{\overline{H}}_{iN}^{(0,1,1)} \cdot \vec{\mu}_N
 \end{aligned}$$

where $\hat{H}^{(mnk)}$ are operators representing interactions m -linear in $\vec{B}$, n -linear in $\vec{\mu}_N$ and k -linear in $\vec{\mu}_e$. Within this notation the individual components of the magnetic Hamiltonian are

$$\hat{H}_a^{(1,0,0)} = \frac{e}{2m_e} \sum_i \hat{l}_{Gia} = \frac{\mu_B}{\hbar} \sum_i \hat{l}_{Gia}$$

$$\hat{H}_{ab}^{(2,0,0)} = \frac{e^2}{8m_e} \sum_i (r_{Gi}^2 \delta_{ab} - r_{Gia} r_{Gib})$$

$$\hat{H}_{Na}^{(0,1,0)} = \frac{\mu_0}{4\pi} \frac{e}{m_e} \sum_i r_{Ni}^{-3} \hat{l}_{Nia}$$

$$\hat{H}_{Nab}^{(1,1,0)} = \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} \sum_i r_{Ni}^{-3} (\vec{r}_{Gi} \cdot \vec{r}_{Ni} \delta_{ab} - r_{Gia} r_{Nib})$$

$$\begin{aligned}
 \hat{H}_{NMab}^{(0,2,0)} = & \left(\frac{\mu_0}{4\pi} \right)^2 \frac{e^2}{2m_e} \sum_i r_{Ni}^{-3} r_{Mi}^{-3} [(\vec{r}_{Ni} \cdot \vec{r}_{Mi}) \delta_{ab} - r_{Mia} r_{Nib}] \\
 & + \frac{\mu_0}{4\pi} r_{NM}^{-5} (r_{NM}^2 \delta_{ab} - 3r_{NMa} r_{NMb})
 \end{aligned}$$

$$\hat{H}_{ia}^{(0,0,1)} = -\frac{\mu_0 \mu_B}{4\pi \hbar} \sum_N Z_N r_{Ni}^{-3} \hat{l}_{Nia}$$

$$\hat{H}_{iab}^{(1,0,1)} = \frac{e^2}{4m_e} \sum_N Z_N r_{Ni}^{-3} [(\vec{r}_{Ni} \cdot \vec{r}_{Gi})\delta_{ab} - r_{Gia}r_{Nib}]$$

$$\hat{H}_{ijab}^{(0,0,2)} = -\frac{\mu_0}{4\pi} \frac{8\pi}{3} \delta(\vec{r}_{ij}) + \frac{\mu_0}{4\pi} r_{ij}^{-5} (r_{ij}^2 \delta_{ab} - 3r_{ija}r_{ijb})$$

$$\hat{H}_{iNab}^{(0,1,1)} = -\frac{\mu_0}{4\pi} \frac{8\pi}{3} \delta(\vec{r}_{Ni}) + \frac{\mu_0}{4\pi} r_{Ni}^{-5} (r_{Ni}^2 \delta_{ab} - 3r_{Nia}r_{Nib})$$

where r_{NM} is the distance between the M th and N th nucleus, r_{ij} is the distance between the j th and i th electron, and $\delta(\vec{r}_{Ni}) = \delta(\vec{r}_i - \vec{r}_N)$ and $\delta(\vec{r}_{ij}) = \delta(\vec{r}_j - \vec{r}_i)$ are the Dirac “delta” functions appearing in the contact terms.

Here we have included also the Hamiltonian terms not mentioned before but following from the relativistic approach: the spin–spin contact interaction and the spin–spin dipolar interaction terms contained in $\hat{H}_{ijab}^{(0,0,2)}$, and the Fermi contact interaction and the dipolar hyperfine interaction contained in $\hat{H}_{iNab}^{(0,1,1)}$.

The spin–spin contact and dipolar terms arise from the interaction between the electronic magnetic moment and the internal magnetic field generated by the other electron at the position of the first electron

$$\hat{H}_{002}(i, j) = -\vec{\mu}_j \cdot \vec{B}_i(\vec{r}_j) = -\vec{\mu}_i \cdot \vec{B}_j(\vec{r}_i)$$

The internal electromagnetic potential at the point $\vec{r}_j$ is

$$\vec{A}_e(\vec{r}_j) = \sum_i \vec{A}_i(\vec{r}_j) = \sum_i \frac{\mu_0}{4\pi} \frac{\vec{\mu}_i \times (\vec{r}_j - \vec{r}_i)}{|\vec{r}_j - \vec{r}_i|^3}$$

and for magnetic induction it holds true that

$$\vec{B}_i(\vec{r}_j) = \vec{\nabla}_j \times \vec{A}_i(\vec{r}_j) = \frac{\mu_0}{4\pi} \vec{\nabla}_j \times \left\{ \vec{\mu}_i \times \frac{(\vec{r}_j - \vec{r}_i)}{|\vec{r}_j - \vec{r}_i|^3} \right\}$$

Using the rule for the double vector product

$$\vec{\nabla} \times (\vec{A} \times \vec{B}) = \vec{A}(\vec{\nabla} \cdot \vec{B}) - (\vec{A} \cdot \vec{\nabla})\vec{B}$$

we get

$$\vec{B}_i(\vec{r}_j) = \frac{\mu_0}{4\pi} \left\{ \vec{\mu}_i \left[\vec{\nabla}_j \cdot \frac{(\vec{r}_j - \vec{r}_i)}{|\vec{r}_j - \vec{r}_i|^3} \right] - (\vec{\mu}_i \cdot \vec{\nabla}_j) \frac{(\vec{r}_j - \vec{r}_i)}{|\vec{r}_j - \vec{r}_i|^3} \right\}$$

The first term is just

$$\left[\vec{\nabla}_j \cdot \frac{(\vec{r}_j - \vec{r}_i)}{|\vec{r}_j - \vec{r}_i|^3} \right] = 4\pi\delta(\vec{r}_j - \vec{r}_i)$$

The second term gives

$$(\vec{\mu}_i \cdot \vec{\nabla}_j) \frac{(\vec{r}_j - \vec{r}_i)}{|\vec{r}_j - \vec{r}_i|^3} = \vec{\mu}_i \frac{4\pi}{3} \delta(\vec{r}_j - \vec{r}_i) + \frac{\vec{\mu}_i}{|\vec{r}_j - \vec{r}_i|^3} - 3 \frac{[\vec{\mu}_i \cdot (\vec{r}_j - \vec{r}_i)]}{|\vec{r}_j - \vec{r}_i|^5} (\vec{r}_j - \vec{r}_i)$$

Then the total electron spin–spin interaction term becomes

$$\hat{H}_{002}(i, j) = -\frac{\mu_0}{4\pi} \left[\frac{8\pi}{3} \delta(\vec{r}_{ij}) \vec{\mu}_i \cdot \vec{\mu}_j \right] + \frac{\mu_0}{4\pi} r_{ij}^{-5} [r_{ij}^2 (\vec{\mu}_i \cdot \vec{\mu}_j) - 3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{r}_{ij} \cdot \vec{\mu}_j)]$$

The contact term

$$\hat{H}_{ijab}^{(0,0,2)}(1) = -\frac{\mu_0}{4\pi} \frac{8\pi}{3} \delta(\vec{r}_{ij}) \delta_{ab}$$

prevents a singularity at $\vec{r}_{ij} = 0$. Its integral form is

$$\int_{-\infty}^{\infty} \psi^*(\vec{r}) \hat{H}_{ijab}^{(0,0,2)}(1) \psi(\vec{r}) d\vec{r} = -\frac{\mu_0}{4\pi} \frac{8\pi}{3} \int_{-\infty}^{\infty} \psi^*(\vec{r}) \psi(\vec{r}) \delta(\vec{r}_{ij}) d\vec{r} = -\frac{\mu_0}{4\pi} \frac{8\pi}{3} |\psi(\vec{r}_0)|^2$$

where $\vec{r}_0 = 0$. The net spin–spin dipolar term is

$$\hat{H}_{ijab}^{(0,0,2)}(2) = \frac{\mu_0}{4\pi} r_{ij}^{-5} (r_{ij}^2 \delta_{ab} - 3r_{ija} r_{ijb})$$

Analogously, the Fermi contact and dipolar hyperfine interaction terms originate in the interaction between the electronic magnetic moment and the internal magnetic field generated by the nucleus

$$\hat{H}_{011}(i, N) = -\vec{B}_N(\vec{r}_i) \cdot \vec{\mu}_i$$

with

$$\vec{B}_N(\vec{r}_i) = \frac{\mu_0}{4\pi} \vec{\nabla}_i \times \left\{ \vec{\mu}_N \times \frac{(\vec{r}_i - \vec{r}_N)}{|\vec{r}_i - \vec{r}_N|^3} \right\}$$

yielding the Fermi contact term

$$\hat{H}_{iNab}^{(0,1,1)}(1) = -\frac{\mu_0}{4\pi} \frac{8\pi}{3} \delta(\vec{r}_{Ni}) \delta_{ab}$$

and the dipolar hyperfine interaction term

$$\hat{H}_{iNab}^{(0,1,1)}(2) = \frac{\mu_0}{4\pi} r_{Ni}^{-5} (r_{Ni}^2 \delta_{ab} - 3r_{Nia} r_{Nib})$$

Notice the expressions for magnetic moments

$$\vec{\mu}_e = -\frac{g_e \mu_B}{\hbar} \vec{S} = -\frac{g_e \mu_B}{\hbar} \sum_i \vec{s}_i$$

and

$$\vec{\mu}_N = \frac{g_N \mu_p}{\hbar} \vec{I}_N$$

3.6.2 Electron–nuclear magnetic parameters

The energy expression, including the electron–nuclear magnetic parameters, is

$$\begin{aligned} E(\vec{B}, \vec{\mu}_N, \vec{\mu}_e) = & E_0 - \vec{\gamma} \cdot \vec{B} - \frac{1}{2} \vec{B} \cdot \vec{\bar{\kappa}} \cdot \vec{B} \\ & - \sum_N \vec{\mu}_N \cdot \vec{B} + \sum_N \vec{\mu}_N \cdot \vec{\bar{\sigma}}_N \cdot \vec{B} \\ & + \frac{1}{2} \sum_N \sum_{M \neq N} \vec{\mu}_N \cdot \vec{\bar{K}}_{NM} \cdot \vec{\mu}_M \\ & - \vec{\mu}_e \cdot \vec{B} + \vec{\mu}_e \cdot \vec{\bar{\Delta g}} \cdot \vec{B} - \frac{1}{2} \vec{\mu}_e \cdot \vec{\bar{D}} \cdot \vec{\mu}_e \\ & + \sum_N \vec{\mu}_e \cdot \vec{\bar{T}}_N \cdot \vec{\mu}_N \end{aligned}$$

Here the first line represents the influence of the magnetic field only, the second and third line the magnetic field–nuclear magnetic moments interaction, the fourth line the magnetic field–electronic magnetic moment interaction and the last one the electronic–nuclear magnetic moments interaction (it is a new term).

The wave function is expanded as

$$\begin{aligned}\Psi(\vec{B}, \vec{\mu}_N, \vec{\mu}_e) = & \Psi^{(0,0,0)} + \vec{\Psi}^{(1,0,0)} \cdot \vec{B} + \sum_N \vec{\Psi}_N^{(0,1,0)} \cdot \vec{\mu}_N \\ & + \sum_i \vec{\Psi}_i^{(0,0,1)} \cdot \vec{\mu}_{ei} + \dots\end{aligned}$$

and the energy expectation value in terms of the perturbation theory

$$E(\vec{B}, \vec{\mu}_N, \vec{\mu}_e) = \left\langle \Psi^{(0,0,0)} \left| \hat{H}(\vec{B}, \vec{\mu}_N, \vec{\mu}_e) \right| \Psi(\vec{B}, \vec{\mu}_N, \vec{\mu}_e) \right\rangle$$

contains 10×4 terms collected according to the same power of variables $(\vec{B}, \vec{\mu}_N, \vec{\mu}_e)$. Now the magnetic parameters are determined as follows

$$-\frac{1}{2}\kappa_{ab}^{\text{dia}} = \left\langle \Psi^{(0,0,0)} \left| \hat{H}_{ab}^{(2,0,0)} \right| \Psi^{(0,0,0)} \right\rangle$$

$$-\frac{1}{2}\kappa_{ab}^{\text{para}} = \left\langle \Psi^{(0,0,0)} \left| \hat{H}_a^{(1,0,0)} \right| \Psi_b^{(1,0,0)} \right\rangle$$

$$\sigma_{Nab}^{\text{dia}} = \left\langle \Psi^{(0,0,0)} \left| \hat{H}_{Nab}^{(1,1,0)} \right| \Psi^{(0,0,0)} \right\rangle$$

$$\sigma_{Nab}^{\text{para}} = \left\langle \Psi^{(0,0,0)} \left| \hat{H}_a^{(1,0,0)} \right| \Psi_{Nb}^{(0,1,0)} \right\rangle + \left\langle \Psi^{(0,0,0)} \left| \hat{H}_{Na}^{(0,1,0)} \right| \Psi_b^{(1,0,0)} \right\rangle$$

$$K_{NMab}^{\text{dia}} = \left\langle \Psi^{(0,0,0)} \left| \hat{H}_{NMab}^{(0,2,0)} \right| \Psi^{(0,0,0)} \right\rangle$$

$$K_{NMab}^{\text{para}} = \left\langle \Psi^{(0,0,0)} \left| \hat{H}_{Na}^{(0,1,0)} \right| \Psi_{Mb}^{(0,1,0)} \right\rangle + S_a^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{H}_{iNab}^{(0,1,1)} \hat{S}_{ia} \right| \Psi_M^{(0,1,1)} \right\rangle$$

$$\begin{aligned}
\Delta g_{ab} &= S_a^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{H}_{iab}^{(1,0,1)} \hat{s}_{ia} \right| \Psi^{(0,0,0)} \right\rangle \\
&\quad + S_a^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{H}_{ia}^{(0,0,1)} \hat{s}_{ia} \right| \Psi_b^{(1,0,0)} \right\rangle \\
&\quad + S_b^{-1} \left\langle \Psi^{(0,0,0)} \left| \hat{H}_a^{(1,0,0)} \left| \sum_i \Psi^{(0,0,1)} \hat{s}_{ib} \right| \right\rangle \\
-\frac{1}{2} D_{ab} &= S_a^{-1} S_b^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{H}_{ia}^{(0,0,1)} \hat{s}_{ia} \right| \sum_j \Psi_{jb}^{(0,0,1)} \hat{s}_{jb} \right\rangle \\
T_{Nab} &= S_a^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{H}_{iNab}^{(0,1,1)} \hat{s}_{ia} \right| \Psi^{(0,0,0)} \right\rangle \\
&\quad + S_a^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{H}_{ia}^{(0,0,1)} \hat{s}_{ia} \right| \Psi_{Nb}^{(0,1,0)} \right\rangle
\end{aligned}$$

3.7 THE EFFECT OF NUCLEAR STRUCTURE

Nuclei behave neither like point charges nor like point dipoles. They have a finite extent and, in general, a non-spherical shape characterised by electric multipole moments.

The electrostatic interaction energy of an electronic charge distribution, ρ_e , and a nuclear charge distribution, ρ_N , is

$$E = \iint \frac{\rho_e(\vec{r}_e) \rho_N(\vec{r}_N)}{|\vec{r}_e - \vec{r}_N|} d\vec{r}_e d\vec{r}_N$$

The protons are the only relevant charge carriers inside the nucleus. Let the position of the proton p in nucleus N be $\vec{r}_{Np}$ (measured relative to the centre of the charge of nucleus) and an electron be at the position $\vec{r}_{Ne}$. Then their interaction energy is

$$E = -e\Phi_e = - \sum_p \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_{Ne} - \vec{r}_{Np}|}$$

In manipulating the denominator we can apply an expansion

$$f(\vec{a} - \vec{b}) = [1 - (\vec{b} \cdot \vec{\nabla}) + \frac{1}{2}(\vec{b} \cdot \vec{\nabla})^2 + \dots] f(\vec{a})$$

so that for $\vec{r}_{Ne} > \vec{r}_{Np}$ (the electron is outside the nucleus) we have

$$\begin{aligned} \frac{1}{|\vec{r}_{Ne} - \vec{r}_{Np}|} &= \left[1 - (\vec{r}_{Np} \cdot \vec{\nabla}) + \frac{1}{2}(\vec{r}_{Np} \cdot \vec{\nabla})^2 + \dots \right] \frac{1}{r_{Ne}} \\ &= \left[\frac{1}{r_{Ne}} - \vec{r}_{Np} \cdot \left(\vec{\nabla} \frac{1}{r_{Ne}} \right) + \frac{1}{2}(\vec{r}_{Np} \cdot \vec{\nabla})(\vec{r}_{Np} \cdot \vec{\nabla}) \frac{1}{r_{Ne}} + \dots \right] \end{aligned}$$

Since there is

$$\vec{\nabla} \left(\frac{1}{r_{Ne}} \right) = -\frac{\vec{r}_{Ne}}{r_{Ne}^3}$$

we get the intermediate result

$$\frac{1}{|\vec{r}_{Ne} - \vec{r}_{Np}|} = \frac{1}{r_{Ne}} + \frac{\vec{r}_{Np} \cdot \vec{r}_{Ne}}{r_{Ne}^3} - \frac{1}{2}(\vec{r}_{Np} \cdot \vec{\nabla}) \frac{\vec{r}_{Np} \cdot \vec{r}_{Ne}}{r_{Ne}^3} + \dots$$

and because of

$$\sum_a \sum_b \nabla_a \left(\frac{r_b}{r^3} \right) = \sum_a \sum_b \left[\frac{4\pi}{3} \delta_{ab} \delta(\vec{r}) + \frac{1}{r^3} \delta_{ab} - \frac{3r_a r_b}{r^5} \right]$$

we arrive at the expression

$$\frac{1}{|\vec{r}_{Ne} - \vec{r}_{Np}|} = \frac{1}{r_{Ne}} + \frac{\vec{r}_{Np} \cdot \vec{r}_{Ne}}{r_{Ne}^3} - \frac{1}{2} \left[\frac{r_{Np}^2}{r_{Ne}^3} - \frac{3(\vec{r}_{Np} \cdot \vec{r}_{Ne})^2}{r_{Ne}^5} \right] + \dots$$

The Dirac function was omitted as an effect of the constraint $\vec{r}_{Ne} > \vec{r}_{Np}$. Then the electrostatic interaction energy becomes

$$E = - \sum_p \frac{e^2}{4\pi\epsilon_0} \left\{ \frac{1}{r_{Ne}} + \frac{\vec{r}_{Np} \cdot \vec{r}_{Ne}}{r_{Ne}^3} - \frac{1}{2} \left[\frac{r_{Np}^2}{r_{Ne}^3} - \frac{3(\vec{r}_{Np} \cdot \vec{r}_{Ne})^2}{r_{Ne}^5} \right] \right\}$$

The first term is the Coulomb interaction of point charges

$$E_0 = - \sum_p \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{Ne}} = - \frac{e^2}{4\pi\epsilon_0} \frac{Z_N}{r_{Ne}}$$

The next term contains the electric dipole moment of the nucleus

$$E_1 = - \sum_p \frac{e^2}{4\pi\epsilon_0} \frac{\vec{r}_{Np} \cdot \vec{r}_{Ne}}{r_{Ne}^3} = - \frac{e}{4\pi\epsilon_0} \frac{\vec{r}_{Ne}}{r_{Ne}^3} \cdot \left(\sum_p e \vec{r}_{Np} \right) = 0$$

which vanishes because $\vec{r}_{Np}$ is the position of a proton relative to the centre of the charge of the nucleus. The term, quadratic in $\vec{r}_{Np}$, can be rewritten as follows

$$\begin{aligned} E_2 &= - \sum_p \frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{1}{2} \left[\frac{r_{Np}^2}{r_{Ne}^3} - \frac{3(\vec{r}_{Np} \cdot \vec{r}_{Ne})^2}{r_{Ne}^5} \right] \right\} \\ &= - \sum_p \frac{e^2}{4\pi\epsilon_0} \left\{ \sum_a \sum_b \frac{(3r_{Npa}r_{Npb} - \delta_{ab}r_{Np}^2)(3r_{Nea}r_{Neb} - \delta_{ab}r_{Ne}^2)}{6r_{Ne}^5} \right\} \\ &= \sum_a \sum_b \frac{1}{6} \left[e \sum_p (3r_{Npa}r_{Npb} - \delta_{ab}r_{Np}^2) \right] \left[-\frac{e}{4\pi\epsilon_0} \frac{(3r_{Nea}r_{Neb} - \delta_{ab}r_{Ne}^2)}{r_{Ne}^5} \right] \end{aligned}$$

and it can be viewed as a scalar product of two second-rank tensors

$$E_2 = \frac{1}{6} \sum_a \sum_b Q_{Nab} V_{Nab} = \frac{1}{6} \bar{Q} \cdot \bar{V}$$

with the *nuclear quadrupole tensor* of nucleus N

$$Q_{Nab} = e \sum_p (3r_{Npa}r_{Npb} - \delta_{ab}r_{Np}^2)$$

and the *electric field gradient tensor* at the nucleus N

$$V_{Nab} = - \frac{e}{4\pi\epsilon_0} \frac{(3r_{Nea}r_{Neb} - \delta_{ab}r_{Ne}^2)}{r_{Ne}^5} = \vec{\nabla}_a \vec{\nabla}_b \left(-\frac{e}{4\pi\epsilon_0} \frac{1}{r_{Ne}} \right)$$

An enlargement of the expansion yields the nuclear octopole moment (which vanishes exactly because of odd parity) and the nuclear hexadecapole moment (whose contribution is negligible).

A non-zero nuclear quadrupole moment implies that the nuclear charge is not distributed spherically; the shape of the nucleus resembles rather an ellipsoid. The nuclear quadrupole moment is better expressed through

$$Q_{Nab} = \int \rho_N(\vec{r}_N) (3r_{Na}r_{Nb} - \delta_{ab}r_N^2) d\vec{r}_N$$

However, it is still a formal, impractical definition since we know neither the exact positions of protons nor the nuclear charge density.

The nuclear quadrupole moment is an expectation value with respect to the nuclear wave function. For the nuclear ground state the nuclear wave function depends upon a radial parameter a , the nuclear spin quantum number I and its projection M_I so that the corresponding ket-vector is denoted as $|a, I, M_I\rangle$. The properties of the nuclear spin (in general, an angular momentum) are well known and they can be fully exploited in expressing such an expectation value. For this purpose let us rewrite the electrostatic interaction energy, making use of the expansion in terms of the spherical harmonic functions

$$\frac{1}{|\vec{r}_e - \vec{r}_N|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{r_N^l}{r_e^{l+1}} Y_{lm}^*(\theta_e, \phi_e) Y_{lm}(\theta_N, \phi_N)$$

since $r_< = r_N$ and $r_> = r_e$. Hence

$$E = \int \rho_e(\vec{r}_e) \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \left(\frac{4\pi}{2l+1} \right)^{1/2} r_e^{-l-1} Y_{lm}^*(\theta_e, \phi_e) A_{l,m}^{(N)} d\vec{r}_e$$

with the spherical tensor characterising the l th moment of the nuclear charge distribution

$$A_{l,m}^{(N)} = \int \rho_N(\vec{r}_N) \left(\frac{4\pi}{2l+1} \right)^{1/2} r_N^l Y_{lm}(\theta_N, \phi_N) d\vec{r}_N$$

The five components of the spherical quadrupole (second-rank, $l = 2$) tensor are

$$A_{2,m}^{(N)} = \left\langle a, I, M_I \left| e \sum_p \left(\frac{4\pi}{5} \right)^{1/2} r_{Np}^2 Y_{2,m}(\theta_{Np}, \phi_{Np}) \right| a, I, M_I \right\rangle$$

with $m = \pm 2, \pm 1, 0$. This integral is in fact a matrix element of the irreducible tensor operator $\hat{A}_{lm}$, which can be rewritten into a form suitable for an application of the Wigner-Eckart theorem

$$\begin{aligned} A_{l,m}^{(N)} &= \left\langle a, I, M_I \left| \hat{A}_{lm} \right| a, I, M_I \right\rangle \\ &= (-1)^{I-M_I} \begin{pmatrix} I & l & I \\ -M_I & m & M_I \end{pmatrix} \left\langle a, I \left\| \hat{A}_l \right\| a, I \right\rangle \end{aligned}$$

where $\langle a, I \| \hat{A}_I \| a, I \rangle$ is a reduced matrix element independent of the projections of the nuclear spin, preceded by an appropriate Clebsch–Gordan coefficient or the $3j$ -symbol. Now the constraint $l \leq 2I$ tell us that only nuclei with the nuclear spin quantum number $I > 1/2$ may have non-zero quadrupole moments; instead, the Clebsch–Gordan coefficient vanishes.

Making use of the properties of nuclear spin (angular momentum), a new spherical second-rank tensor operator can be constructed with the components [5]

$$\hat{B}_{2,0} = \langle b, I \| \hat{B}_I \| b, I \rangle \left[\frac{1}{2} (3\hat{I}_z^2 - \hat{I}^2) \right]$$

$$\hat{B}_{2,\pm 1} = \langle b, I \| \hat{B}_I \| b, I \rangle \left[\mp \sqrt{\frac{3}{8}} (\hat{I}_z \hat{I}_{\pm} + \hat{I}_{\pm} \hat{I}_z) \right]$$

$$\hat{B}_{2,\pm 2} = \langle b, I \| \hat{B}_I \| b, I \rangle \left[\sqrt{\frac{3}{8}} (\hat{I}_{\pm})^2 \right]$$

This tensor can be subject to the Wigner–Eckart theorem

$$\begin{aligned} B_{l,m} &= \langle b, I, M_I | \hat{B}_{lm} | b, I, M_I \rangle \\ &= (-1)^{I-M_I} \begin{pmatrix} I & l & I \\ -M_I & m & M_I \end{pmatrix} \langle b, I \| \hat{B}_I \| b, I \rangle \end{aligned}$$

and we can see that the same coefficient as before occurs. Therefore it holds true that

$$\frac{A_{l,m}^{(N)}}{B_{l,m}} = \frac{\langle a, I \| \hat{A}_I \| a, I \rangle}{\langle b, I \| \hat{B}_I \| b, I \rangle}$$

The constant factor $\langle b, I \| \hat{B}_I \| b, I \rangle$ is determined by the condition that $\hat{B}_{2,0}$ and $\hat{A}_{2,0}$ have the same expectation value in the substate with the maximum spin projection, i.e. $M_I = +I$. The only constant which is necessary is denoted (eQ) and is termed the *nuclear quadrupole moment*—see Table 3.2.

TABLE 3.2

The properties of selected nuclei

Isotope	Natural abundance (%)	Spin quantum number (I)	Nuclear g -factor (g_N)	Quadrupole moment (10^{-28} m^2 (barn))
^1H	99.98	1/2	+5.5856912	0
^2H	0.0156	1	+0.8574376	+0.002875
^6Li	7.42	1	+0.8220467	-0.000644
^7Li	92.58	3/2	+2.170949	-0.0366
^9Be	100	3/2	-0.7852	+0.053
^{10}B	19.58	3	+0.600217	+0.008472
^{11}B	80.42	3/2	+1.792425	+0.04065
^{13}C	1.108	1/2	+1.404822	0
^{14}N	99.63	1	+0.4037607	+0.0156
^{15}N	0.37	1/2	-0.5663784	0
^{17}O	0.037	5/2	-0.75752	-0.02578
^{19}F	100	1/2	+5.257732	0
^{21}Ne	0.257	3/2	-0.441197	+0.1029
^{23}Na	100	3/2	+1.478347	+0.101
^{25}Mg	10.13	5/2	-0.34218	+0.22
^{27}Al	100	5/2	+1.456602	+0.140
^{29}Si	4.7	1/2	-0.11058	0
^{31}P	100	1/2	+2.26320	0
^{33}S	0.76	3/2	+0.429214	-0.064
^{35}Cl	75.53	3/2	+0.5479157	-0.08249
^{37}Cl	24.47	3/2	+0.4560820	-0.06493
^{39}K	93.1	3/2	+0.2609772	+0.049
^{41}K	6.88	3/2	+0.1432466	+0.060
^{43}Ca	0.145	7/2	-0.37636	0
^{45}Sc	100	7/2	+1.358995	-0.22
^{47}Ti	7.28	5/2	-0.31539	+0.29
^{49}Ti	5.51	7/2	-0.31548	+0.24
^{50}V	0.24	6	+0.557908	+0.05
^{51}V	99.76	7/2	+1.47183	-0.052
^{53}Cr	9.55	3/2	-0.31636	-0.022
^{55}Mn	100	5/2	+1.3813	+0.4
^{57}Fe	2.19	1/2	+0.1812459	0
^{59}Co	100	7/2	+1.322	+0.404
^{61}Ni	1.19	3/2	-0.50001	+0.162
^{63}Cu	69.09	3/2	+1.4822	-0.209
^{65}Cu	30.91	3/2	+1.5878	-0.195
^{67}Zn	4.11	5/2	+0.350191	+0.150
^{69}Ga	60.4	3/2	+1.34439	+0.168
^{71}Ga	39.6	3/2	+1.70818	+0.106
^{73}Ge	7.76	9/2	-0.1954371	-0.173
^{75}As	100	3/2	+0.95965	+0.29
^{77}Se	7.58	1/2	+1.07012	0
^{79}Br	50.54	3/2	+1.404266	+0.293
^{81}Br	49.46	3/2	+1.513707	+0.27

(contd.)

TABLE 3.2

The properties of selected nuclei (*contd.*)

Isotope	Natural abundance (%)	Spin quantum number (I)	Nuclear g -factor (g_N)	Quadrupole moment (10^{-28} m^2 (barn))
^{83}Kr	11.55	9/2	-0.215704	+0.270
^{85}Rb	72.15	5/2	+0.54121	+0.274
^{87}Rb	27.85	3/2	+1.83416	+0.132
^{87}Sr	7.02	9/2	-0.242849	+0.15
^{89}Y	100	1/2	-0.2748306	0
^{91}Zr	11.23	5/2	-0.52145	0
^{93}Nb	100	9/2	+1.37122	-0.36
^{95}Mo	15.72	5/2	-0.3657	-0.019
^{97}Mo	9.46	5/2	-0.3734	-0.102
^{99}Tc	0	9/2	+1.262	+0.3
^{99}Ru	12.72	5/2	-0.2565	+0.076
^{101}Ru	17.07	5/2	-0.2875	+0.44
^{103}Rh	100	1/2	-0.17680	0
^{105}Pd	22.23	5/2	-0.2568	+0.8
^{107}Ag	51.82	1/2	-0.227140	0
^{109}Ag	48.18	1/2	-0.2613810	0
^{111}Cd	12.75	1/2	-1.1897712	0
^{113}Cd	12.26	1/2	-1.2446010	0
^{113}In	4.28	9/2	+1.22864	+0.846
^{115}In	95.72	9/2	+1.23129	+0.861
^{115}Sn	0.35	1/2	-0.183766	0
^{117}Sn	7.61	1/2	-2.00208	0
^{119}Sn	8.58	1/2	-2.09456	0
^{121}Sb	57.25	5/2	+1.34536	-0.20
^{123}Sb	42.75	7/2	+0.72851	-0.26
^{123}Te	0.87	1/2	-1.47358	0
^{125}Te	6.99	1/2	-1.77656	0
^{127}I	100	5/2	+1.12531	-0.789
^{129}Xe	26.44	1/2	-1.555952	0
^{131}Xe	21.18	3/2	+0.461241	-0.120
^{133}Cs	100	7/2	+0.7377209	-0.003
^{135}Ba	6.59	3/2	+0.558629	+0.18
^{137}Ba	11.32	3/2	+0.624910	+0.28
^{138}La	0.089	5	+0.74278	+0.51
^{139}La	99.911	7/2	+0.79520	+0.22
^{141}Pr	100	5/2	+1.6544	-0.0589
^{143}Nd	12.17	7/2	-0.3043	-0.484
^{145}Nd	8.30	7/2	-0.1874	-0.253
^{147}Pm	0	7/2	+0.737	+0.74
^{147}Sm	14.97	7/2	-0.23280	-0.18
^{149}Sm	13.83	7/2	-0.19191	+0.052
^{151}Eu	47.82	5/2	+1.3887	+1.15
^{153}Eu	52.18	5/2	+0.6132	+2.94
^{155}Gd	14.73	3/2	-0.1727	+1.59

TABLE 3.2
The properties of selected nuclei (*contd.*)

Isotope	Natural abundance (%)	Spin quantum number (I)	Nuclear g -factor (g_N)	Quadrupole moment (10^{-28} m^2 (barn))
^{157}Gd	15.68	3/2	-0.2265	+2.03
^{159}Tb	100	3/2	+1.343	+1.18
^{161}Dy	18.88	5/2	-0.1922	+2.44
^{163}Dy	24.97	5/2	+0.2690	+2.57
^{165}Ho	100	7/2	+1.1923	+2.73
^{167}Er	22.94	7/2	-0.16186	+2.827
^{169}Tm	100	1/2	-0.4632	0
^{171}Yb	14.31	1/2	+0.98734	0
^{173}Yb	16.13	5/2	-0.271956	+2.8
^{175}Lu	97.41	7/2	+0.63791	+5.68
^{176}Lu	2.59	7	+0.456	+8
^{177}Hf	18.5	7/2	+0.22671	+4.5
^{179}Hf	13.75	9/2	-0.14242	+5.1
^{181}Ta	99.99	7/2	+0.6771	+3.9
^{183}W	14.40	1/2	+0.2355694	0
^{185}Re	37.07	5/2	+1.2748	+2.36
^{187}Re	62.93	5/2	+1.2879	+2.24
^{187}Os	1.64	1/2	+0.12930	0
^{189}Os	16.10	3/2	+0.439955	+0.91
^{191}Ir	37.30	3/2	+0.0974	+0.78
^{193}Ir	62.70	3/2	+0.1061	+0.70
^{195}Pt	33.80	1/2	+1.21898	0
^{197}Au	100	3/2	+0.098772	+0.594
^{199}Hg	16.84	1/2	+1.0117702	0
^{201}Hg	13.22	3/2	-0.373483	+0.455
^{203}Tl	29.50	1/2	+3.244514	0
^{205}Tl	70.50	1/2	+3.2764268	0
^{207}Pb	22.60	1/2	+1.16438	0
^{209}Bi	100	9/2	+0.91347	-0.46
^{235}U	0.72	7/2	-0.10	+4.55

Hence

$$\begin{aligned}
 \frac{eQ}{2} &= \langle a, I, I | \hat{A}_{2,0} | a, I, I \rangle = \langle b, I, I | \hat{B}_{2,0} | b, I, I \rangle \\
 &= \langle b, I | \hat{B}_I | b, I \rangle \left\langle b, I, I \left| \left[\frac{1}{2} (3\hat{I}_z^2 - \hat{I}^2) \right] \right| b, I, I \right\rangle \\
 &= \langle b, I | \hat{B}_I | b, I \rangle \frac{I(2I-1)}{2}
 \end{aligned}$$

which implies

$$\langle b, I \| \hat{B}_I \| b, I \rangle = \frac{eQ}{I(2I-1)}$$

Now the energy of the nuclear quadrupole interaction with one electron is

$$E_2 = \int \rho_e(\vec{r}_e) \sum_{m=-2}^{+2} \left(\frac{4\pi}{5} \right)^{1/2} \frac{1}{r_e^3} Y_{2,m}^*(\theta_e, \phi_e) A_{2,m}^{(N)} d\vec{r}_e$$

and the corresponding Hamiltonian for more electrons becomes

$$\hat{H}^q = -\frac{e}{4\pi\epsilon_0} \sum_i \sum_{m=-2}^{+2} \left(\frac{4\pi}{5} \right)^{1/2} \frac{1}{r_{Ni}^3} Y_{2,m}^*(\theta_{Ni}, \phi_{Ni}) A_{2,m}^{(N)}$$

where the electron position is measured relative to the nucleus. The spherical coordinates can be expressed in terms of Cartesian ones and thus

$$\left(\frac{4\pi}{5} \right)^{1/2} \frac{1}{r_{Ni}^3} Y_{2,0}^*(\theta_{Ni}, \phi_{Ni}) = \frac{1}{r_{Ni}^5} \frac{1}{2} (3z_{Ni}^2 - r_{Ni}^2)$$

$$\left(\frac{4\pi}{5} \right)^{1/2} \frac{1}{r_{Ni}^3} Y_{2,\pm 1}^*(\theta_{Ni}, \phi_{Ni}) = \frac{1}{r_{Ni}^5} \frac{\sqrt{6}}{2} z_{Ni} (x_{Ni} \pm iy_{Ni})$$

$$\left(\frac{4\pi}{5} \right)^{1/2} \frac{1}{r_{Ni}^3} Y_{2,\pm 2}^*(\theta_{Ni}, \phi_{Ni}) = \frac{1}{r_{Ni}^5} \frac{\sqrt{6}}{4} (x_{Ni} \pm iy_{Ni})^2$$

In terms of Cartesian coordinates the operator of the *nuclear quadrupole interaction* of the N th nucleus is written as

$$\hat{H}_N^q = \vec{I}_N \cdot \vec{\bar{q}}_N \cdot \vec{I}_N = \sum_a \sum_b \hat{I}_{Na} \hat{q}_{Nab} \hat{I}_{Nb}$$

with

$$\hat{q}_{Nab} = -\frac{e^2}{4\pi\epsilon_0} \frac{Q_N}{2I_N(2I_N-1)} \sum_i \frac{1}{r_{Ni}^5} (3r_{Nia}r_{Nib} - r_{Ni}^2 \delta_{ab})$$

The total nuclear quadrupole interaction operator is

$$\hat{H}^q = - \sum_i \sum_N \frac{e^2}{4\pi\epsilon_0} \frac{Q_N}{2I_N(2I_N - 1)} \left[\frac{3}{r_{Ni}^5} (\vec{I}_N \cdot \vec{r}_{Ni})^2 - \frac{1}{r_{Ni}^3} \vec{I}_N^2 \right]$$

SUMMARY

1. The electronic orbital angular momentum, the electron spin and the nuclear spins belong to the magnetoactive components of a molecule. When the energy of the molecule depends upon the magnetic field induction, the electronic magnetic moment and the nuclear magnetic moments, its second derivatives represent a set of magnetic parameters: the (reduced) magnetic susceptibility tensor, the differential electron *g*-tensor, the electron spin–spin interaction tensor, the magnetic shielding tensors, the nuclear spin–spin interaction tensors and the electron–nuclear hyperfine coupling tensors.
2. The electron spin can be introduced phenomenologically through the Pauli equation which is a natural extension of the Schrödinger equation. The energy shift due to the electron spin interacting with the magnetic field is the Zeeman effect. The spin–orbit interaction term, which will assume a crucial importance in transition metal and lanthanide atoms, can be introduced through some mechanistic speculations.
3. The magnetic parameters can be expressed in terms of the (sum over the states) perturbation theory in which the appropriate perturbation operators, individual for the given type of magnetic interaction, occur. These operators can be derived from the electromagnetic potential acting on the electrons and nuclei. The effect of the nuclear structure is expressed through the nuclear quadrupole moment and the corresponding Hamiltonian term.

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Relativistic Approach

4.1 QUANTISATION OF RELATIVISTIC HAMILTON FUNCTION

The combination of well known relativistic formulae

$$m = \frac{m_0}{\sqrt{1 - (v/c)^2}}$$

$$E = mc^2$$

$$E_0 = m_0c^2$$

$$\vec{p} = m\vec{v}$$

yields the following expression for the mechanical energy

$$E^2 = E_0^2 + c^2p^2$$

or

$$E = c(m_0^2c^2 + p^2)^{1/2}$$

When a charged particle is moving under the influence of electromagnetic potentials (the vector potential $\vec{A}$ and the scalar potential Φ) then the relativistic expression for the energy (the relativistic Hamilton function) is

$$H = c(m_0^2c^2 + \pi^2)^{1/2} + q\Phi$$

with mechanical linear momentum

$$\vec{\pi} = \vec{p} - q\vec{A}$$

For a slow-moving particle ($1 \gg v/c$) the expansion of the square root in powers of π/m_0c is possible

$$\begin{aligned}
 H &= m_0 c^2 [1 + (\pi/m_0 c)^2]^{1/2} + q\Phi \\
 &= m_0 c^2 \left[1 + \frac{1}{2} (\pi/m_0 c)^2 - \frac{1}{8} (\pi/m_0 c)^4 + O(\pi/m_0 c)^6 \right] + q\Phi
 \end{aligned}$$

Restricting ourselves to only the lowest two terms we get

$$H \approx m_0 c^2 + \frac{1}{2m_0} \pi^2 + q\Phi$$

The quantum mechanical equation is obtained by substituting the energy and momentum for corresponding operators

$$\hat{H} \rightarrow i\hbar \left(\frac{\partial}{\partial t} \right)$$

$$\vec{p} \rightarrow -i\hbar \vec{\nabla}$$

Thus we arrive at the equation

$$i\hbar \left(\frac{\partial}{\partial t} \right) \Psi = \left\{ m_0 c^2 + \frac{1}{2m_0} \pi^2 + q\Phi \right\} \Psi$$

which, except for the constant term $m_0 c^2$, is just the time-dependent Schrödinger equation for a charged particle in an electromagnetic field. The presence of the $m_0 c^2$ term can be annihilated by introducing an appropriate phase factor into the wave function. All the terms of such a Hamiltonian have been already analysed and there is nothing new in it.

4.2 THE DIRAC EQUATION FOR A FREE ELECTRON

The quadratic form of the relativistic Hamilton function is inappropriate for its operator form because the second derivative with respect to time is involved

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \Psi = (m_0^2 c^4 + p^2 c^2) \Psi$$

Consequently the integral of $|\Psi|^2$ over all space varies with time so that the probability is not conserved.

For further purposes the operator $\vec{p}_0$ is introduced

$$\vec{p}_0 = \frac{i\hbar}{c} \frac{\partial}{\partial t}$$

and the quadratic operator form is rewritten as

$$\{\hat{p}_0^2 - \hat{p}_x^2 - \hat{p}_y^2 - \hat{p}_z^2 - m_0^2 c^2\} \Psi_{KG} = 0$$

This is known as the *Klein–Gordon equation*.

The equation linear in time derivatives postulated by Dirac [1] is

$$\{\hat{\alpha}_0 \hat{p}_0 - \hat{\alpha}_x \hat{p}_x - \hat{\alpha}_y \hat{p}_y - \hat{\alpha}_z \hat{p}_z - \hat{\beta} m_0 c\} \Psi_D(x, y, z, t) = 0$$

The set of new operators ($\hat{\alpha}_0, \hat{\alpha}_x, \hat{\alpha}_y, \hat{\alpha}_z, \hat{\beta}$) must be independent of canonical variables ($p_x, p_y, p_z, p_0, x, y, z, t$) and they are determined in the following way. The Dirac equation is multiplied on the left by the operator

$$\hat{o} = \{\hat{\alpha}_0 \hat{p}_0 + \hat{\alpha}_x \hat{p}_x + \hat{\alpha}_y \hat{p}_y + \hat{\alpha}_z \hat{p}_z + \hat{\beta} m_0^2 c^2\}$$

yielding the condition

$$\begin{aligned} & \{\hat{\alpha}_0 \hat{p}_0 + \hat{\alpha}_x \hat{p}_x + \hat{\alpha}_y \hat{p}_y + \hat{\alpha}_z \hat{p}_z + \hat{\beta} m_0 c\} \\ & \{\hat{\alpha}_0 \hat{p}_0 - \hat{\alpha}_x \hat{p}_x - \hat{\alpha}_y \hat{p}_y - \hat{\alpha}_z \hat{p}_z - \hat{\beta} m_0 c\} \Psi_D \\ &= \{\hat{\alpha}_0^2 \hat{p}_0^2 - \hat{\alpha}_x^2 \hat{p}_x^2 - \hat{\alpha}_y^2 \hat{p}_y^2 - \hat{\alpha}_z^2 \hat{p}_z^2 - \hat{\beta}^2 m_0^2 c^2\} \Psi_D \\ & - \{(\hat{\alpha}_x \hat{\alpha}_y + \hat{\alpha}_y \hat{\alpha}_x) \hat{p}_x \hat{p}_y + (\hat{\alpha}_y \hat{\alpha}_z + \hat{\alpha}_z \hat{\alpha}_y) \hat{p}_y \hat{p}_z + (\hat{\alpha}_z \hat{\alpha}_x + \hat{\alpha}_x \hat{\alpha}_z) \hat{p}_z \hat{p}_x\} \Psi_D \\ & - m_0 c \{(\hat{\alpha}_x \hat{\beta} + \hat{\beta} \hat{\alpha}_x) \hat{p}_x + (\hat{\alpha}_y \hat{\beta} + \hat{\beta} \hat{\alpha}_y) \hat{p}_y + (\hat{\alpha}_z \hat{\beta} + \hat{\beta} \hat{\alpha}_z) \hat{p}_z\} \Psi_D = 0 \end{aligned}$$

This expression is identical to the Klein–Gordon equation under the assumption that the following relationships (idempotency and anticommutation) hold true

$$\hat{\alpha}_x^2 = \hat{\alpha}_y^2 = \hat{\alpha}_z^2 = \hat{\beta}^2 = 1$$

$$(\hat{\alpha}_x \hat{\alpha}_y + \hat{\alpha}_y \hat{\alpha}_x) = (\hat{\alpha}_y \hat{\alpha}_z + \hat{\alpha}_z \hat{\alpha}_y) = (\hat{\alpha}_z \hat{\alpha}_x + \hat{\alpha}_x \hat{\alpha}_z) = 0$$

$$(\hat{\alpha}_x \hat{\beta} + \hat{\beta} \hat{\alpha}_x) = (\hat{\alpha}_y \hat{\beta} + \hat{\beta} \hat{\alpha}_y) = (\hat{\alpha}_z \hat{\beta} + \hat{\beta} \hat{\alpha}_z) = 0$$

The operator $\hat{\alpha}_0$ is identity. Because of the anticommutation relations, the Dirac operators cannot be multiplicative operators (numbers). They are not differential operators either because of the independence of $p_x, p_y, p_z, p_0, x, y, z, t$. But what variable (degree of freedom) do the Dirac operators act upon? In the chapter dealing with the electron spin we saw that there are the Pauli matrix operators (which obey the idempotency and anticommutation) acting on a two-component wave function (the two-component spinor)

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \begin{cases} \hat{\sigma}_x |\alpha\rangle = |\beta\rangle \\ \hat{\sigma}_x |\beta\rangle = |\alpha\rangle \end{cases}$$

$$\hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \begin{cases} \hat{\sigma}_y |\alpha\rangle = -i|\beta\rangle \\ \hat{\sigma}_y |\beta\rangle = i|\alpha\rangle \end{cases}$$

$$\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \begin{cases} \hat{\sigma}_z |\alpha\rangle = |\alpha\rangle \\ \hat{\sigma}_z |\beta\rangle = -|\beta\rangle \end{cases}$$

with

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Thus the Dirac operators are somehow related to the Pauli matrix operators. They can be represented by 4×4 matrices, viz.

$$\hat{\alpha}_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \hat{\sigma}_x \\ \hat{\sigma}_x & \mathbf{0} \end{pmatrix}$$

$$\hat{\alpha}_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \hat{\sigma}_y \\ \hat{\sigma}_y & \mathbf{0} \end{pmatrix}$$

$$\hat{\alpha}_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \hat{\sigma}_z \\ \hat{\sigma}_z & \mathbf{0} \end{pmatrix}$$

$$\hat{\beta} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}$$

completed by the unit matrix

$$\hat{\alpha}_0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}$$

The matrices on the right contain 2×2 matrices. Let us introduce the matrix operator

$$\hat{\rho} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ \mathbf{1} & \mathbf{0} \end{pmatrix}$$

with $\hat{\rho}^2 = 1$. Then each Dirac $\hat{\alpha}_i$ operator ($i = x, y, z$) can be written as

$$\hat{\alpha}_i = \hat{\rho} \hat{\sigma}_i$$

and a vector formed from the Dirac operators can be viewed as

$$\vec{\alpha} = \hat{\rho} \vec{\sigma}$$

Having determined the Dirac operators, the Dirac equation for a free particle can be rewritten in the form

$$\left\{ c\hat{\alpha}_x\hat{p}_x + c\hat{\alpha}_y\hat{p}_y + c\hat{\alpha}_z\hat{p}_z + \hat{\beta}m_0c^2 \right\} \Psi_D(x, y, z, t) = c\hat{\alpha}_0\hat{p}_0 \Psi_D(x, y, z, t)$$

and for stationary (time-independent) states when

$$E \rightarrow i\hbar \left(\frac{\partial}{\partial t} \right) = c\hat{p}_0$$

we obtain

$$\left\{ c\hat{\alpha}_x\hat{p}_x + c\hat{\alpha}_y\hat{p}_y + c\hat{\alpha}_z\hat{p}_z + \hat{\beta}E_0 \right\} \Psi_D(x, y, z) = E\Psi_D(x, y, z)$$

The Dirac form of the Hamiltonian is represented by a 4×4 matrix

$$\hat{H}_D = \begin{pmatrix} E_0 & 0 & c\hat{p}_z & c(\hat{p}_x - i\hat{p}_y) \\ 0 & E_0 & c(\hat{p}_x + i\hat{p}_y) & -c\hat{p}_z \\ c\hat{p}_z & c(\hat{p}_x - i\hat{p}_y) & -E_0 & 0 \\ c(\hat{p}_x + i\hat{p}_y) & -c\hat{p}_z & 0 & -E_0 \end{pmatrix}$$

Now it is evident that this operator acts on a wave function in the form of a *four-component spinor* represented by a four-component column vector

$$\Psi_D = \begin{pmatrix} \Psi_1(x, y, z) \\ \Psi_2(x, y, z) \\ \Psi_3(x, y, z) \\ \Psi_4(x, y, z) \end{pmatrix}$$

Therefore the Dirac equation for stationary states represents in fact a system of coupled equations

$$E_0\Psi_1 + c\hat{p}_z\Psi_3 + c(\hat{p}_x - i\hat{p}_y)\Psi_4 = E\Psi_1$$

$$E_0\Psi_2 + c(\hat{p}_x + i\hat{p}_y)\Psi_3 - c\hat{p}_z\Psi_4 = E\Psi_2$$

$$c\hat{p}_z\Psi_1 + c(\hat{p}_x - i\hat{p}_y)\Psi_2 - E_0\Psi_3 = E\Psi_3$$

$$c(\hat{p}_x + i\hat{p}_y)\Psi_1 - c\hat{p}_z\Psi_2 - E_0\Psi_4 = E\Psi_4$$

to be satisfied simultaneously.

Let us consider a slow-moving electron, i.e. the magnitude of the linear momentum $\vec{p}$ is negligible compared to m_0c . Then the eigenvalues of the Dirac equation are dominated by $\pm E_0$; hence

$$E_1 = E_0 + O(c\vec{p})$$

$$E_2 = E_0 + O(c\vec{p})$$

$$E_3 = -E_0 + O(c\vec{p})$$

$$E_4 = -E_0 + O(c\vec{p})$$

where $O(c\vec{p})$ are much smaller corrections due to coupling by the components of $\vec{p}$. It can be shown that if the positive energy solutions correspond to an electron ($q = -e$), then the negative energy solutions correspond to a positron ($q = +e$). The energy solutions are doubled because they correspond to different spin orientations, as we will see later. In the first pair of the Dirac set of equations the components Ψ_1 and Ψ_2 prevail whereas in the second pair the components Ψ_3 and Ψ_4 dominate. Thus it seems to be appropriate formally to split the Dirac state vector into an *upper two-component spinor* Ψ_u and a *lower two-component spinor* Ψ_l

$$\Psi_D = \begin{pmatrix} \Psi_1(x, y, z) \\ \Psi_2(x, y, z) \\ \Psi_3(x, y, z) \\ \Psi_4(x, y, z) \end{pmatrix} = \begin{pmatrix} \Psi_u(x, y, z) \\ \Psi_l(x, y, z) \end{pmatrix}$$

with

$$\Psi_u(x, y, z) = \begin{pmatrix} \Psi_1(x, y, z) \\ \Psi_2(x, y, z) \end{pmatrix}$$

$$\Psi_l(x, y, z) = \begin{pmatrix} \Psi_3(x, y, z) \\ \Psi_4(x, y, z) \end{pmatrix}$$

For electron solutions, $E \approx E_0$, $|\Psi_u| \gg |\Psi_l|$ holds true whereas for positron solutions it is $|\Psi_u| \ll |\Psi_l|$.

4.3 THE DIRAC EQUATION FOR AN ELECTRON IN THE ELECTROMAGNETIC FIELD

The presence of an electromagnetic field is reflected in the linear momentum

$$\vec{\pi} = \vec{p} - q\vec{A} = \vec{p} + e\vec{A}$$

and the potential energy

$$V = q\Phi = -e\Phi$$

Then the Dirac Hamiltonian adopts the form of

$$\hat{H}_D = c\hat{\alpha}_x\hat{\pi}_x + c\hat{\alpha}_y\hat{\pi}_y + c\hat{\alpha}_z\hat{\pi}_z + \hat{\beta}E_0 - \hat{\alpha}_0e\Phi$$

or, using a vector representation of the Dirac matrices

$$\hat{H}_D + \hat{\alpha}_0 e\Phi = c\vec{\alpha} \cdot \vec{\pi} + \hat{\beta}E_0$$

Its square becomes

$$\begin{aligned} (\hat{H}_D + \hat{\alpha}_0 e\Phi)^2 &= (c\vec{\alpha} \cdot \vec{\pi} + \hat{\beta}E_0)^2 \\ &= c^2(\vec{\alpha} \cdot \vec{\pi})^2 + c\vec{\alpha} \cdot \vec{\pi}\hat{\beta}E_0 + \hat{\beta}E_0c\vec{\alpha} \cdot \vec{\pi} + (\hat{\beta}E_0)^2 \\ &= c^2(\vec{\alpha} \cdot \vec{\pi})^2 + cE_0(\vec{\alpha}\hat{\beta} + \hat{\beta}\vec{\alpha}) \cdot \vec{\pi} + (\hat{\beta}E_0)^2 \end{aligned}$$

In the above manipulations we used the property that $\vec{\alpha}$ and $\hat{\beta}$ both commute with $\vec{\pi}$. Because of anticommutation, the cross-term vanishes and the expression reduces to

$$(\hat{H}_D + \hat{\alpha}_0 e\Phi)^2 = c^2(\vec{\alpha} \cdot \vec{\pi})^2 + (\hat{\beta}E_0)^2$$

Now the square of the scalar product will be analysed in more detail. Hence

$$(\vec{\alpha} \cdot \vec{\pi})^2 = (\hat{\rho}\vec{\sigma} \cdot \vec{\pi})(\hat{\rho}\vec{\sigma} \cdot \vec{\pi}) = \hat{\rho}^2(\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{\pi})$$

Notice that the squares

$$\hat{\beta}^2 = \hat{\rho}^2 = \hat{\alpha}_0^2 = 1$$

are all the unit matrix. Then we obtain

$$(\hat{H}_D + \hat{\alpha}_0 e\Phi)^2 = 1[c^2(\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{\pi}) + E_0^2]$$

The relationship

$$(\vec{\sigma} \cdot \vec{A})(\vec{\sigma} \cdot \vec{B}) = (\vec{A} \cdot \vec{B}) + i\vec{\sigma} \cdot (\vec{A} \times \vec{B})$$

will be helpful provided that the vector $\vec{\sigma}$ commutes with the vectors $\vec{A}$ and $\vec{B}$. Making use of this formula, we get

$$(\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{\pi}) = (\vec{\pi} \cdot \vec{\pi}) + i\vec{\sigma} \cdot (\vec{\pi} \times \vec{\pi})$$

The second term involves

$$\vec{\pi} \times \vec{\pi} = (\vec{p} + e\vec{A}) \times (\vec{p} + e\vec{A}) = \vec{p} \times \vec{p} + e(\vec{p} \times \vec{A} + \vec{A} \times \vec{p}) + e^2 \vec{A} \times \vec{A}$$

The first and the last vector products vanish but the middle term survives. Let us use a vector product relationship

$$\vec{\nabla} \times \vec{A} \Psi = \Psi(\vec{\nabla} \times \vec{A}) - (\vec{A} \times \vec{\nabla})\Psi$$

since

$$\vec{p} = -i\hbar\vec{\nabla}$$

Then the middle term above becomes

$$\begin{aligned} \vec{p} \times \vec{A} + \vec{A} \times \vec{p} &= -i\hbar[(\vec{\nabla} \times \vec{A}) - (\vec{A} \times \vec{\nabla})] - i\hbar(\vec{A} \times \vec{\nabla}) \\ &= -i\hbar(\vec{\nabla} \times \vec{A}) = -i\hbar\vec{B} \end{aligned}$$

where the magnetic induction $\vec{B} = \vec{\nabla} \times \vec{A}$ appears. Coming back, we have

$$(\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{\pi}) = (\vec{\pi} \cdot \vec{\pi}) + i\vec{\sigma} \cdot (-e\hbar\vec{B}) = \hat{\pi}^2 + e\hbar\vec{\sigma} \cdot \vec{B}$$

and

$$(\hat{H}_D + \hat{\alpha}_0 e\Phi)^2 = \mathbf{1}[c^2\hat{\pi}^2 + c^2 e\hbar\vec{\sigma} \cdot \vec{B} + E_0^2]$$

In the absence of electromagnetic fields the square of the Dirac Hamiltonian reduces to

$$(\hat{H}_D)^2 = \mathbf{1}[c^2\hat{p}^2 + E_0^2]$$

which is nothing else but four equivalent relativistic expressions for the energy of a free particle. Thus we can conclude that, as long as the electromagnetic field is present, a new term appears in the quadratic form of the Dirac equation.

The explicit form of the square operator is

$$\begin{aligned}
 & [(\hat{H}_D + \hat{\alpha}_0 e \Phi)^2 - \mathbf{1} E_0^2] / c^2 = (\vec{\sigma} \cdot \vec{\pi})^2 \\
 &= \begin{pmatrix} 0 & 0 & \hat{\pi}_z & \hat{\pi}_x - i\hat{\pi}_y \\ 0 & 0 & \hat{\pi}_x + i\hat{\pi}_y & -\hat{\pi}_z \\ \hat{\pi}_z & \hat{\pi}_x - i\hat{\pi}_y & 0 & 0 \\ \hat{\pi}_x + i\hat{\pi}_y & -\hat{\pi}_z & 0 & 0 \end{pmatrix} \\
 &= \begin{pmatrix} 0 & 0 & \hat{\pi}_z & \hat{\pi}_x - i\hat{\pi}_y \\ 0 & 0 & \hat{\pi}_x + i\hat{\pi}_y & -\hat{\pi}_z \\ \hat{\pi}_z & \hat{\pi}_x - i\hat{\pi}_y & 0 & 0 \\ \hat{\pi}_x + i\hat{\pi}_y & -\hat{\pi}_z & 0 & 0 \end{pmatrix} \\
 &= \begin{pmatrix} \hat{\pi}^2 + \hat{Z} & \hat{X} & 0 & 0 \\ \hat{X}^+ & \hat{\pi}^2 - \hat{Z} & 0 & 0 \\ 0 & 0 & \hat{\pi}^2 + \hat{Z} & \hat{X} \\ 0 & 0 & \hat{X}^+ & \hat{\pi}^2 - \hat{Z} \end{pmatrix}
 \end{aligned}$$

with the operator

$$\begin{aligned}
 \hat{X} &= \hat{\pi}_z(\hat{\pi}_x - i\hat{\pi}_y) - (\hat{\pi}_x - i\hat{\pi}_y)\hat{\pi}_z \\
 &= [\hat{\pi}_z, \hat{\pi}_x] + i[\hat{\pi}_y, \hat{\pi}_z] = e\hbar(B_x - iB_y)
 \end{aligned}$$

its complex conjugate being

$$\hat{X}^+ = (\hat{\pi}_x + i\hat{\pi}_y)\hat{\pi}_z - \hat{\pi}_z(\hat{\pi}_x + i\hat{\pi}_y) = e\hbar(B_x + iB_y)$$

and

$$\hat{Z} = i[\hat{\pi}_x, \hat{\pi}_y] = e\hbar B_z$$

$$\begin{aligned}
 \hat{\pi}^2 &= (\vec{p} + e\vec{A}) \cdot (\vec{p} + e\vec{A}) = \hat{p}^2 + e\vec{p} \cdot \vec{A} + e\vec{A} \cdot \vec{p} + e^2 A^2 \\
 &= \hat{p}^2 + 2e\vec{A} \cdot \vec{p} + e^2 A^2
 \end{aligned}$$

When the vector potential is expressed through the magnetic induction

$$\vec{A} = \frac{1}{2} \vec{B} \times (\vec{r} - \vec{G})$$

with the position vector measured relative to the gauge origin, then one gets

$$\begin{aligned} \hat{\pi}^2 &= \hat{p}^2 + e\vec{B} \times (\vec{r} - \vec{G}) \cdot \vec{p} + \frac{e^2}{4} [\vec{B} \times (\vec{r} - \vec{G})]^2 \\ &= \hat{p}^2 + e\vec{B} \cdot \vec{l}_{Ge} + \frac{e^2}{4} [\vec{B} \times (\vec{r} - \vec{G})]^2 \end{aligned}$$

Here the angular momentum vector was introduced

$$\vec{l}_{Ge} = (\vec{r} - \vec{G}) \times \vec{p}$$

All the derivations made up to now have been rigorous. We are interested in comparing the relativistic and the non-relativistic Hamiltonian terms, which can be done approximately in the following way. The Dirac Hamiltonian is assumed in the form of the dominating term for the positive energy solutions E_0 and the small perturbation $\hat{H}_{NR}$ due to a slow-moving electron

$$\hat{H}_D = 1(E_0 + \hat{H}_{NR})$$

By substituting into the quadratic form we get

$$1(E_0 + \hat{H}_{NR} + \hat{\alpha}_0 e\Phi)^2 = 1[c^2\pi^2 + c^2 e\hbar\vec{\sigma} \cdot \vec{B} + E_0^2]$$

and making use of the square it holds that

$$\begin{aligned} [E_0^2 + (\hat{H}_{NR})^2 + (e\Phi)^2 + 2E_0 e\Phi + 2E_0 \hat{H}_{NR} + 2e\Phi \hat{H}_{NR}]/c^2 \\ = \hat{\pi}^2 + e\hbar\vec{\sigma} \cdot \vec{B} + E_0^2/c^2 \end{aligned}$$

The leading terms on the left side, with the use of $E_0/c^2 = m_0$, are

$$m_0^2 c^2 + 2m_0 \hat{H}_{NR} + 2m_0 e\Phi = \hat{\pi}^2 + e\hbar\vec{\sigma} \cdot \vec{B} + m_0^2 c^2$$

since the remaining terms are of the order $(1/c^2)$ and thus negligible. By a rearrangement this gives an expression

$$\hat{H}_{\text{NR}} = -e\Phi + \frac{1}{2m_0}\hat{\pi}^2 + \frac{e\hbar}{2m_0}\vec{\sigma} \cdot \vec{B}$$

This is the well known non-relativistic Hamiltonian in the presence of the external electromagnetic field except for the last term

$$\hat{H}^{(s-B)} = \frac{e\hbar}{2m_0}\vec{\sigma} \cdot \vec{B} = -\vec{\mu}_e \cdot \vec{B}$$

This new term represents an interaction of the external magnetic field with the intrinsic magnetic moment of an electron

$$\vec{\mu}_e = -\frac{e\hbar}{2m_0}\vec{\sigma} = -\frac{e}{m_0}\left(\frac{\hbar}{2}\vec{\sigma}\right) = -\frac{2\mu_B}{\hbar}\vec{s}_e$$

Now the electron spin has appeared explicitly.

The Hamiltonian of a free electron in the non-relativistic theory is

$$\hat{H}_{\text{NR}} = \frac{1}{2m_0}\hat{p}^2$$

and it is easy to demonstrate that it commutes with the angular momentum

$$[\hat{l}_a, \hat{H}_{\text{NR}}] = \frac{1}{2m_0}[\hat{l}_a, \hat{p}^2] = 0$$

so that the angular momentum is a constant of motion. However, the angular momentum operator $\vec{l}$ does not commute with the Dirac Hamiltonian

$$[\hat{l}_a, \hat{H}_D] = c[\hat{l}_a, (\vec{\alpha} \cdot \vec{p})] = c\vec{\alpha} \cdot [\hat{l}_a, \vec{p}] = c\hat{\rho}\vec{\sigma} \cdot [\hat{l}_a, \vec{p}] = ic\hat{\rho}(\vec{\sigma} \times \vec{p})_a$$

and therefore the angular momentum $\vec{l}$ is no longer a constant of motion. Also, the spin operator does not commute with the Dirac Hamiltonian

$$[\hat{\sigma}_a, \hat{H}_D] = c[\hat{\sigma}_a, (\vec{\alpha} \cdot \vec{p})] = c[\hat{\sigma}_a, \vec{\alpha}] \cdot \vec{p} = c\hat{\rho}[\hat{\sigma}_a, \vec{\sigma}] \cdot \vec{p} = -2ic\hat{\rho}(\vec{\sigma} \times \vec{p})_a$$

Let us introduce the *total angular momentum* as a sum of the orbital and spin contribution

$$\vec{j} = \vec{l} + \frac{\hbar}{2} \vec{\sigma}$$

For such an operator the commutators of $[\hat{l}_a, \hat{H}_D]$ and $\frac{1}{2}[\hat{\sigma}_a, \hat{H}_D]$ just cancel so that this operator commutes with the Dirac Hamiltonian

$$[\hat{j}_a, \hat{H}_D] = [\hat{l}_a + \frac{1}{2}\hat{\sigma}_a, \hat{H}_D] = 0$$

and thus it can be taken as a new constant of motion.

It must be mentioned again that the Dirac equation was not derived—it was postulated. However, it is useful in describing the correct behaviour of electrons. One example is the magnetogyric factor for the electron, defined as the ratio of the intrinsic magnetic moment to the intrinsic angular momentum, expressed in units of $(q/2m)$

$$g_e = \left(\frac{\vec{\mu}_e}{\vec{s}_e} \right) / \left(-\frac{e}{2m_e} \right) = \left(\frac{-2\mu_B}{\hbar} \frac{\vec{s}_e}{\vec{s}_e} \right) / \left(-\frac{e}{2m_e} \right) = -2, \quad [\text{true}]$$

This value cannot be properly derived from the non-relativistic theory because the application of the classical expression for the magnetic moment of a charged particle associated with some angular momentum $\vec{l}$

$$\vec{\mu} = \frac{q}{2m} \vec{l}$$

would predict for electrons

$$g_e = \left(\frac{\vec{\mu}}{\vec{l}} \right) / \left(\frac{q}{2m} \right) = -1, \quad [\text{false}]$$

4.4 APPROXIMATE SOLUTION OF THE DIRAC EQUATION

Although the Dirac equation in its four-component form can be solved exactly for a few systems (the hydrogen-like atom, electron in a uniform magnetic field), normally a decoupling to the two-component form has to be done [2–6]. For this purpose two techniques were developed: the Foldy–Wouthuysen transformation and the partitioning method (for a small component). We will follow the second approach, which is based on these steps:

- (a) annihilation of the rest mass energy from the positive energy states;
- (b) application of the matrix partitioning method to eliminate the lower component spinor;
- (c) utilisation of the commutator equations to shift a resolvent operator to the right side;
- (d) application of the resolvent operator to the upper component spinor;
- (e) renormalisation of the upper component spinor;
- (f) transformation of the approximate Dirac operator into the basis of the renormalised upper component spinor.

The rest mass energy for the positive energy states can be removed by introducing an appropriate phase factor into the wave function

$$\begin{pmatrix} \Psi_u \\ \Psi_l \end{pmatrix} \rightarrow \exp(-im_0c^2t/\hbar) \begin{pmatrix} \Psi_u \\ \Psi_l \end{pmatrix}$$

The Dirac (time-dependent) equation for an electron in the presence of an external electromagnetic field can be arranged into the form

$$\begin{pmatrix} (-e\Phi - c\hat{p}_0)\mathbf{1} & c\vec{\sigma} \cdot \vec{\pi} \\ c\vec{\sigma} \cdot \vec{\pi} & (-2m_0c^2 - e\Phi - c\hat{p}_0)\mathbf{1} \end{pmatrix} \begin{pmatrix} \Psi_u \\ \Psi_l \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

This is equivalent, in fact, to a system of two coupled matrix equations

$$(-e\Phi - c\hat{p}_0)\mathbf{1}\Psi_u + c(\vec{\sigma} \cdot \vec{\pi})\Psi_l = 0$$

$$c(\vec{\sigma} \cdot \vec{\pi})\Psi_u + (-2m_0c^2 - e\Phi - c\hat{p}_0)\mathbf{1}\Psi_l = 0$$

The second equation can be utilised to express the lower (small) component spinor in terms of the upper (large) component spinor

$$\Psi_l = [(2m_0c^2 + e\Phi + c\hat{p}_0)\mathbf{1}]^{-1} c\vec{\sigma} \cdot \vec{\pi}\Psi_u$$

provided that the resolvent

$$\hat{K} = [(2m_0c^2 + e\Phi + c\hat{p}_0)\mathbf{1}]^{-1}$$

or

$$\hat{k} = 2m_0c^2\hat{K} = 2m_0c^2[(2m_0c^2 + e\Phi + c\hat{p}_0)\mathbf{1}]^{-1} = \left[\left(1 + \frac{e\Phi + c\hat{p}_0}{2m_0c^2} \right) \mathbf{1} \right]^{-1}$$

exists. After the substitution for Ψ_I , the first equation adopts a form where only the upper component spinor occurs

$$\left\{ \frac{1}{2m_0} (\vec{\sigma} \cdot \vec{\pi}) \hat{k} (\vec{\sigma} \cdot \vec{\pi}) - (e\Phi + c\hat{p}_0) \mathbf{1} \right\} \Psi_u = 0$$

The presence of the new operator $\hat{k}$ in this equation brings some complications and therefore we would like to shift its position somewhere to the right. However, owing to non-commutations this is not a trivial problem. For this purpose we apply two tricks. By a rearrangement of the expression defining the operator $\hat{k}$ one gets

$$(e\Phi + c\hat{p}_0) \mathbf{1} = 2m_0 c^2 (\hat{k}^{-1} - \mathbf{1})$$

and after a multiplication from the left by $\hat{k}$ we obtain the expression

$$\left\{ \frac{1}{4m_0^2 c^2} \hat{k} (\vec{\sigma} \cdot \vec{\pi}) \hat{k} (\vec{\sigma} \cdot \vec{\pi}) - (\mathbf{1} - \hat{k}) \right\} \Psi_u = 0$$

or

$$\hat{k} \Psi_u = \left\{ \mathbf{1} - \frac{1}{4m_0^2 c^2} \hat{k} (\vec{\sigma} \cdot \vec{\pi}) \hat{k} (\vec{\sigma} \cdot \vec{\pi}) \right\} \Psi_u$$

This equation shows us explicitly how the operator $\hat{k}$, when staying on the right side, acts on the upper component spinor. The second trick will indicate how we can shift the $\hat{k}$ operator to the right side. For this purpose let us consider an identity fulfilled for any operators

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = \hat{B}[\hat{B}^{-1}, \hat{A}]\hat{B}$$

and in particular, when $\hat{A} = (\vec{\sigma} \cdot \vec{\pi})$ and $\hat{B} = \hat{k}$ it holds true that

$$\begin{aligned} [(\vec{\sigma} \cdot \vec{\pi}), \hat{k}] &= \hat{k}[\hat{k}^{-1}, (\vec{\sigma} \cdot \vec{\pi})]\hat{k} \\ &= \hat{k} \left[1 + \frac{e\Phi + c\hat{p}_0}{2m_0 c^2}, (\vec{\sigma} \cdot \vec{\pi}) \right] \hat{k} \\ &= \frac{1}{2m_0 c^2} \hat{k} [e\Phi + c\hat{p}_0, (\vec{\sigma} \cdot \vec{\pi})] \hat{k} \end{aligned}$$

The new commutator, with the help of $\vec{p} = -i\hbar\vec{\nabla}$ and $c\hat{p}_0 = i\hbar(\partial/\partial t)$, can be manipulated as follows

$$\begin{aligned} [\hat{\sigma}_x \hat{\pi}_x, e\Phi + c\hat{p}_0] &= \hat{\sigma}_x \left[\hat{p}_x + eA_x, e\Phi + i\hbar \frac{\partial}{\partial t} \right] \\ &= \hat{\sigma}_x \left(-i\hbar e \frac{\partial \Phi}{\partial x} - i\hbar e \frac{\partial A_x}{\partial t} \right) = i\hbar e \hat{\sigma}_x \left(-\nabla_x \Phi - \frac{\partial A_x}{\partial t} \right) \\ &= i\hbar e \hat{\sigma}_x E_x \end{aligned}$$

where the electric field strength $\vec{E} = -\vec{\nabla}\Phi - (\partial\vec{A}/\partial t)$ appears explicitly. Thus the commutator expression becomes

$$[(\vec{\sigma} \cdot \vec{\pi}), \hat{k}] = (\vec{\sigma} \cdot \vec{\pi})\hat{k} - \hat{k}(\vec{\sigma} \cdot \vec{\pi}) = -\frac{i\hbar e}{2m_0 c^2} \hat{k}(\vec{\sigma} \cdot \vec{E})\hat{k}$$

or

$$\hat{k}(\vec{\sigma} \cdot \vec{\pi}) = (\vec{\sigma} \cdot \vec{\pi})\hat{k} + \frac{i\hbar e}{2m_0 c^2} \hat{k}(\vec{\sigma} \cdot \vec{E})\hat{k}$$

We have arrived at the system of three rigorous equations which allow us to solve the Dirac equation in the two-component form to an arbitrary degree of accuracy. Starting from the two-component equation

$$\left\{ \frac{1}{2m_0} (\vec{\sigma} \cdot \vec{\pi})\hat{k}(\vec{\sigma} \cdot \vec{\pi}) - (e\Phi + c\hat{p}_0)\mathbf{1} \right\} \Psi_u = 0$$

the $\hat{k}$ operator is shifted to the right side at the expense of introducing the additional but much smaller term

$$\hat{k}(\vec{\sigma} \cdot \vec{\pi}) = (\vec{\sigma} \cdot \vec{\pi})\hat{k} + \frac{i\hbar e}{2m_0 c^2} \hat{k}(\vec{\sigma} \cdot \vec{E})\hat{k}$$

and then the effect of the $\hat{k}$ operator is evaluated

$$\hat{k}\Psi_u = \left\{ \mathbf{1} - \frac{1}{4m_0^2 c^2} \hat{k}(\vec{\sigma} \cdot \vec{\pi})\hat{k}(\vec{\sigma} \cdot \vec{\pi}) \right\} \Psi_u$$

In the first iteration we obtain

$$\left\{ \frac{1}{2m_0} (\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{\pi}) \left[1 - \frac{1}{4m_0^2 c^2} \hat{k}(\vec{\sigma} \cdot \vec{\pi}) \hat{k}(\vec{\sigma} \cdot \vec{\pi}) \right] \right. \\ \left. + \frac{1}{2m_0} (\vec{\sigma} \cdot \vec{\pi}) \frac{i\hbar e}{2m_0 c^2} \hat{k}(\vec{\sigma} \cdot \vec{E}) \left[1 - \frac{1}{4m_0^2 c^2} \hat{k}(\vec{\sigma} \cdot \vec{\pi}) \hat{k}(\vec{\sigma} \cdot \vec{\pi}) \right] \right. \\ \left. - e\Phi - c\hat{p}_0 \right\} \Psi_u = 0$$

To the first order of accuracy we assume

$$\hat{k}\Psi_u = \left\{ 1 - \frac{1}{4m_0^2 c^2} (\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{\pi}) + O(\alpha^4) \right\} \Psi_u$$

where the remainder $O(\alpha^4)$ is neglected (the fine structure constant is expressed as $\alpha = \mu_0 e^2 c / 2\hbar \approx 1/137$). Then the expansion of the Dirac Hamiltonian $\hat{H}_D \rightarrow c\hat{p}_0$ becomes

$$\hat{H}_D = -e\Phi + \frac{1}{2m_0} (\vec{\sigma} \cdot \vec{\pi})^2 - \frac{1}{8m_0^3 c^2} (\vec{\sigma} \cdot \vec{\pi})^4 + \frac{i\hbar e}{4m_0^2 c^2} (\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{E}) \\ + O(m_0 c^2 \alpha^6)$$

There are, however, two features which should be reanalysed: the upper component spinor was not normalised and the last term in the expansion of the Dirac Hamiltonian is not Hermitian. Thus we introduce a renormalised upper component spinor

$$\Phi_u = \hat{N}\Psi_u$$

through the assumption that the probability density associated with Φ_u is the same as that for the four-component spinor

$$\Psi^+ \Psi = \Psi_u^+ \Psi_u + \Psi_l^+ \Psi_l = \Phi_u^+ \Phi_u$$

Now, using the expression of the lower component spinor in terms of the upper component spinor

$$\Psi_l = \frac{1}{2m_0 c^2} \hat{k}(\vec{\sigma} \cdot \vec{\pi}) \Psi_u$$

the probability density adopts the form of

$$\Phi_u^+ \Phi_u = \hat{N}^+ \hat{N} \Psi_u^+ \Psi_u = \left[1 + \frac{1}{4m_0^2 c^2} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}^2 (\vec{\sigma} \cdot \vec{\pi}) \right] \Psi_u^+ \Psi_u$$

and therefore the normalisation (Hermitian) operator is

$$\hat{N} = \left[1 + \frac{1}{4m_0^2 c^2} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}^2 (\vec{\sigma} \cdot \vec{\pi}) \right]^{1/2}$$

Within the accuracy of the order $1/c^2$ it is

$$\hat{N} = \left[1 + \frac{1}{8m_0^2 c^2} (\vec{\sigma} \cdot \vec{\pi})^2 \right] + O(\alpha^4) = 1 + \hat{X}$$

and its inverse is

$$\hat{N}^{-1} = \left[1 - \frac{1}{8m_0^2 c^2} (\vec{\sigma} \cdot \vec{\pi})^2 \right] + O(\alpha^4) = 1 - \hat{X}$$

with

$$\hat{X} = \frac{1}{8m_0^2 c^2} (\vec{\sigma} \cdot \vec{\pi})^2$$

The renormalised upper component spinor satisfies the time-dependent Dirac equation in the form

$$\hat{H}'_D \Phi_u = c \hat{p}_0 \Phi_u$$

with the transformed Hamiltonian $\hat{H}'_D$ being Hermitian. Its actual form is derived in the following way. For the unnormalised upper component spinor the Dirac equation was

$$\hat{H}_D \Psi_u = c \hat{p}_0 \Psi_u$$

and using the transformation relationship

$$\Psi_u = \hat{N}^{-1} \Phi_u$$

and, by premultiplication throughout $\hat{N}$ from the left, we get

$$\hat{N}\hat{H}_D\hat{N}^{-1}\Phi_u = \hat{N}c\hat{p}_0\hat{N}^{-1}\Phi_u$$

The application of the operator identity to the shift of the $\hat{p}_0$ to the right side yields

$$[\hat{p}_0, \hat{N}^{-1}] = \hat{p}_0\hat{N}^{-1} - \hat{N}^{-1}\hat{p}_0 = \hat{N}^{-1}[\hat{N}, \hat{p}_0]\hat{N}^{-1}$$

and the above expression relaxes to

$$\hat{N}\hat{H}_D\hat{N}^{-1}\Phi_u = \hat{N}\hat{N}^{-1}c\hat{p}_0 + \hat{N}\hat{N}^{-1}[\hat{N}, c\hat{p}_0]\hat{N}^{-1}\Phi_u$$

which can be rearranged as

$$\{\hat{N}\hat{H}_D\hat{N}^{-1} - [\hat{N}, c\hat{p}_0]\hat{N}^{-1}\}\Phi_u = c\hat{p}_0\Phi_u$$

This is the desired form of the Dirac equation with the transformed Hamiltonian

$$\hat{H}'_D = \hat{N}\hat{H}_D\hat{N}^{-1} - [\hat{N}, c\hat{p}_0]\hat{N}^{-1}$$

which can be rewritten as

$$\hat{H}'_D = \hat{N}(\hat{H}_D - c\hat{p}_0)\hat{N}^{-1} + c\hat{p}_0$$

Now the expansion of the normalisation operator and the original Dirac Hamiltonian is applied to the certain order of accuracy

$$\begin{aligned}\hat{H}'_D &= (1 + \hat{X})(-e\Phi - c\hat{p}_0 + \hat{Y})(1 - \hat{X}) + c\hat{p}_0 \\ &= -e\Phi - c\hat{p}_0 + \hat{Y} + (-e\Phi - c\hat{p}_0 + \hat{Y})(-\hat{X}) + \hat{X}(-e\Phi - c\hat{p}_0 + \hat{Y}) \\ &\quad + \hat{X}(-e\Phi - c\hat{p}_0 + \hat{Y})(-\hat{X}) + c\hat{p}_0\end{aligned}$$

with the operator

$$\hat{Y} = \frac{1}{2m_0}(\vec{\sigma} \cdot \vec{\pi})\hat{k}(\vec{\sigma} \cdot \vec{\pi})$$

commuting with $\hat{X}$. If the result is required to be accurate only to the order of $m_0c^2\alpha^4$, we may write

$$\hat{H}'_D = (-e\Phi + \hat{Y}) + [e\Phi + c\hat{p}_0, \hat{X}] + O(m_0c^2\alpha^6)$$

or

$$\hat{H}'_D = \hat{H}_D + \left[e\Phi + c\hat{p}_0, \frac{1}{8m_0^2c^2}(\vec{\sigma} \cdot \vec{\pi})^2 \right] + O(m_0c^2\alpha^6)$$

The commutator can be evaluated as

$$\begin{aligned} [e\Phi + c\hat{p}_0, (\vec{\sigma} \cdot \vec{\pi})^2] &= [e\Phi + c\hat{p}_0, (\vec{\sigma} \cdot \vec{\pi})](\vec{\sigma} \cdot \vec{\pi}) - (\vec{\sigma} \cdot \vec{\pi})[e\Phi + c\hat{p}_0, (\vec{\sigma} \cdot \vec{\pi})] \\ &= -i\hbar e[(\vec{\sigma} \cdot \vec{E}), (\vec{\sigma} \cdot \vec{\pi})] \end{aligned}$$

because of the validity

$$[e\Phi + c\hat{p}_0, (\vec{\sigma} \cdot \vec{\pi})] = -i\hbar e(\vec{\sigma} \cdot \vec{E})$$

Then

$$\hat{H}'_D = \hat{H}_D - \frac{i\hbar e}{8m_0^2c^2}[(\vec{\sigma} \cdot \vec{E}), (\vec{\sigma} \cdot \vec{\pi})] + O(m_0c^2\alpha^6)$$

Using the expansion of the untransformed Dirac Hamiltonian we arrive at the Hermitian form

$$\hat{H}'_D = -e\Phi + \frac{1}{2m_0}(\vec{\sigma} \cdot \vec{\pi})^2 - \frac{1}{8m_0^3c^2}(\vec{\sigma} \cdot \vec{\pi})^4 - \frac{i\hbar e}{8m_0^2c^2}[(\vec{\sigma} \cdot \vec{E}), (\vec{\sigma} \cdot \vec{\pi})]$$

Here the products involving two or more Pauli operators can be simplified by the use of the expression

$$(\vec{\sigma} \cdot \vec{A})(\vec{\sigma} \cdot \vec{B}) = \vec{A} \cdot \vec{B} + i\vec{\sigma} \cdot (\vec{A} \times \vec{B})$$

and

$$(\vec{\sigma} \cdot \vec{\pi})^2 = \hat{\pi}^2 + e\hbar\vec{\sigma} \cdot \vec{B}$$

4.5 RELATIVISTIC ONE-ELECTRON HAMILTONIAN TERMS

For stationary states the time-dependent operator reduces to the energy E

$$c\hat{p}_0 = i\hbar \frac{\partial}{\partial t} \rightarrow E$$

Making use of

$$E = m_0 c^2 + W$$

where W is the energy in excess of that associated with the rest mass, the stationary two-component Dirac equation adopts the form

$$\left\{ \frac{1}{2m_0} (\vec{\sigma} \cdot \vec{\pi}) \hat{k} (\vec{\sigma} \cdot \vec{\pi}) - (e\Phi + W) \mathbf{1} \right\} \Psi_u = 0$$

since the rest mass energy has been removed by an appropriate phase factor in the wave function. For the vanishing scalar potential $\Phi = 0$ the resolvent operator $\hat{k}$ reduces to a number

$$\hat{k} \rightarrow k = \left(1 - \frac{W}{2m_0 c^2} \right)^{-1}$$

and the two-component Dirac equation simplifies to

$$\left\{ \frac{k}{2m_0} (\vec{\sigma} \cdot \vec{\pi}) (\vec{\sigma} \cdot \vec{\pi}) - (e\Phi) \mathbf{1} \right\} \Psi_u = W \Psi_u$$

For further partitioning and classification of the Hamiltonian terms some assumptions concerning the electromagnetic field will be accepted:

(a) the electric field strength is divided into two parts

$$\vec{E} = \vec{E}_{\text{int}} + \vec{E}_{\text{ext}}$$

where the internal field is stationary and the external field does not arise from point sources, so that

$$\vec{E}_{\text{int}} = -\vec{\nabla} \Phi_{\text{int}}$$

$$\vec{E}_{\text{ext}} = -\vec{\nabla} \Phi_{\text{ext}} - \frac{\partial \vec{A}}{\partial t}$$

(b) the magnetic field $\vec{B}$ does not arise from point sources

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

Then the resolvent operator can be written in the form

$$\hat{k} = \left[\hat{k}_0^{-1} + \frac{\lambda}{2} (e\Phi_{\text{ext}} + W) \right]^{-1}$$

where the internal field contribution is

$$\hat{k}_0 = \left[1 + \frac{\lambda}{2} e\Phi_{\text{int}} \right]^{-1}$$

and the convergence parameter is

$$\lambda = \frac{1}{m_0 c^2} \ll 1$$

The operator $\hat{k}$ can be expanded according to the identity fulfilled for any operators

$$(\hat{A} + \hat{B})^{-1} = \hat{A}^{-1} \sum_{n=0}^{\infty} (-\hat{B}\hat{A}^{-1})^n$$

so that we obtain an expansion where the operators occurring in the denominator have been transferred to the numerator

$$\hat{k} = \hat{k}_0 \sum_{n=0}^{\infty} \left[-\frac{\lambda}{2} (e\Phi_{\text{ext}} + W) \hat{k}_0 \right]^n$$

Inside this expression the commutation relations of individual terms hold true. The Dirac equation for the upper component spinor can be written in the form

$$\left\{ \frac{1}{2m_0} (\vec{\sigma} \cdot \vec{\pi}) \hat{k} (\vec{\sigma} \cdot \vec{\pi}) - (e\Phi_{\text{int}}) \mathbf{1} \right\} \Psi_u = (W + e\Phi_{\text{ext}}) \Psi_u$$

By substituting for $\hat{k}$ one gets

$$\begin{aligned} \hat{O} &= (\vec{\sigma} \cdot \vec{\pi}) \hat{k} (\vec{\sigma} \cdot \vec{\pi}) = (\vec{\sigma} \cdot \vec{\pi}) \hat{k}_0 \sum_{n=0}^{\infty} \left[-\frac{\lambda}{2} (e\Phi_{\text{ext}} + W) \hat{k}_0 \right]^n (\vec{\sigma} \cdot \vec{\pi}) \\ &= \sum_{n=0}^{\infty} \left(-\frac{\lambda}{2} \right)^n (\vec{\sigma} \cdot \vec{\pi}) (e\Phi_{\text{ext}} + W)^n \hat{k}_0^{n+1} (\vec{\sigma} \cdot \vec{\pi}) \end{aligned}$$

Then, using the commutator relations, all factors $(e\Phi_{\text{ext}} + W)$ can be moved to the right, which allows us to write

$$\hat{O} = \sum_{n=0}^{\infty} \hat{C}_n (e\Phi_{\text{ext}} + W)^n$$

The operators $\hat{C}_n$, independent of $(e\Phi_{\text{ext}} + W)$, are defined as coefficients of this expansion. Since the commutator corrections may contain additional factors proportional to λ , the new coefficients $\hat{C}_{nk}$ independent of λ can be introduced

$$\hat{C}_n = \sum_{k=n}^{\max(n)} \lambda^k \hat{C}_{nk}$$

The expressions for these coefficients are listed in Table 4.1. Equivalently, the factors $(e\Phi_{\text{ext}} + W)$ can be moved to the left

$$\hat{O} = \sum_{n=0}^{\infty} \sum_{k=n}^{\max(n)} \lambda^k (e\Phi_{\text{ext}} + W)^n (\hat{C}_{nk})^+$$

TABLE 4.1
Expansion coefficients $\hat{C}_{nk}$

n	k	$\hat{C}_{nk}$
0	0	$(\vec{\sigma} \cdot \vec{\pi}) \hat{k}_0 (\vec{\sigma} \cdot \vec{\pi})$
0	1	$\frac{i\hbar e}{2} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}_0^2 (\vec{\sigma} \cdot \vec{E}_{\text{ext}})$
0	2	$\frac{\hbar^2 e}{4} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}_0^3 (\vec{\sigma} \cdot \vec{E}_{\text{ext}})$
1	1	$-\frac{1}{2} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}_0^2 (\vec{\sigma} \cdot \vec{\pi})$
1	2	$-\frac{i\hbar e}{2} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}_0^3 (\vec{\sigma} \cdot \vec{E}_{\text{ext}})$
2	2	$\frac{1}{4} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}_0^3 (\vec{\sigma} \cdot \vec{\pi})$

The Hermiticity is guaranteed when working with half the sum at each order

$$\hat{O} = \frac{1}{2} \sum_{n=0}^{\infty} \sum_{k=n}^{\max(n)} \lambda^k [\hat{C}_{nk}(e\Phi_{\text{ext}} + W)^n + (e\Phi_{\text{ext}} + W)^n(\hat{C}_{nk})^+]$$

Using these expressions, the upper-component Dirac equation for stationary states can be written as

$$\left\{ \sum_{n=0}^{\infty} \sum_{k=n}^{\max(n)} \frac{\lambda^k}{4m_0} \left[(e\Phi_{\text{ext}} + W)^n (\hat{C}_{nk})^+ + (\hat{C}_{nk})(e\Phi_{\text{ext}} + W)^n \right] - (e\Phi_{\text{int}})\mathbf{1} \right\} \Psi_u = (W + e\Phi_{\text{ext}})\Psi_u$$

The Dirac Hamiltonian can be formally decomposed to the N th order terms

$$\hat{H}_D = \sum_{N=0} \hat{H}^{(N)}$$

and only the lowest order contributions are relevant since the rest is of the higher powers of $(1/c)$. These are

$$\begin{aligned} \hat{H}^{(0)} &= -e\Phi_{\text{int}} - e\Phi_{\text{ext}} + \frac{1}{2}[(\hat{C}_{00})^+ + \hat{C}_{00}] \\ &= -e\Phi + \frac{1}{2m_0}(\vec{\sigma} \cdot \vec{\pi})\hat{k}_0(\vec{\sigma} \cdot \vec{\pi}) \end{aligned}$$

and

$$\begin{aligned} \hat{H}^{(1)} &= \frac{i\hbar e}{8m_0^2 c^2} [(\vec{\sigma} \cdot \vec{\pi})\hat{k}_0^2(\vec{\sigma} \cdot \vec{E}_{\text{ext}}) - (\vec{\sigma} \cdot \vec{E}_{\text{ext}})\hat{k}_0^2(\vec{\sigma} \cdot \vec{\pi})] \\ &\quad - \frac{1}{16m_0^3 c^2} [(\vec{\sigma} \cdot \vec{\pi})\hat{k}_0(\vec{\sigma} \cdot \vec{\pi})^2\hat{k}_0^2(\vec{\sigma} \cdot \vec{\pi}) + (\vec{\sigma} \cdot \vec{\pi})\hat{k}_0^2(\vec{\sigma} \cdot \vec{\pi})^2\hat{k}_0(\vec{\sigma} \cdot \vec{\pi})] \\ &\quad + \frac{e}{8m_0^2 c^2} [\Phi(\vec{\sigma} \cdot \vec{\pi})\hat{k}_0^2(\vec{\sigma} \cdot \vec{\pi}) + (\vec{\sigma} \cdot \vec{\pi})\hat{k}_0^2(\vec{\sigma} \cdot \vec{\pi})\Phi] \end{aligned}$$

In transferring all the $\hat{k}_0$ operators to the far right or the far left the following commutator relation is useful

$$\hat{k}_0(\vec{\sigma} \cdot \vec{\pi}) - (\vec{\sigma} \cdot \vec{\pi})\hat{k}_0 = \frac{i\hbar e}{2m_0 c^2} \hat{k}_0^2(\vec{\sigma} \cdot \vec{E}_{\text{int}})$$

The application to the $\hat{H}^{(0)}$ yields

$$\begin{aligned}\hat{H}^{(0)} = & -e\Phi \\ & + \frac{1}{4m_0} \{(\vec{\sigma} \cdot \vec{\pi})[(\vec{\sigma} \cdot \vec{\pi})\hat{k}_0 + \frac{i\hbar e}{2m_0 c^2} \hat{k}_0^2(\vec{\sigma} \cdot \vec{E}_{\text{int}})] \\ & + [\hat{k}_0(\vec{\sigma} \cdot \vec{\pi}) - \frac{i\hbar e}{2m_0 c^2} \hat{k}_0^2(\vec{\sigma} \cdot \vec{E}_{\text{int}})](\vec{\sigma} \cdot \vec{\pi})\}\end{aligned}$$

$$\begin{aligned}\hat{H}^{(0)} = & -e\Phi \\ & + \frac{1}{4m_0} [\hat{k}_0(\vec{\sigma} \cdot \vec{\pi})^2 + (\vec{\sigma} \cdot \vec{\pi})^2 \hat{k}_0] \\ & - \frac{i\hbar e}{8m_0^2 c^2} [\hat{k}_0^2(\vec{\sigma} \cdot \vec{E}_{\text{int}})(\vec{\sigma} \cdot \vec{\pi}) - (\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{E}_{\text{int}})\hat{k}_0^2]\end{aligned}$$

The last term can be combined with the first term of $\hat{H}^{(1)}$ to yield a term containing the total electric field strength $\vec{E} = \vec{E}_{\text{int}} + \vec{E}_{\text{ext}}$. The commutator corrections from terms in $\hat{H}^{(1)}$ are much smaller (of the order $1/c^4$) and are thus neglected, so that $\hat{k}_0$ is simply shifted either to the far left or the far right. The final relativistic one-electron Hamiltonian terms are collected in Table 4.2.

TABLE 4.2
Relativistic one-electron Hamiltonian terms

	Hamiltonian term
$\hat{H}^{0a}$	$-e\Phi$
$\hat{H}^{0b}$	$\frac{1}{4m_0} [\hat{k}_0(\vec{\sigma} \cdot \vec{\pi})^2 + (\vec{\sigma} \cdot \vec{\pi})^2 \hat{k}_0]$
$\hat{H}^{0c}$	$-\frac{i\hbar e}{8m_0^2 c^2} [\hat{k}_0^2(\vec{\sigma} \cdot \vec{E}_{\text{int}})(\vec{\sigma} \cdot \vec{\pi}) - (\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{E}_{\text{int}})\hat{k}_0^2]$
$\hat{H}^{1a}$	$-\frac{i\hbar e}{8m_0^2 c^2} [\hat{k}_0^2(\vec{\sigma} \cdot \vec{E}_{\text{ext}})(\vec{\sigma} \cdot \vec{\pi}) - (\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{E}_{\text{ext}})\hat{k}_0^2]$
$\hat{H}^{1b}$	$-\frac{1}{16m_0^3 c^2} [\hat{k}_0^3(\vec{\sigma} \cdot \vec{\pi})^4 + (\vec{\sigma} \cdot \vec{\pi})^4 \hat{k}_0^3]$
$\hat{H}^{1c}$	$\frac{e}{8m_0^2 c^2} [\hat{k}_0^2 \Phi(\vec{\sigma} \cdot \vec{\pi})^2 + (\vec{\sigma} \cdot \vec{\pi})^2 \Phi \hat{k}_0^2]$

The terms of each order are Hermitian, independent of the energy W , and do not lead to divergent integrals.

The Hamiltonian terms just derived, albeit through a rigorous treatment, are rather far from practical utilisation. For such a purpose we need to specify the components of the electromagnetic field in more detail. Since we are interested in molecular systems, the internal fields under consideration are:

(a) the nuclear Coulomb (scalar) potential

$$\Phi_{\text{int}} = \sum_N \Phi_N$$

with the single nucleus contribution

$$\Phi_N = \frac{e}{4\pi\epsilon_0} \frac{Z_N}{r_{Ne}}$$

where the electron–nuclear distance is $r_{Ne} = |\vec{r}_{Ne}| = |\vec{r}_e - \vec{r}_N|$;

(b) the internal electric field strength

$$\vec{E}_{\text{int}} = \sum_N \vec{E}_N = -\vec{\nabla}\Phi_{\text{int}} = -\sum_N \vec{\nabla}\Phi_N$$

with

$$\vec{E}_N = -\vec{\nabla}\Phi_N = \frac{e}{4\pi\epsilon_0} \frac{Z_N}{r_{Ne}^3} \vec{r}_{Ne}$$

(c) the internal vector potential arising from the nuclear magnetic moments $\vec{\mu}_N$

$$\vec{A}_{\text{int}} = \sum_N \vec{A}_N$$

with

$$\vec{A}_N = \frac{\mu_0}{4\pi} \frac{1}{r_{Ne}^3} (\vec{\mu}_N \times \vec{r}_{Ne})$$

(d) the internal magnetic induction

$$\vec{B}_{\text{int}} = \sum_N \vec{B}_N$$

with

$$\vec{B}_N = \frac{\mu_0}{4\pi} \left[-\frac{1}{r_{Ne}^3} \vec{\mu}_N + 3 \frac{1}{r_{Ne}^5} (\vec{\mu}_N \cdot \vec{r}_{Ne}) \vec{r}_{Ne} \right]$$

(e) the external vector potential

$$\vec{A}_{\text{ext}} = \frac{1}{2} (\vec{B}_{\text{ext}} \times \vec{r}_{Ge})$$

where the position of the electron is measured relative to a gauge origin, i.e. $\vec{r}_{Ge} = \vec{r}_e - \vec{G}$.

Under these assumptions the individual Hamiltonian terms can be discussed as follows. The term

$$\hat{H}^{0a} = -e\Phi = -e\Phi_{\text{ext}} - \sum_N \frac{e^2}{4\pi\epsilon_0} \frac{Z_N}{r_{Ne}}$$

contains the interaction with the external electric field as well as the well known *electron–nuclear attraction* present in the non-relativistic Hamiltonian.

The Hamiltonian term, $\hat{H}^{0b}$, after expanding

$$(\vec{\sigma} \cdot \vec{\pi})^2 = (\vec{\pi} \cdot \vec{\pi}) + i\vec{\sigma} \cdot (\vec{\pi} \times \vec{\pi}) = (\vec{p} + e\vec{A})^2 + e\hbar\vec{\sigma} \cdot \vec{B}$$

brings the following contributions

$$\hat{H}^{0b}(1) = \frac{1}{4m_0} [\hat{k}_0 \hat{p}^2 + \hat{p}^2 \hat{k}_0]$$

$$\hat{H}^{0b}(2) = \frac{e}{4m_0} [\hat{k}_0 (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) \hat{k}_0]$$

$$\hat{H}^{0b}(3) = \frac{e^2}{2m_0} \hat{k}_0 \vec{A}^2$$

$$\hat{H}^{0b}(4) = \frac{e\hbar}{2m_0} \hat{k}_0 \vec{\sigma} \cdot \vec{B}$$

In treating the effect of $\hat{k}_0$ let us reconsider its definition

$$\hat{k}_0 = \frac{1}{1 + \hat{\eta}}$$

with

$$\hat{\eta} = \frac{e}{2m_0c^2} \Phi_{\text{int}}$$

from which

$$\hat{k}_0(1 + \hat{\eta}) = 1$$

and hence a recurrence formula results

$$\hat{k}_0^{(i+1)} = 1 - \hat{\eta}\hat{k}_0^{(i)}$$

Alternatively, one can apply the operator identity

$$\frac{1}{1 + \hat{\eta}} = \sum_{n=0}^{\infty} (-\hat{\eta})^n$$

This series is strongly convergent for $\hat{\eta} \ll 1$ so that only the lowest two terms are relevant. However, for $\hat{\eta} \gg 1$ the expansion is divergent but $\hat{k}_0$ approaches zero.

A substitution for $\hat{k}_0 = 1 - \hat{\eta}\hat{k}_0$ into $\hat{H}^{0b}(1)$ yields

$$\hat{H}^{0b}(1) = \frac{1}{2m_0} \hat{p}^2 - \frac{e}{8m_0^2c^2} (\hat{k}_0 \Phi_{\text{int}} \hat{p}^2 + \hat{p}^2 \Phi_{\text{int}} \hat{k}_0)$$

Here the first term is the *non-relativistic kinetic energy*. The second term, hereafter $\hat{H}^{0b}(1^*)$, is transferred to the higher order of $(1/c)$ and will be discussed later.

The contribution $\hat{H}^{0b}(2)$ contains the products

$$\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} = 2\vec{A} \cdot \vec{p} - i\hbar \vec{\nabla} \cdot \vec{A}$$

in which the last term, under the assumption of the Coulomb gauge ($\vec{\nabla} \cdot \vec{A} = 0$), vanishes. The vector potential, however, consists of internal and external contributions

$$\vec{A} = \vec{A}_{\text{ext}} + \vec{A}_{\text{int}} = \vec{A}_{\text{ext}} + \sum_N \vec{A}_N$$

The external field brings an effect of

$$\vec{A}_{\text{ext}} \cdot \vec{p} = \frac{1}{2}(\vec{B}_{\text{ext}} \times \vec{r}_{Ge}) \cdot \vec{p} = \frac{1}{2}(\vec{B}_{\text{ext}} \cdot \vec{l}_{Ge})$$

and the Hamiltonian contribution, after the application of $\hat{k}_0$, is

$$\hat{H}^{0b}(2a) = \frac{e}{2m_0}(\vec{B}_{\text{ext}} \cdot \vec{l}_{Ge}) - \frac{e^2}{8m_0^2c^2}[\hat{k}_0\Phi_{\text{int}}(\vec{B}_{\text{ext}} \cdot \vec{l}_{Ge}) + (\vec{B}_{\text{ext}} \cdot \vec{l}_{Ge})\Phi_{\text{int}}\hat{k}_0]$$

The first product is the *orbital Zeeman term*. The second term is a higher-order correction in which a commutation relation can be used

$$[\vec{l}_{Ge}, \hat{k}_0] = -\frac{i\hbar e}{2m_0c^2}\hat{k}_0^3(\vec{r}_{Ge} \times \vec{E}_{\text{int}})$$

The internal (dipolar) field brings an effect of

$$\vec{A}_N \cdot \vec{p} = \frac{\mu_0}{4\pi} \frac{1}{r_{Ne}^3}(\vec{\mu}_N \times \vec{r}_{Ne}) \cdot \vec{p} = \frac{\mu_0}{4\pi} \frac{1}{r_{Ne}^3}(\vec{\mu}_N \cdot \vec{l}_{Ne})$$

and the Hamiltonian contribution $\hat{H}_N^{0b}(2b)$ is

$$\begin{aligned} \hat{H}_N^{0b}(2b) &= \frac{e}{2m_0}[\hat{k}_0(\vec{A}_N \cdot \vec{p}) + (\vec{A}_N \cdot \vec{p})\hat{k}_0] \\ &= \frac{\mu_0}{4\pi} \frac{e}{2m_0} \left[\hat{k}_0 \frac{1}{r_{Ne}^3}(\vec{\mu}_N \cdot \vec{l}_{Ne}) + \frac{1}{r_{Ne}^3}(\vec{\mu}_N \cdot \vec{l}_{Ne})\hat{k}_0 \right] \end{aligned}$$

Since the nuclear magnetic moments are small in magnitude, the corrections arising from the commutator relations can be neglected. However, it is convenient to retain $\hat{k}_0$ as a convergence factor so that we arrive at the *orbital hyperfine interaction* in the form

$$\hat{H}_N^{0b}(2b) = \frac{\mu_0}{4\pi} \frac{e}{m_0} \hat{k}_0 \frac{1}{r_{Ne}^3}(\vec{\mu}_N \cdot \vec{l}_{Ne})$$

The Hamiltonian term $\hat{H}^{0b}(3)$ contains contributions from

$$\vec{A}^2 = \vec{A}_{\text{ext}}^2 + 2 \sum_N \vec{A}_{\text{ext}} \cdot \vec{A}_N + \sum_N \sum_M \vec{A}_N \cdot \vec{A}_M$$

The term involving only the external field is

$$\hat{H}^{0b}(3a) = \frac{e^2}{2m_0} \hat{k}_0 \vec{A}_{\text{ext}}^2 = \frac{e^2}{2m_0} \vec{A}_{\text{ext}}^2 - \frac{e^3}{8m_0^2 c^2} (\hat{k}_0 \Phi_{\text{int}} \vec{A}_{\text{ext}}^2 + \vec{A}_{\text{ext}}^2 \Phi_{\text{int}} \hat{k}_0)$$

The first contribution is simply the *diamagnetic term*

$$\hat{H}^{0b}(3a') = \frac{e^2}{2m_0} \vec{A}_{\text{ext}}^2 = \frac{e^2}{8m_0} [B_{\text{ext}}^2 r_{Ge}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Ge})^2]$$

The second contribution, arising when $\hat{k}_0$ is transferred to a higher order, is thought to be negligible and will be treated later

$$\hat{H}_N^{0b}(3a'') = -\frac{e^3}{8m_0^2 c^2} (\hat{k}_0 \Phi_N \vec{A}_{\text{ext}}^2 + \vec{A}_{\text{ext}}^2 \Phi_N \hat{k}_0)$$

The term involving both the external field and the internal (dipolar) field is the *electron–nuclear Zeeman correction*

$$\begin{aligned} \hat{H}_N^{0b}(3b) &= \frac{e^2}{m_0} \hat{k}_0 (\vec{A}_{\text{ext}} \cdot \vec{A}_N) \\ &= \frac{\mu_0}{4\pi} \frac{e^2}{2m_0} \hat{k}_0 r_{Ne}^{-3} [(\vec{B}_{\text{ext}} \cdot \vec{\mu}_N)(\vec{r}_{Ge} \cdot \vec{r}_{Ne}) - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Ne})(\vec{r}_{Ge} \cdot \vec{\mu}_N)] \end{aligned}$$

The last term involving two nuclear dipolar fields is the *electron coupled nuclear spin–spin interaction*

$$\begin{aligned} \hat{H}_{NM}^{0b}(3c) &= \frac{e^2}{2m_0} \hat{k}_0 (\vec{A}_N \cdot \vec{A}_M) \\ &= \left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^2}{2m_0} \hat{k}_0 r_{Ne}^{-3} r_{Me}^{-3} [(\vec{\mu}_N \cdot \vec{\mu}_M)(\vec{r}_{Ne} \cdot \vec{r}_{Me}) \\ &\quad - (\vec{\mu}_N \cdot \vec{r}_{Me})(\vec{\mu}_M \cdot \vec{r}_{Ne})] \end{aligned}$$

This term is counted for $M < N$, $M > N$ (where it is convergent) as well as for $M = N$ (where, however, it is divergent).

In the above terms $\hat{H}_N^{0b}(2b)$, $\hat{H}_N^{0b}(3b)$ and $\hat{H}_{NM}^{0b}(3c)$ the effect of $\hat{k}_0$ improves the convergence of integrals. In the vicinity of the N th nucleus the internal scalar field behaves effectively as $\Phi_{\text{int}} = (e/4\pi\epsilon_0) Z_N r_{Ne}^{-1}$. Therefore for small distances r_{Ne} the operator $\hat{k}_0$ is proportional to r_{Ne} and the product $\hat{k}_0 r_{Ne}^{-3}$ reduces to r_{Ne}^{-2} so that the integrals present no problem. For two dipolar fields

the single $\hat{k}_0$ factor is still not capable of securing the convergence because the overall behaviour near the nucleus is like r_{Ne}^{-3} and the integrals will diverge.

The Hamiltonian term $\hat{H}^{0b}(4)$ can be split into two contributions. The first arises from the external magnetic field and is the *Zeeman term*

$$\hat{H}^{0b}(4a) = \frac{e\hbar}{2m_0} (\vec{\sigma} \cdot \vec{B}_{\text{ext}})$$

The effect of $\hat{k}_0$ is transferred to a higher order where it is negligible. The second contribution involves the internal (dipolar) magnetic field and represents the *dipolar hyperfine interaction term*

$$\begin{aligned} \hat{H}_N^{0b}(4b) &= \frac{e\hbar}{2m_0} \hat{k}_0 (\vec{\sigma} \cdot \vec{B}_{\text{int}}) \\ &= -\frac{\mu_0}{4\pi} \frac{e\hbar}{2m_0} \hat{k}_0 r_{Ne}^{-5} [r_{Ne}^2 (\vec{\sigma} \cdot \vec{\mu}_N) - 3(\vec{\sigma} \cdot \vec{r}_{Ne})(\vec{\mu}_N \cdot \vec{r}_{Ne})] \end{aligned}$$

For a vanishing electron–nuclear distance we would expect an appearance of the Fermi contact term. However, due to the presence of $\hat{k}_0$, such a term disappears

$$\lim_{r(N_e) \rightarrow 0} \hat{H}_N^{0b}(4b) = 0$$

We will see later that the Fermi contact term follows from another Hamiltonian term.

The Hamiltonian terms $\hat{H}^{1a} + \hat{H}^{0c}$, after expanding the operator $\vec{\pi} = \vec{p} + e\vec{A}$, are manipulated using the identity

$$(\vec{\sigma} \cdot \vec{X})(\vec{\sigma} \cdot \vec{Y}) = \vec{X} \cdot \vec{Y} + i\vec{\sigma} \cdot (\vec{X} \times \vec{Y})$$

In particular

$$\begin{aligned} (\vec{\sigma} \cdot \vec{E})(\vec{\sigma} \cdot \vec{\pi}) &= \vec{E} \cdot \vec{\pi} + i\vec{\sigma} \cdot (\vec{E} \times \vec{\pi}) \\ &= \vec{E} \cdot \vec{p} + e\vec{E} \cdot \vec{A} + i\vec{\sigma} \cdot (\vec{E} \times \vec{p}) + ie\vec{\sigma} \cdot (\vec{E} \times \vec{A}) \\ (\vec{\sigma} \cdot \vec{\pi})(\vec{\sigma} \cdot \vec{E}) &= \vec{\pi} \cdot \vec{E} + i\vec{\sigma} \cdot (\vec{\pi} \times \vec{E}) \\ &= \vec{p} \cdot \vec{E} + e\vec{A} \cdot \vec{E} + i\vec{\sigma} \cdot (\vec{p} \times \vec{E}) + ie\vec{\sigma} \cdot (\vec{A} \times \vec{E}) \end{aligned}$$

Notice the action of the differential operator $\vec{p} = -i\hbar\vec{\nabla}$

$$\vec{p} \cdot \vec{E}\Psi = \vec{E} \cdot (\vec{p}\Psi) + \Psi(\vec{p} \cdot \vec{E}) = \vec{E} \cdot (\vec{p}\Psi) - i\hbar\Psi(\vec{\nabla} \cdot \vec{E})$$

A combination of these expressions leads to the following contributions

$$\hat{H}^{1a}(1) = -\frac{i\hbar e}{8m_0^2 c^2} [\hat{k}_0^2 (\vec{E} \cdot \vec{p}) - (\vec{E} \cdot \vec{p}) \hat{k}_0^2]$$

$$\hat{H}^{1a}(2) = \frac{\hbar^2 e}{8m_0^2 c^2} \hat{k}_0^2 (\vec{\nabla} \cdot \vec{E})$$

$$\hat{H}^{1a}(3) = \frac{\hbar e}{8m_0^2 c^2} [\hat{k}_0^2 \vec{\sigma} \cdot (\vec{E} \times \vec{p}) - \vec{\sigma} \cdot (\vec{p} \times \vec{E}) \hat{k}_0^2]$$

$$\hat{H}^{1a}(4) = -\frac{i\hbar e^2}{8m_0^2 c^2} [\hat{k}_0^2 (\vec{E} \cdot \vec{A}) - (\vec{E} \cdot \vec{A}) \hat{k}_0^2] \equiv 0$$

$$\hat{H}^{1a}(5) = \frac{\hbar e^2}{8m_0^2 c^2} [\hat{k}_0^2 \vec{\sigma} \cdot (\vec{E} \times \vec{A}) - \vec{\sigma} \cdot (\vec{A} \times \vec{E}) \hat{k}_0^2]$$

The term $\hat{H}^{1a}(1)$ can be rewritten when one effect of $\hat{k}_0 = (1 - \hat{\eta})$ is considered, with $\hat{\eta} = (e/2m_0 c^2) \Phi_{\text{int}}$, as follows

$$\begin{aligned} \hat{H}^{1a}(1) &= -\frac{i\hbar e}{8m_0^2 c^2} [\hat{k}_0 (1 - \hat{\eta}) (\vec{E} \cdot \vec{p}) - (\vec{E} \cdot \vec{p}) (1 - \hat{\eta}) \hat{k}_0] \\ &= -\frac{i\hbar e}{8m_0^2 c^2} [\hat{k}_0 (\vec{E} \cdot \vec{p}) - \hat{k}_0 \hat{\eta} (\vec{E} \cdot \vec{p}) - (\vec{E} \cdot \vec{p}) \hat{k}_0 + (\vec{E} \cdot \vec{p}) \hat{\eta} \hat{k}_0] \\ &\approx \frac{i\hbar e}{8m_0^2 c^2} [(\vec{E} \cdot \vec{p}), \hat{k}_0] \end{aligned}$$

The surviving commutator is

$$\begin{aligned} [(\vec{E} \cdot \vec{p}), \hat{k}_0] &= \hat{k}_0 [\hat{k}_0^{-1}, (\vec{E} \cdot \vec{p})] \hat{k}_0 = -\frac{e}{2m_0 c^2} \hat{k}_0^2 [\Phi_{\text{int}}, (\vec{E} \cdot \vec{p})] \\ &= \frac{e}{2m_0 c^2} \hat{k}_0^2 \vec{E} \cdot [\vec{p}, \Phi_{\text{int}}] = \frac{i\hbar e}{2m_0 c^2} \hat{k}_0^2 \vec{E} \cdot [-\vec{\nabla}, \Phi_{\text{int}}] \\ &= \frac{i\hbar e}{2m_0 c^2} \hat{k}_0^2 \vec{E} \cdot \vec{E}_{\text{int}} \end{aligned}$$

so that we arrive at the result

$$\hat{H}^{1a}(1) = \frac{\hbar^2 e^2}{16m_0^3 c^4} \hat{k}_0^2 (\vec{E} \cdot \vec{E}_{\text{int}})$$

Despite the low order of $(1/c^4)$ this term may contribute in the vicinity of the nucleus. For the Coulomb field due to the nuclei

$$\Phi_N = \frac{e}{4\pi\epsilon_0} \frac{Z_N}{r_{Ne}}$$

$$\vec{E}_N = -\vec{\nabla}\Phi_N = \frac{e}{4\pi\epsilon_0} \frac{Z_N}{r_{Ne}^3} \vec{r}_{Ne}$$

the scalar product of the electric field strengths is

$$\vec{E} \cdot \vec{E}_{\text{int}} \approx \vec{E}_N \cdot \vec{E}_N = \left(\frac{e}{4\pi\epsilon_0} \right)^2 \frac{Z_N^2}{r_{Ne}^4}$$

The Hamiltonian term

$$\hat{H}_N^{1a}(1) = \frac{\hbar^2 e^2}{8m_0^2 c^2} \frac{Z_N}{4\pi\epsilon_0} F(r_{Ne})$$

involves the function

$$F(r) = \frac{C}{\left(1 + \frac{C}{r}\right)^2 r^4}$$

with

$$C = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2m_0 c^2} Z_N$$

Such a function can be integrated in polar coordinates as

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} F(r) r^2 dr \sin \vartheta d\vartheta d\varphi = 4\pi \int_0^\infty F(r) r^2 dr$$

For $r \gg C$ the integral presents no problem and, owing to a small coefficient, the result can be neglected. For $r \ll C$, however, there is a near-singularity of the integrand which behaves like a Dirac “delta” function $\delta(r)$. Clearly it holds true that

$$\frac{d}{dr} \left(\frac{1}{1 + C/r} \right) = \frac{C/r^2}{(1 + C/r)^2} = F(r)r^2$$

and consequently the integral is

$$I = 4\pi \int_0^\infty F(r)r^2 dr = 4\pi \frac{1}{1 + C/r} \Big|_0^\infty = 4\pi$$

Using these expressions, the Hamiltonian term becomes the *Darwin term*

$$\hat{H}_N^{1a}(1) = \frac{\hbar^2 e^2}{8m_0^2 c^2} \frac{1}{4\pi\epsilon_0} Z_N 4\pi\delta(\vec{r}_{Ne}) = \frac{\hbar^2 e^2}{8\epsilon_0 m_0^2 c^2} Z_N \delta(\vec{r}_{Ne})$$

This term is a correction to the interaction of the charge of an electron with an electric field due to the “Zitterbewegung”—a trembling motion (a highly oscillatory part of the motion with a frequency of the order $2m_0c^2/\hbar$ and an amplitude of the order $\hbar/m_0c$).

In the Hamiltonian term $\hat{H}^{1a}(2)$ for the Coulomb field

$$\vec{E}_N = -\vec{\nabla}\Phi_N = -\frac{eZ_N}{4\pi\epsilon_0} \vec{\nabla}(r_{Ne}^{-1})$$

the divergence of the electric field strength results in the Dirac function

$$\vec{\nabla} \cdot \vec{E}_N = -\frac{eZ_N}{4\pi\epsilon_0} \vec{\nabla} \cdot (\vec{\nabla} r_{Ne}^{-1}) = -\frac{eZ_N}{4\pi\epsilon_0} (-4\pi)\delta(\vec{r}_{Ne})$$

and one would expect

$$\hat{H}_N^{1a}(2) = \frac{\hbar^2 e}{8m_0^2 c^2} \hat{k}_0^2 (\vec{\nabla} \cdot \vec{E}_N) = \frac{\hbar^2 e^2}{8\epsilon_0 m_0^2 c^2} Z_N \hat{k}_0^2 \delta(\vec{r}_{Ne})$$

As an effect of $\hat{k}_0$, however, this term vanishes ($\hat{k}_0 = 0$ for $r_{Ne} = 0$).

The Hamiltonian term $\hat{H}^{1a}(3)$ contains a vector product for which the following formula is applicable

$$\vec{\nabla} \times \vec{X}\phi = (\vec{\nabla} \times \vec{X})\phi + \phi(\vec{\nabla} \times \vec{X})$$

In fact

$$\vec{\nabla} \times \vec{E}\hat{k}_0^2 = (\vec{\nabla} \times \vec{E})\hat{k}_0^2 + \hat{k}_0^2(\vec{\nabla} \times \vec{E})$$

or

$$-i\hbar\vec{\nabla} \times \vec{E}\hat{k}_0^2 = (\vec{p} \times \vec{E})\hat{k}_0^2 + \hat{k}_0^2(\vec{p} \times \vec{E})$$

The expression on the left vanishes since it is the rotation of a gradient

$$\vec{\nabla} \times \vec{E}\hat{k}_0^2 = -\vec{\nabla} \times (\vec{\nabla}\Phi)\hat{k}_0^2 = -\text{rot}(\text{grad}\Phi)\hat{k}_0^2 = 0$$

Consequently the Hamiltonian term $\hat{H}^{1a}(3)$ becomes

$$\hat{H}^{1a}(3) = \frac{\hbar e}{4m_0^2 c^2} \hat{k}_0^2 \vec{\sigma} \cdot (\vec{E} \times \vec{p})$$

and for the Coulomb field

$$\vec{E}_N = \frac{e}{4\pi\epsilon_0} Z_N r_{Ne}^{-3} \vec{r}_{Ne}$$

this is the *spin-orbit interaction* term

$$\begin{aligned} \hat{H}_N^{1a}(3) &= \frac{1}{4\pi\epsilon_0} \frac{\hbar e^2}{4m_0^2 c^2} Z_N \hat{k}_0^2 r_{Ne}^{-3} \vec{\sigma} \cdot (\vec{r}_{Ne} \times \vec{p}) \\ &= \frac{\hbar e^2}{16\pi\epsilon_0 m_0^2 c^2} Z_N \hat{k}_0^2 r_{Ne}^{-3} (\vec{\sigma} \cdot \vec{l}_{Ne}) \end{aligned}$$

The Hamiltonian term $\hat{H}^{1a}(4)$ equals zero because all the operators involved ($\vec{E}, \vec{A}, \hat{k}_0$) commute.

In the Hamiltonian term $\hat{H}^{1a}(5)$ the vector product alters the sign when the factors are reversed and thus the two contributions are equivalent

$$\hat{H}^{1a}(5) = \frac{\hbar e^2}{4m_0^2 c^2} \hat{k}_0^2 \vec{\sigma} \cdot (\vec{E} \times \vec{A})$$

For an external magnetic field $\vec{A}_{\text{ext}} = (1/2)(\vec{B}_{\text{ext}} \times \vec{r}_{Ge})$ and a Coulomb field we have

$$\begin{aligned} \hat{H}_N^{1a}(5a) &= \frac{\hbar e^2}{4m_0^2 c^2} \hat{k}_0^2 \vec{\sigma} \cdot (\vec{E}_N \times \vec{A}_{\text{ext}}) \\ &= \frac{1}{4\pi\epsilon_0} \frac{\hbar e^3}{8m_0^2 c^2} Z_N \hat{k}_0^2 r_{Ne}^{-3} \vec{\sigma} \cdot [\vec{r}_{Ne} \times (\vec{B}_{\text{ext}} \times \vec{r}_{Ge})] \end{aligned}$$

Using the vector identity

$$\vec{A} \times (\vec{B} \times \vec{C}) = (\vec{A} \cdot \vec{C})\vec{B} - (\vec{A} \cdot \vec{B})\vec{C}$$

the *spin-orbit Zeeman gauge correction* results in the form of

$$\hat{H}_N^{1a}(5a) = \frac{1}{4\pi\epsilon_0} \frac{\hbar e^3}{8m_0^2 c^2} Z_N \hat{k}_0^2 r_{Ne}^{-3} [(\vec{r}_{Ne} \cdot \vec{r}_{Ge})(\vec{\sigma} \cdot \vec{B}_{ext}) - (\vec{\sigma} \cdot \vec{r}_{Ge})(\vec{r}_{Ne} \cdot \vec{B}_{ext})]$$

For the second possibility, when the internal (dipolar) magnetic field

$$\vec{A}_N = \frac{\mu_0}{4\pi} r_{Ne}^{-3} (\vec{\mu}_N \times \vec{r}_{Ne})$$

is involved, we get the *spin-orbit hyperfine correction*

$$\begin{aligned} \hat{H}_{NM}^{1a}(5b) &= \frac{\hbar e^2}{4m_0^2 c^2} \hat{k}_0^2 \vec{\sigma} \cdot (\vec{E}_M \times \vec{A}_N) \\ &= \frac{\mu_0}{4\pi} \frac{1}{4\pi\epsilon_0} \frac{\hbar e^3}{4m_0^2 c^2} Z_M [\hat{k}_0(r_{Me})]^2 r_{Ne}^{-3} r_{Me}^{-3} \vec{\sigma} \cdot [\vec{r}_{Me} \times (\vec{\mu}_N \times \vec{r}_{Ne})] \\ &= \frac{\mu_0}{4\pi} \frac{1}{4\pi\epsilon_0} \frac{\hbar e^3}{4m_0^2 c^2} Z_M [\hat{k}_0(r_{Me})]^2 r_{Ne}^{-3} r_{Me}^{-3} [(\vec{r}_{Ne} \cdot \vec{r}_{Me})(\vec{\sigma} \cdot \vec{\mu}_N) \\ &\quad - (\vec{\sigma} \cdot \vec{r}_{Ne})(\vec{\mu}_N \cdot \vec{r}_{Me})] \end{aligned}$$

This term represents a higher-order correction which can be neglected (because of a small coefficient) except in the case when $\vec{r}_{Ne} = 0$ for $N = M$. Then the operator can be arranged as follows

$$\begin{aligned} \hat{H}_{NN}^{1a}(5b) &= \frac{\mu_0}{4\pi} \frac{1}{4\pi\epsilon_0} \frac{\hbar e^3}{4m_0^2 c^2} Z_N [\hat{k}_0(r_{Ne})]^2 r_{Ne}^{-4} [(\vec{\sigma} \cdot \vec{\mu}_N) \\ &\quad - r_{Ne}^{-2} (\vec{\sigma} \cdot \vec{r}_{Ne})(\vec{\mu}_N \cdot \vec{r}_{Ne})] \end{aligned}$$

and one can use its expression through irreducible tensor components

$$\begin{aligned} &(\vec{\sigma} \cdot \vec{\mu}_N) - r_{Ne}^{-2} (\vec{\sigma} \cdot \vec{r}_{Ne})(\vec{\mu}_N \cdot \vec{r}_{Ne}) \\ &= \frac{2}{3} (\vec{\sigma} \cdot \vec{\mu}_N) + \left[\frac{1}{3} (\vec{\sigma} \cdot \vec{\mu}_N) - r_{Ne}^{-2} (\vec{\sigma} \cdot \vec{r}_{Ne})(\vec{\mu}_N \cdot \vec{r}_{Ne}) \right] \\ &= \sum_a \sum_b \sigma_a T_{ab}^{(0)} \mu_{Nb} + \sum_a \sum_b \sigma_a T_{ab}^{(2)} \mu_{Nb} \end{aligned}$$

For the spherically symmetric $T^{(0)}$ component and a Coulomb field we have

$$\begin{aligned}\hat{H}_{NN}^{1a}(5b') &= \frac{\mu_0}{4\pi} \frac{1}{4\pi\epsilon_0} \frac{\hbar e^3}{4m_0^2 c^2} Z_N \frac{1}{\left(1 + \frac{c}{r_{Ne}}\right)^2} \frac{2}{3} r_{Ne}^{-4} (\vec{\sigma} \cdot \vec{\mu}_N) \\ &= \frac{\mu_0}{4\pi} \frac{\hbar e}{2m_0} \frac{2}{3} F(r_{Ne}) (\vec{\sigma} \cdot \vec{\mu}_N)\end{aligned}$$

where the identical function $F(r)$ has been introduced as in the derivation of $\hat{H}_N^{1a}(1)$. Since $F(r_{Ne}) = 4\pi\delta(r_{Ne})$, we have arrived at the *Fermi contact hyperfine term*

$$\hat{H}_{NN}^{1a}(5b') = \frac{\mu_0}{4\pi} \frac{\hbar e}{2m_0} \frac{8\pi}{3} \delta(r_{Ne}) (\vec{\sigma} \cdot \vec{\mu}_N)$$

The $T^{(2)}$ component can be integrated without difficulty and exhibits no singularities. The result will be negligible because of the small coefficient.

The Hamiltonian term $\hat{H}^{1b}$ contains the scalar product expanded as

$$\begin{aligned}(\vec{\sigma} \cdot \vec{\pi})^4 &= [\hat{p}^2 + e(\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) + e^2 \vec{A}^2 + e\hbar \vec{\sigma} \cdot \vec{B}] \\ &\quad [\hat{p}^2 + e(\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) + e^2 \vec{A}^2 + e\hbar \vec{\sigma} \cdot \vec{B}]\end{aligned}$$

leading to the following contributions

$$\hat{H}^{1b}(1) = -\frac{1}{16m_0^3 c^2} \{\hat{k}_0^3 \hat{p}^4 + \hat{p}^4 \hat{k}_0^3\}$$

$$\begin{aligned}\hat{H}^{1b}(2) &= -\frac{e}{16m_0^3 c^2} \{\hat{k}_0^3 [\hat{p}^2 (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) + (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) \hat{p}^2] \\ &\quad + [\hat{p}^2 (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) + (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) \hat{p}^2] \hat{k}_0^3\}\end{aligned}$$

$$\hat{H}^{1b}(3) = -\frac{e^2}{16m_0^3 c^2} \{\hat{k}_0^3 [\hat{p}^2 \vec{A}^2 + \vec{A}^2 \hat{p}^2] + [\hat{p}^2 \vec{A}^2 + \vec{A}^2 \hat{p}^2] \hat{k}_0^3\}$$

$$\hat{H}^{1b}(4) = -\frac{e\hbar}{16m_0^3 c^2} \{\hat{k}_0^3 [\hat{p}^2 (\vec{B} \cdot \vec{\sigma}) + (\vec{B} \cdot \vec{\sigma}) \hat{p}^2] + [\hat{p}^2 (\vec{B} \cdot \vec{\sigma}) + (\vec{B} \cdot \vec{\sigma}) \hat{p}^2] \hat{k}_0^3\}$$

$$\hat{H}^{1b}(5) = -\frac{e^2}{16m_0^3 c^2} \{\hat{k}_0^3 [(\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A})^2 + (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A})^2] \hat{k}_0^3\}$$

$$\hat{H}^{1b}(6) = -\frac{e^3}{16m_0^3c^2} \{ \hat{k}_0^3 [\vec{A}^2 (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) + (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) \vec{A}^2] \\ + [\vec{A}^2 (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) + (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) \vec{A}^2] \hat{k}_0^3 \}$$

$$\hat{H}^{1b}(7) = -\frac{e^4}{16m_0^3c^2} \{ \hat{k}_0^3 \vec{A}^4 + \vec{A}^4 \hat{k}_0^3 \}$$

$$\hat{H}^{1b}(8) = -\frac{e^3\hbar}{16m_0^3c^2} \{ \hat{k}_0^3 [\vec{A}^2 (\vec{B} \cdot \vec{\sigma}) + (\vec{B} \cdot \vec{\sigma}) \vec{A}^2] + [\vec{A}^2 (\vec{B} \cdot \vec{\sigma}) + (\vec{B} \cdot \vec{\sigma}) \vec{A}^2] \hat{k}_0^3 \}$$

$$\hat{H}^{1b}(9) = -\frac{e^2\hbar^2}{16m_0^3c^2} \{ \hat{k}_0^3 (\vec{B} \cdot \vec{\sigma})^2 + (\vec{B} \cdot \vec{\sigma})^2 \hat{k}_0^3 \}$$

In these terms the effect of $\hat{k}_0$ is not essential. Normally it is transferred to a higher order and the associated commutator ignored. Thus a few terms of interest follow.

The relativistic *correction to the kinetic energy* is

$$\hat{H}^{1b}(1) = -\frac{1}{8m_0^3c^2} \hat{p}^4$$

and this term is substantial for heavy atoms.

The kinetic energy–electromagnetic field cross-term is

$$\hat{H}^{1b}(2) = -\frac{e\hbar}{2m_0^3c^2} \hat{k}_0^3 \hat{p}^2 (\vec{A} \cdot \vec{p})$$

which for the external magnetic field becomes the *orbital Zeeman–kinetic energy correction*

$$\hat{H}^{1b}(2a) = -\frac{e\hbar}{4m_0^3c^2} \hat{k}_0^3 \hat{p}^2 (\vec{B}_{\text{ext}} \cdot \vec{l}_{Ge})$$

and for the nuclear dipolar field it is the *orbital hyperfine correction*

$$\hat{H}_N^{1b}(2b) = -\frac{\mu_0}{4\pi} \frac{e\hbar}{2m_0^3c^2} \hat{k}_0^3 \hat{p}^2 r_{Ne}^{-3} (\vec{\mu}_N \cdot \vec{l}_{Ne})$$

The cross-term kinetic energy–magnetic field–electron spin yields the *Zeeman–kinetic energy correction*

$$\hat{H}^{1b}(4a) = -\frac{e\hbar}{4m_0^3c^2} \hat{k}_0^3 (\vec{B}_{\text{ext}} \cdot \vec{\sigma}) \hat{p}^2$$

The other terms originating in $\hat{H}^{1b}$ are usually omitted.

The Hamiltonian term $\hat{H}^{1c}$, after the expansion of $(\vec{\sigma} \cdot \vec{\pi})$, consists of the following contributions

$$\hat{H}^{1c}(1) = \frac{e}{8m_0^2c^2} \{\hat{k}_0^2 \Phi \hat{p}^2 + \hat{p}^2 \Phi \hat{k}_0^2\}$$

$$\hat{H}^{1c}(2) = \frac{e^2}{8m_0^2c^2} \{\hat{k}_0^2 \Phi (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) \Phi \hat{k}_0^2\}$$

$$\hat{H}^{1c}(3) = \frac{e^3}{8m_0^2c^2} \{\hat{k}_0^2 \Phi \vec{A}^2 + \vec{A}^2 \Phi \hat{k}_0^2\}$$

$$\hat{H}^{1c}(4) = \frac{e^2\hbar}{8m_0^2c^2} \{\hat{k}_0^2 \Phi (\vec{\sigma} \cdot \vec{B}) + (\vec{\sigma} \cdot \vec{B}) \Phi \hat{k}_0^2\}$$

The first term $\hat{H}^{1c}(1)$ can be combined with that arising from $\hat{H}^{0b}(1)$ and the effect of $\hat{k}_0$ ignored (transferred to a higher order), so that we get

$$\hat{H}^{1c}(1) + \hat{H}^{0b}(1^*) = \frac{e}{8m_0^2c^2} \{(\Phi - \Phi_{\text{int}}) \hat{p}^2 + \hat{p}^2 (\Phi - \Phi_{\text{int}})\}$$

When the external scalar potential is absent, then $\Phi = \Phi_{\text{int}}$, and consequently this contribution vanishes.

The second term $\hat{H}^{1c}(2)$, for the case of a Coulomb gauge ($\vec{\nabla} \cdot \vec{A} = 0$), yields

$$\hat{H}^{1c}(2) = \frac{e^2}{4m_0^2c^2} \{\hat{k}_0^2 \Phi (\vec{A} \cdot \vec{p}) + (\vec{A} \cdot \vec{p}) \Phi \hat{k}_0^2\}$$

This term again can be combined with that arising from $\hat{H}^{0b}(2a)$ and the effect of $\hat{k}_0$ ignored

$$\hat{H}^{1c}(2) + \hat{H}^{0b}(2^*) = \frac{e^2}{4m_0^2c^2} \{(\Phi - \Phi_{\text{int}}) (\vec{A} \cdot \vec{p}) + (\vec{A} \cdot \vec{p}) (\Phi - \Phi_{\text{int}})\}$$

This contribution vanishes in the absence of an external scalar field.

The third Hamiltonian term $\hat{H}^{1c}(3)$ can be combined with that arising from $\hat{H}^{0b}(3)$ and, when the effect of $\hat{k}_0$ is ignored, then

$$\hat{H}^{1c}(3) + \hat{H}^{0b}(3^*) = \frac{e^3}{4m_0^2c^2}(\Phi - \Phi_{\text{int}})\vec{A}^2$$

Again, in the absence of an external scalar field, this contribution vanishes.

The last Hamiltonian term $\hat{H}^{1c}(4)$ yields a contribution vanishing in the absence of an external scalar field

$$\hat{H}^{1c}(4) + \hat{H}^{0b}(4^*) = \frac{e^2\hbar}{4m_0^2c^2}(\Phi - \Phi_{\text{int}})(\vec{\sigma} \cdot \vec{B})$$

The relevant one-electron Hamiltonian terms are collected in Table 4.3. However, this table cannot be complete since one can generate the Hamiltonian terms of higher order in $(1/c)$. It is irrelevant to go beyond the order c^{-2} . Some Hamiltonian terms contain the vector of Pauli matrices which is interrelated with the electron spin via $\vec{s} = (\hbar/2)\vec{\sigma}$.

4.6 RELATIVISTIC TWO-ELECTRON HAMILTONIAN TERMS

The derivation of the electron–electron interaction needs deep analysis originating in the special theory of relativity. Let us consider two coordinate systems: $C(x, y, z, \tau)$ and $C'(x', y', z', \tau')$ with the time-related coordinate $\tau = ict$. Let the inertial frame C' be moving along the x -direction with a constant velocity v relative to C . The systems of coordinates are interrelated by the *Lorentz transformation* and its inverse according to Table 4.4, where the dimensionless time dilation factor

$$\gamma = (1 - v^2/c^2)^{-1/2}$$

is introduced.

Any four-vector $X\{X_1(x), X_2(y), X_3(z), X_4(t)\}$ obeys a similar transformation. The electromagnetic potential four-vector is $\Xi = \{A_x, A_y, A_z, i\Phi/c\}$ and its transformation becomes

$$A_x = \gamma(A'_x + v\Phi'/c^2)$$

$$A_y = A'_y$$

TABLE 4.3

Nominal one-electron Hamiltonian terms

	Hamiltonian term	Meaning
$\hat{H}^{0a}(1)$	$-e\Phi_{\text{ext}}$	electron-external field interaction
$\hat{H}_N^{0a}(2)$	$-\frac{e^2}{4\pi\epsilon_0} \frac{Z_N}{r_{Ne}}$	electron-nuclear attraction
$\hat{H}^{0b}(1)$	$\frac{1}{2m_0} \hat{p}^2$	non-relativistic kinetic energy
	$-\frac{e}{8m_0^2c^2} (\hat{k}_0 \Phi_{\text{int}} \hat{p}^2 + \hat{p}^2 \Phi_{\text{int}} \hat{k}_0)$	higher-order correction
$\hat{H}^{0b}(2a)$	$\frac{e}{2m_0} (\vec{B}_{\text{ext}} \cdot \vec{l}_{Ge})$	orbital Zeeman term
	$-\frac{e^2}{8m_0^2c^2} [\hat{k}_0 \Phi_{\text{int}} (\vec{B}_{\text{ext}} \cdot \vec{l}_{Ge}) + (\vec{B}_{\text{ext}} \cdot \vec{l}_{Ge}) \Phi_{\text{int}} \hat{k}_0]$	higher-order correction
$\hat{H}_N^{0b}(2b)$	$\frac{\mu_0}{4\pi} \frac{e}{m_0} \hat{k}_0 r_{Ne}^{-3} (\vec{\mu}_N \cdot \vec{l}_{Ne})$	orbital hyperfine interaction
$\hat{H}^{0b}(3a)$	$\frac{e^2}{8m_0} [\vec{B}_{\text{ext}}^2 r_{Ge}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Ge})^2]$	diamagnetic term
	$-\frac{e^3}{8m_0^2c^2} (\hat{k}_0 \Phi_{\text{int}} \vec{A}_{\text{ext}}^2 + \vec{A}_{\text{ext}}^2 \Phi_{\text{int}} \hat{k}_0)$	higher-order correction
$\hat{H}_N^{0b}(3b)$	$\frac{\mu_0}{4\pi} \frac{e^2}{2m_0} \hat{k}_0 r_{Ne}^{-3} [(\vec{B}_{\text{ext}} \cdot \vec{\mu}_N)(\vec{r}_{Ge} \cdot \vec{r}_{Ne}) - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Ne})(\vec{r}_{Ge} \cdot \vec{\mu}_N)]$	electron-nuclear Zeeman correction
$\hat{H}_{NM}^{0b}(3c)$	$\left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^2}{2m_0} \hat{k}_0 r_{Ne}^{-3} r_{Me}^{-3} [(\vec{\mu}_N \cdot \vec{\mu}_M)(\vec{r}_{Ne} \cdot \vec{r}_{Me}) - (\vec{\mu}_N \cdot \vec{r}_{Me})(\vec{\mu}_M \cdot \vec{r}_{Ne})]$	electron-coupled nuclear spin-spin interaction
$\hat{H}^{0b}(4a)$	$\frac{e\hbar}{2m_0} (\vec{\sigma} \cdot \vec{B}_{\text{ext}})$	Zeeman term
$\hat{H}^{0b}(4b)$	$-\frac{\mu_0}{4\pi} \frac{e\hbar}{2m_0} \hat{k}_0 r_{Ne}^{-5} [r_{Ne}^2 (\vec{\sigma} \cdot \vec{\mu}_N) - 3(\vec{\sigma} \cdot \vec{r}_{Ne})(\vec{\mu}_N \cdot \vec{r}_{Ne})]$	dipolar hyperfine interaction
$\hat{H}_N^{1a}(1)$	$\frac{\hbar^2 e^2}{8\epsilon_0 m_0^2 c^2} Z_N \delta(\vec{r}_{Ne})$	Darwin term

(contd.)

TABLE 4.3

Nominal one-electron Hamiltonian terms (*contd.*)

	Hamiltonian term	Meaning
$\hat{H}_N^{1a}(3)$	$\frac{\hbar e^2}{16\pi\epsilon_0 m_0^2 c^2} Z_N \hat{k}_0^2 r_{Ne}^{-3} (\vec{\sigma} \cdot \vec{l}_{Ne})$	spin-orbit interaction
$\hat{H}_N^{1a}(5a)$	$\frac{1}{4\pi\epsilon_0} \frac{\hbar e^3}{8m_0^2 c^2} Z_N \hat{k}_0^2 r_{Ne}^{-3} [(\vec{r}_{Ne} \cdot \vec{r}_{Ge})(\vec{\sigma} \cdot \vec{B}_{ext}) - (\vec{\sigma} \cdot \vec{r}_{Ge})(\vec{r}_{Ne} \cdot \vec{B}_{ext})]$	spin-orbit Zeeman gauge correction
$\hat{H}_{NM}^{1a}(5b)$	$\left(\frac{\mu_0}{4\pi}\right) \frac{1}{4\pi\epsilon_0} \frac{\hbar e^3}{4m_0^2 c^2} Z_M [\hat{k}_0(r_{Me})]^2 r_{Ne}^{-3} r_{Me}^{-3} [(\vec{r}_{Ne} \cdot \vec{r}_{Me})(\vec{\sigma} \cdot \vec{\mu}_N) - (\vec{\sigma} \cdot \vec{r}_{Ne})(\vec{\mu}_N \cdot \vec{r}_{Me})]$	spin-orbit hyperfine correction
$\hat{H}_{NN}^{1a}(5b')$	$\frac{\mu_0}{4\pi} \frac{\hbar e}{2m_0} \frac{8\pi}{3} \delta(r_{Ne})(\vec{\sigma} \cdot \vec{\mu}_N)$	Fermi contact hyperfine term
$\hat{H}^{1b}(1)$	$-\frac{1}{8m_0^3 c^2} \hat{p}^4$	kinetic energy correction
$\hat{H}^{1b}(2a)$	$-\frac{e\hbar}{4m_0^3 c^2} \hat{k}_0^3 \hat{p}^2 (\vec{B}_{ext} \cdot \vec{l}_{Ge})$	orbital Zeeman-kinetic energy correction
$\hat{H}_N^{1b}(2b)$	$-\frac{\mu_0}{4\pi} \frac{e\hbar}{2m_0^3 c^2} \hat{k}_0^3 \hat{p}^2 r_{Ne}^{-3} (\vec{\mu}_N \cdot \vec{l}_{Ne})$	orbital hyperfine correction
$\hat{H}^{1b}(4a)$	$-\frac{e\hbar}{4m_0^3 c^2} \hat{k}_0^3 (\vec{B}_{ext} \cdot \vec{\sigma}) \hat{p}^2$	Zeeman-kinetic energy correction

TABLE 4.4

Relativistic invariant transformations

Lorentz transformation of coordinates	Inverse transformation of coordinates	Lorentz transformation of a four-vector
$x = \gamma(x' + vt')$	$x' = \gamma(x - vt)$	$X_1 = \gamma(X'_1 - ivX'_4/c)$
$y = y'$	$y' = y$	$X_2 = X'_2$
$z = z'$	$z' = z$	$X_3 = X'_3$
$t = \gamma(vx'/c^2 + t')$	$t' = \gamma(-vx/c^2 + t)$	$X_4 = \gamma(ivX'_1/c + X'_4)$

$$A_z = A'_z$$

$$\Phi = \gamma(vA'_x + \Phi')$$

For the observer in the C' frame the scalar field is stationary and the magnitude of the field is only the function of a distance from the electron with charge $-e$, and thus

$$\Phi' = -\frac{e}{4\pi\epsilon_0} \frac{1}{r'}$$

Such a stationary point charge is not a source of the magnetic field and, since $\vec{B} = 0$, also $\vec{A} = 0$. For the observer in the C frame, however, the vector potential arises

$$A_x = \gamma v \Phi' / c^2 = -\frac{e}{4\pi\epsilon_0 c^2} \gamma v \frac{1}{r'}$$

and this can be generalised to an electron moving in space with velocity $\vec{v}$ as follows

$$\vec{A} = -\frac{e}{4\pi\epsilon_0 c^2} \gamma \vec{v} \frac{1}{r'}$$

The scalar potential adopts the form of

$$\Phi' = -\frac{e}{4\pi\epsilon_0} \gamma \frac{1}{r'}$$

The inverse Lorentz transformation can be expressed in the form

$$\vec{r}' = \vec{r} + (\gamma - 1)|v|^{-2}(\vec{v} \cdot \vec{r})\vec{v}$$

and

$$r' = r \left[1 + \frac{(\vec{v} \cdot \vec{r})^2 \gamma^2}{c^2 r^2} \right]^{1/2}$$

Here $\vec{r}$ is a position of the electron moving at a constant velocity relative to the observer. The electromagnetic potential evaluated at the time of observation has the components

$$\vec{A} = \vec{v}\Phi/c^2$$

and

$$\Phi = -\frac{e}{4\pi\epsilon_0}\gamma\frac{1}{r}\left[1 + \frac{(\vec{v} \cdot \vec{r})^2\gamma^2}{c^2r^2}\right]^{-1/2}$$

Now, for a slowly moving electron ($v \ll c$), expansion as a power series in (v/c) is possible. Hence

$$\vec{A} = -\frac{e}{4\pi\epsilon_0 c} \frac{1}{r} \left[\frac{\vec{v}}{c} + O(v^3/c^3) \right]$$

and

$$\Phi = -\frac{e}{4\pi\epsilon_0} \frac{1}{r} \left[1 + \frac{v^2}{2c^2} - \frac{(\vec{v} \cdot \vec{r})^2}{2c^2r^2} + O(v^4/c^4) \right]$$

It is advantageous to introduce a Coulomb gauge in which the divergence of the vector potential vanishes. For this purpose one can introduce a scalar function

$$f(r) = -e(\vec{v} \cdot \vec{r})/2c^2r$$

Remember now that a gradient of any scalar function added to the vector potential satisfies the Coulomb gauge because

$$\vec{\nabla} \cdot (\vec{A} + \vec{\nabla}f) = \text{div}(\vec{A}) + \text{div}[\text{grad}(f)] = 0$$

With no loss of generality, the electromagnetic potentials become

$$\vec{A} = -\frac{e}{4\pi\epsilon_0} \frac{1}{r} \left[\frac{\vec{v}}{2c^2} + \frac{(\vec{v} \cdot \vec{r})\vec{r}}{2c^2r^2} \right] + O((v/c)^3)$$

$$\Phi = -\frac{e}{4\pi\epsilon_0} \frac{1}{r} + O((v/c)^4)$$

In terms of linear momentum the vector potential adopts the form of

$$\vec{A} = -\frac{e}{4\pi\epsilon_0} \frac{1}{2m_0c^2} \left[\frac{\vec{p}}{r} + \frac{(\vec{p} \cdot \vec{r})\vec{r}}{r^3} \right] + O(m_0c\alpha^5/e)$$

The derivation of the Hamiltonian resembles the standard procedure: the classical Lagrange function is constructed first, then it is used to express the classical Hamilton function and then quantisation is applied by substituting the canonical variables for corresponding quantum-mechanical operators. There are two additional requirements: the Hamiltonian should be symmetric with respect to the interchange of two electrons, and it should be Hermitian.

The classical relativistic Lagrange function for one particle (electron) due to the kinetic energy, the vector and scalar potentials is

$$L_1 = -T_1 + q_1(\vec{A} \cdot \vec{v}_1) - q_1\Phi = -T_1 - e(\vec{A}_2 \cdot \vec{v}_1) + e\Phi_2$$

If the potentials at the position $\vec{r}_1$ of the electron arise from the movement of the second electron (labelled 2), then

$$\vec{A}_2(\vec{r}_1) = -\frac{e}{4\pi\epsilon_0} \frac{1}{2c^2} \left[\frac{\vec{v}_2}{r_{12}} + \frac{(\vec{v}_2 \cdot \vec{r}_{12})\vec{r}_{12}}{r_{12}^3} \right] + O((v_2/c)^3)$$

$$\Phi_2(r_1) = -\frac{e}{4\pi\epsilon_0} \frac{1}{r_{12}} + O((v_2/c)^4)$$

with $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1 = -\vec{r}_{21}$ being the position of electron 2 relative to electron 1. For the two interacting electrons the *Lagrange function* becomes

$$\begin{aligned} L_{12} &= -T_1 - T_2 - e(\vec{A}_2 \cdot \vec{v}_1) + e\Phi_2 = -T_1 - T_2 - e(\vec{A}_1 \cdot \vec{v}_2) + e\Phi_1 \\ &= -m_0c^2(1 - v_1^2/c^2)^{1/2} - m_0c^2(1 - v_2^2/c^2)^{1/2} \\ &\quad + \frac{e^2}{4\pi\epsilon_0} \frac{1}{2c^2} \left[\frac{(\vec{v}_1 \cdot \vec{v}_2)}{r_{12}} + \frac{(\vec{v}_1 \cdot \vec{r}_{12})(\vec{v}_2 \cdot \vec{r}_{12})}{r_{12}^3} \right] - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}} + O((v/c)^4) \end{aligned}$$

The kinetic energy term can be expanded as

$$m_0c^2(1 - v_1^2/c^2)^{1/2} = -m_0c^2 + \frac{1}{2}m_0v^2 + \frac{1}{8c^2}m_0v^4 + \dots$$

With the Lagrange function constructed, the linear momentum of the first electron is

$$\begin{aligned} \vec{p}_1 &= \frac{\partial L_{12}}{\partial \vec{v}_1} = m_0\vec{v}_1 + \frac{1}{2c^2}m_0\vec{v}_1^3 + \frac{e^2}{4\pi\epsilon_0} \frac{1}{2c^2} \left[\frac{\vec{v}_2}{r_{12}} + \frac{(\vec{v}_2 \cdot \vec{r}_{12})\vec{r}_{12}}{r_{12}^3} \right] \\ &\quad + O(m_0c(v/c)^5) \end{aligned}$$

and an analogous expression holds for $\vec{p}_2$, the linear momentum of the second electron. Then the velocity of electron 1, expressed in terms of momenta, results in the form of

$$\vec{v}_1 = \frac{\vec{p}_1}{m_0} - \frac{\vec{p}_1^3}{2m_0^3c^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{2m_0^2c^2} \left[\frac{\vec{p}_1}{r_{12}} + \frac{(\vec{p}_2 \cdot \vec{r}_{12})\vec{r}_{12}}{r_{12}^3} \right] + O(c(p/m_0c)^5)$$

and analogously for electron 2.

The *Hamilton function* is constructed via

$$\begin{aligned} H_{12} &= \vec{v}_1 \cdot \vec{p}_1 + \vec{v}_2 \cdot \vec{p}_2 - L_{12} \\ &= \sum_{i=1,2} \left[m_0c^2 + \frac{p_i^2}{2m_0} - \frac{p_i^4}{8m_0^3c^2} \right] + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}} \\ &\quad - \frac{e^2}{4\pi\epsilon_0} \frac{1}{2m_0^2c^2} \left[\frac{(\vec{p}_1 \cdot \vec{p}_2)}{r_{12}} + \frac{(\vec{p}_2 \cdot \vec{r}_{12})(\vec{p}_1 \cdot \vec{r}_{12})}{r_{12}^3} \right] + O(m_0c^2(p/m_0c)^6) \end{aligned}$$

Except for the last term, this is the relativistic one-electron Hamilton function for two electrons with an added classical expression for the Coulomb inter-electron repulsion. The new term is the *Breit interaction*

$$\begin{aligned} B(1, 2) &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2m_0^2c^2} \left[\frac{(\vec{p}_1 \cdot \vec{p}_2)}{r_{12}} + \frac{(\vec{p}_2 \cdot \vec{r}_{12})(\vec{p}_1 \cdot \vec{r}_{12})}{r_{12}^3} \right] \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2c^2} \left[\frac{(\vec{v}_1 \cdot \vec{v}_2)}{r_{12}} + \frac{(\vec{v}_2 \cdot \vec{r}_{12})(\vec{v}_1 \cdot \vec{r}_{12})}{r_{12}^3} \right] \end{aligned}$$

which represents an approximate relativistic correction to the interaction of two electrons.

Going to an operator form, let us remember that in the Dirac theory the operator corresponding to a velocity $\vec{v}$ is

$$\hat{v}_i \rightarrow c\vec{\alpha}_i$$

so that the Breit operator is

$$\hat{B}(1, 2) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2r_{12}} \left[(\vec{\alpha}_1 \cdot \vec{\alpha}_2) + \left(\vec{\alpha}_1 \cdot \frac{\vec{r}_{12}}{r_{12}} \right) \left(\vec{\alpha}_2 \cdot \frac{\vec{r}_{12}}{r_{12}} \right) \right]$$

The approximate relativistic equation for two electrons is known as the *Breit equation*

$$\hat{H}_B \Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

with the Breit Hamiltonian

$$\hat{H}_B(1, 2) = \hat{H}_D(1) + \hat{H}_D(2) + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \hat{B}(1, 2)$$

where $\hat{H}_D(i)$ is the Dirac Hamiltonian for electron i . The Breit Hamiltonian is not fully Lorentz-invariant because of approximations introduced in its “derivation”. The wave function is represented by a sixteen-component spinor written as

$$\Psi(1, 2) = \begin{pmatrix} \Psi_{uu} \\ \Psi_{ul} \\ \Psi_{lu} \\ \Psi_{ll} \end{pmatrix}$$

as an effect of the matrix representation of the Breit operator; this involves matrices of order 16 as they result from the direct product of the matrix representations of the components of the Dirac operators $\vec{\alpha}_1$ and $\vec{\alpha}_2$. The four-component spinors are labelled according to the energy of the electrons: Ψ_{uu} , for example, has four components for which both the electrons have a positive energy but different spin orientations. Just this wave function is of interest to us.

The reduction of the Breit equation into a four-component form of interest is a complicated, tedious and not fully exact process since the Breit operator itself is precise only to the order of $1/c^2$ (the reader should consult more specialised literature [3–6]). For this purpose it is convenient to consider *even operators* of the form

$$\hat{E} = \begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix}$$

and *odd operators* of the form

$$\hat{O} = \begin{pmatrix} 0 & c \\ d & 0 \end{pmatrix}$$

Any operator can be separated into odd and even contributions. The Dirac operator $\hat{\beta}$ commutes with an even operator and anticommutes with an odd operator. The Breit Hamiltonian can be decomposed into even–even (EE), even–odd (EO), odd–even (OE) and odd–odd (OO) components, depending on whether the part of the operator acting on electrons one and two, respectively, is even or odd

$$\left\{ m_1 c^2 \hat{\beta}_1 + m_2 c^2 \hat{\beta}_2 + (EE) + (EO) + (OE) + (OO) \right\} \Psi = E \Psi$$

with

$$(EE) = e_1 \Phi(\vec{r}_1) + e_2 \Phi(\vec{r}_2) + V_{12}$$

$$(EO) = c(\vec{\alpha}_2 \cdot \vec{\pi}_2)$$

$$(OE) = c(\vec{\alpha}_1 \cdot \vec{\pi}_1)$$

$$(OO) = -\hat{B}$$

with

$$V_{12} = \frac{e_1 e_2}{4\pi\epsilon_0} \frac{1}{r_{12}}$$

The scalar potential $\Phi(\vec{r})$ involves contributions from any sources (nuclei, external field) other than the two electrons. The vector potential contributes to the generalised momenta

$$\vec{\pi}_i = \vec{p}_i + e\vec{A}(\vec{r}_i)$$

The separated upper-upper part of the Breit Hamiltonian is satisfactory to the order of $1/c^2$ and is

$$\begin{aligned}
 \hat{H}_B(uu) = & m_1 c^2 + m_2 c^2 + (EE) + \frac{1}{2m_1 c^2} (OE)^2 + \frac{1}{2m_2 c^2} (EO)^2 \\
 & - \frac{1}{8m_1^3 c^6} (OE)^4 - \frac{1}{8m_2^3 c^6} (EO)^4 \\
 & + \frac{1}{8m_1^2 c^4} [[(OE), (EE)], (OE)] + \frac{1}{8m_2^2 c^4} [[(EO), (EE)], (EO)] \\
 & + \frac{1}{8m_1 m_2 c^4} \{ [[(OE), (OO)]_+, (EO)]_+ + [[(EO), (OO)]_+, (EO)]_+ \} \\
 & + \frac{m_1 - m_2}{2(m_1^2 - m_2^2)} (OO)^2
 \end{aligned}$$

The last term, however, brings a singularity when the rest mass of both the electrons is equal. Since we wish to apply first-order perturbation theory to the Breit operator, the $(OO)^2$ term will be neglected.

The individual contributions are

$$\begin{aligned}
 \frac{1}{2m_0 c^2} (OE)^2 &= \frac{1}{2m_0} (\vec{\alpha}_1 \cdot \vec{\pi}_1)^2 \\
 -\frac{1}{8m_0^3 c^6} (OE)^4 &= -\frac{1}{8m_0^3 c^2} (\vec{\alpha}_1 \cdot \vec{\pi}_1)^4 \\
 \frac{1}{8m_0^2 c^4} [[(OE), (EE)], (OE)] &= \frac{1}{8m_0^2 c^2} [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), e\Phi(\vec{r}_1) + e\Phi(\vec{r}_2) \\
 &\quad + V_{12}], (\vec{\alpha}_1 \cdot \vec{\pi}_1)] \\
 &= \frac{1}{8m_0^2 c^2} [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), e\Phi(\vec{r}_1)], (\vec{\alpha}_1 \cdot \vec{\pi}_1)] \\
 &\quad + \frac{1}{8m_0^2 c^2} [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), V_{12}], (\vec{\alpha}_1 \cdot \vec{\pi}_1)] \\
 \frac{1}{2m_0 c^2} (EO)^2 &= \frac{1}{2m_0} (\vec{\alpha}_2 \cdot \vec{\pi}_2)^2 \\
 -\frac{1}{8m_0^3 c^6} (EO)^4 &= -\frac{1}{8m_0^3 c^2} (\vec{\alpha}_2 \cdot \vec{\pi}_2)^4
 \end{aligned}$$

$$\begin{aligned}
\frac{1}{8m_0^2c^4} [[(EO), (EE)], (EO)] &= \frac{1}{8m_0^2c^2} [[(\vec{\alpha}_2 \cdot \vec{\pi}_2), e\Phi(\vec{r}_1) + e\Phi(\vec{r}_2) \\
&\quad + V_{12}], (\vec{\alpha}_2 \cdot \vec{\pi}_2)] \\
&= \frac{1}{8m_0^2c^2} [[(\vec{\alpha}_2 \cdot \vec{\pi}_2), e\Phi(\vec{r}_2)], (\vec{\alpha}_2 \cdot \vec{\pi}_2)] \\
&\quad + \frac{1}{8m_0^2c^2} [[(\vec{\alpha}_2 \cdot \vec{\pi}_2), V_{12}], (\vec{\alpha}_2 \cdot \vec{\pi}_2)] \\
\frac{1}{8m_0^2c^4} \{ &[[(OE), (OO)]_+, (EO)]_+ + [[(EO), (OO)]_+, (EO)]_+ \} \\
&= -\frac{1}{8m_0^2c^2} \{ [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), \hat{B}]_+, (\vec{\alpha}_2 \cdot \vec{\pi}_2)]_+ + [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), \hat{B}]_+, (\vec{\alpha}_2 \cdot \vec{\pi}_2)]_+ \}
\end{aligned}$$

Now the Breit Hamiltonian can be expressed in the form

$$\hat{H}_B(1, 2) = \hat{H}_D(1) + \hat{H}_D(2) + \hat{H}_{12}$$

The one-electron Dirac operators will appear in the form

$$\begin{aligned}
\hat{H}_D(i) &= m_0c^2 + e\Phi(\vec{r}_i) + \frac{1}{2m_0} (\vec{\alpha}_i \cdot \vec{\pi}_i)^2 - \frac{1}{8m_0^3c^2} (\vec{\alpha}_i \cdot \vec{\pi}_i)^4 \\
&\quad + \frac{1}{8m_0^2c^2} [[(\vec{\alpha}_i \cdot \vec{\pi}_i), e\Phi(\vec{r}_i)], (\vec{\alpha}_i \cdot \vec{\pi}_i)]
\end{aligned}$$

and the electron–electron interaction term becomes

$$\begin{aligned}
\hat{H}_{12} &= V_{12} + \frac{1}{8m_0^2c^2} [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), V_{12}], (\vec{\alpha}_1 \cdot \vec{\pi}_1)] \\
&\quad + \frac{1}{8m_0^2c^2} [[(\vec{\alpha}_2 \cdot \vec{\pi}_2), V_{12}], (\vec{\alpha}_2 \cdot \vec{\pi}_2)] \\
&\quad - \frac{1}{8m_0^2c^2} \{ [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), \hat{B}]_+, (\vec{\alpha}_2 \cdot \vec{\pi}_2)]_+ + [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), \hat{B}]_+, (\vec{\alpha}_2 \cdot \vec{\pi}_2)]_+ \}
\end{aligned}$$

Here the first term represents the *Coulomb electron–electron repulsion*

$$\hat{H}_{12}^a = V_{12} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$$

In treating the second term the following manipulations hold valid

$$\begin{aligned}
 [(\vec{\alpha}_1 \cdot \vec{\pi}_1), V_{12}] &= \frac{e^2}{4\pi\epsilon_0} \left[(\vec{\alpha}_1 \cdot \{\vec{p}_1 + e\vec{A}_1\}), \frac{1}{r_{12}} \right] = \frac{e^2}{4\pi\epsilon_0} \left[(\vec{\alpha}_1 \cdot \vec{p}_1), \frac{1}{r_{12}} \right] \\
 &= -\frac{i\hbar e^2}{4\pi\epsilon_0} \left[(\vec{\alpha}_1 \cdot \vec{\nabla}_1), \frac{1}{r_{12}} \right] = \frac{i\hbar e^2}{4\pi\epsilon_0} \frac{1}{r_{12}^3} (\vec{\alpha}_1 \cdot \vec{r}_{21}) \\
 &= -\frac{i\hbar e^2}{4\pi\epsilon_0} \frac{1}{r_{12}^3} (\vec{\alpha}_1 \cdot \vec{r}_{12})
 \end{aligned}$$

so that we arrive at

$$\begin{aligned}
 \frac{1}{2} \hat{H}_{12}^b &= \frac{1}{8m_0^2 c^2} [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), V_{12}], (\vec{\alpha}_1 \cdot \vec{\pi}_1)] \\
 &= \frac{e^2}{4\pi\epsilon_0} \frac{i\hbar}{8m_0^2 c^2} \left[\frac{1}{r_{12}^3} (\vec{\alpha}_1 \cdot \vec{r}_{21}), (\vec{\alpha}_1 \cdot \vec{\pi}_1) \right] \\
 &= \frac{e^2}{4\pi\epsilon_0} \frac{i\hbar}{8m_0^2 c^2} \left\{ \frac{1}{r_{12}^3} \left[(\vec{r}_{21} \cdot \vec{\pi}_1) + i\vec{\sigma}_1 \cdot \vec{r}_{21} \times \vec{\pi}_1 \right] \right. \\
 &\quad \left. - \left[(\vec{\pi}_1 \cdot \vec{r}_{21}) + i\vec{\sigma}_1 \cdot \vec{\pi}_1 \times \vec{r}_{21} \right] \frac{1}{r_{12}^3} \right\}
 \end{aligned}$$

The third term of $\hat{H}_{12}$ is identical with the second one except for the interchange of electrons, so that the individual contributions should be counted twice. These two terms can be rewritten as a sum of three contributions; the first is the *electron Darwin term*

$$\hat{H}_{12}^b(1) = \frac{e^2}{4\pi\epsilon_0} \frac{\hbar^2}{4m_0^2 c^2} (-4\pi) \delta(\vec{r}_{21}) = -\left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right)^2 4\pi \delta(\vec{r}_{21})$$

The next contribution is the *electron-electron spin-orbit term*

$$\begin{aligned}
 \hat{H}_{12}^b(2) &= -\frac{e^2}{4\pi\epsilon_0} \frac{\hbar}{8m_0^2 c^2} \left[\frac{1}{r_{12}^3} (\vec{\sigma}_1 \cdot \vec{r}_{21} \times \vec{p}_1 - \vec{\sigma}_2 \cdot \vec{r}_{21} \times \vec{p}_2) \right. \\
 &\quad \left. - (\vec{\sigma}_1 \cdot \vec{p}_1 \times \vec{r}_{21} - \vec{\sigma}_2 \cdot \vec{p}_2 \times \vec{r}_{21}) \frac{1}{r_{12}^3} \right] \\
 &= -\left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right)^2 \frac{1}{\hbar} \frac{1}{r_{12}^3} (\vec{\sigma}_1 \cdot \vec{r}_{21} \times \vec{p}_1 + \vec{\sigma}_2 \cdot \vec{r}_{12} \times \vec{p}_2)
 \end{aligned}$$

The remaining contribution contains the vector potential

$$\begin{aligned}
 \hat{H}_{12}^b(3) &= -\frac{e^2}{4\pi\epsilon_0} \frac{e\hbar}{8m_0^2c^2} \left\{ \frac{1}{r_{12}^3} [\vec{\sigma}_1 \cdot \vec{r}_{21} \times \vec{A}(\vec{r}_1) \right. \\
 &\quad \left. - \vec{\sigma}_2 \cdot \vec{r}_{21} \times \vec{A}(\vec{r}_2)] - [\vec{\sigma}_1 \cdot \vec{A}(\vec{r}_1) \times \vec{r}_{21} - \vec{\sigma}_2 \cdot \vec{A}(\vec{r}_2) \times \vec{r}_{21}] \frac{1}{r_{12}^3} \right\} \\
 &= -\left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{2m_0} \frac{1}{r_{12}^3} [\vec{\sigma}_1 \cdot \vec{r}_{21} \times \vec{A}(\vec{r}_1) + \vec{\sigma}_2 \cdot \vec{r}_{12} \times \vec{A}(\vec{r}_2)]
 \end{aligned}$$

This can be split into the external field $\vec{A}_{\text{ext}}(\vec{r}_i) = (1/2)(\vec{B}_{\text{ext}} \times \vec{r}_{Gi})$ and the internal dipolar field $\vec{A}_N(\vec{r}_i) = (\mu_0/4\pi)r_{Ni}^{-3}(\vec{\mu}_N \times \vec{r}_{Ni})$ contributions. The term containing the external field represents the *electron-electron spin-orbit Zeeman gauge correction*

$$\begin{aligned}
 \hat{H}_{12}^b(3a) &= -\left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{4m_0} \frac{1}{r_{12}^3} [\vec{\sigma}_1 \cdot \vec{r}_{21} \times (\vec{B}_{\text{ext}} \times \vec{r}_{G1}) \\
 &\quad + \vec{\sigma}_2 \cdot \vec{r}_{12} \times (\vec{B}_{\text{ext}} \times \vec{r}_{G2})] \\
 &= \left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{4m_0} \frac{1}{r_{12}^3} [(\vec{\sigma}_1 \cdot \vec{r}_{G1})(\vec{r}_{21} \cdot \vec{B}_{\text{ext}}) \\
 &\quad - (\vec{r}_{21} \cdot \vec{r}_{G1})(\vec{\sigma}_1 \cdot \vec{B}_{\text{ext}}) + (\vec{\sigma}_2 \cdot \vec{r}_{G2})(\vec{r}_{12} \cdot \vec{B}_{\text{ext}}) \\
 &\quad - (\vec{r}_{12} \cdot \vec{r}_{G2})(\vec{\sigma}_2 \cdot \vec{B}_{\text{ext}})]
 \end{aligned}$$

The internal dipolar contribution yields the *electron-electron spin-orbit hyperfine correction*

$$\begin{aligned}
 \hat{H}_{12}^b(3b) &= -\left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{2m_0} \frac{1}{r_{12}^3} \\
 &\quad \sum_N \left[\frac{1}{r_{N1}^3} \vec{\sigma}_1 \cdot \vec{r}_{21} \times (\vec{\mu}_N \times \vec{r}_{N1}) + \frac{1}{r_{N2}^3} \vec{\sigma}_2 \cdot \vec{r}_{12} \times (\vec{\mu}_N \times \vec{r}_{N2}) \right] \\
 &= \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{2m_0} \frac{1}{r_{12}^3} \\
 &\quad \sum_N \left(\frac{1}{r_{N1}^3} \left[(\vec{r}_{12} \cdot \vec{r}_{N1})(\vec{\mu}_N \cdot \vec{\sigma}_1) - (\vec{r}_{12} \cdot \vec{\mu}_N)(\vec{r}_{N1} \cdot \vec{\sigma}_1) \right] \right. \\
 &\quad \left. + \frac{1}{r_{N2}^3} \left[(\vec{r}_{21} \cdot \vec{r}_{N2})(\vec{\mu}_N \cdot \vec{\sigma}_2) - (\vec{r}_{21} \cdot \vec{\mu}_N)(\vec{r}_{N2} \cdot \vec{\sigma}_2) \right] \right)
 \end{aligned}$$

The last two-electron Hamiltonian term involving the Breit operator

$$\hat{H}_{12}^c = -\frac{1}{8m_0^2c^2} \{ [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), \hat{B}]_+, (\vec{\alpha}_2 \cdot \vec{\pi}_2)]_+ + [[(\vec{\alpha}_1 \cdot \vec{\pi}_1), \hat{B}]_+, (\vec{\alpha}_2 \cdot \vec{\pi}_2)]_+ \}$$

produces a number of contributions leading effectively to the following list

$$\hat{H}_{12}^c(1) = -\frac{e^2}{4\pi\epsilon_0} \frac{\hbar}{2m_0^2c^2} \frac{1}{r_{12}^3} [\vec{\sigma}_1 \cdot \vec{r}_{12} \times \vec{\pi}_2 + \vec{\sigma}_2 \cdot \vec{r}_{21} \times \vec{\pi}_1]$$

$$\hat{H}_{12}^c(2) = \frac{e^2}{4\pi\epsilon_0} \frac{\hbar^2}{4m_0^2c^2} \frac{1}{r_{12}^3} [\vec{\sigma}_1 \cdot \vec{\sigma}_2 - 3r_{12}^{-2}(\vec{\sigma}_1 \cdot \vec{r}_{21})(\vec{\sigma}_2 \cdot \vec{r}_{21})]$$

$$\hat{H}_{12}^c(3) = -\frac{e^2}{4\pi\epsilon_0} \frac{\hbar^2}{4m_0^2c^2} \frac{8\pi}{3} (\vec{\sigma}_1 \cdot \vec{\sigma}_2) \delta(\vec{r}_{21})$$

$$\hat{H}_{12}^c(4) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2m_0^2c^2} \frac{1}{r_{12}} [\vec{p}_1 \cdot \vec{p}_2 + r_{12}^{-2}(\vec{r}_{21} \cdot \vec{p}_1)(\vec{r}_{21} \cdot \vec{p}_2)]$$

$$\hat{H}_{12}^c(5) = \frac{e^2}{4\pi\epsilon_0} \frac{i\hbar}{4m_0^2c^2} \frac{1}{r_{12}^3} [(\vec{r}_{21} \cdot \vec{p}_1) + (\vec{r}_{12} \cdot \vec{p}_2)]$$

$$\hat{H}_{12}^c(6) = \frac{e^2}{4\pi\epsilon_0} \frac{i\hbar}{4m_0^2c^2} (-4\pi) \delta(\vec{r}_{21}) [(\vec{r}_{21} \cdot \vec{p}_1) + (\vec{r}_{12} \cdot \vec{p}_2)]$$

The first contribution, using $\vec{\pi}_i = \vec{p}_i + e\vec{A}_{\text{ext}}(\vec{r}_i) + e\sum_N \vec{A}_N(\vec{r}_i)$, yields the *spin-orbit* term first

$$\begin{aligned} \hat{H}_{12}^c(1a) &= -\frac{e^2}{4\pi\epsilon_0} \frac{\hbar}{2m_0^2c^2} \frac{1}{r_{12}^3} [\vec{\sigma}_1 \cdot \vec{r}_{12} \times \vec{p}_2 + \vec{\sigma}_2 \cdot \vec{r}_{21} \times \vec{p}_1] \\ &= -\left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right)^2 \frac{2}{\hbar} \frac{1}{r_{12}^3} [\vec{\sigma}_1 \cdot \vec{r}_{12} \times \vec{p}_2 + \vec{\sigma}_2 \cdot \vec{r}_{21} \times \vec{p}_1] \end{aligned}$$

This term represents the interaction of the magnetic moment generated by the first electron with the magnetic field produced by the orbital motion of the other electron.

The external vector potential $\vec{A}_{\text{ext}}(\vec{r}_i) = (1/2)(\vec{B}_{\text{ext}} \times \vec{r}_{Gi})$, for a uniform magnetic field, gives the *spin–other orbit Zeeman gauge correction* term

$$\begin{aligned} \hat{H}_{12}^c(1b) = & -\frac{e^2}{4\pi\epsilon_0} \frac{e\hbar}{4m_0^2c^2} \frac{1}{r_{12}^3} [(\vec{\sigma}_1 \cdot \vec{r}_{12}) \times (\vec{B}_{\text{ext}} \times \vec{r}_{G2}) + (\vec{\sigma}_2 \cdot \vec{r}_{21}) \\ & \times (\vec{B}_{\text{ext}} \times \vec{r}_{G1})] = -\left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{2m_0} \frac{1}{r_{12}^3} \\ & [(\vec{r}_{12} \cdot \vec{r}_{G2})(\vec{\sigma}_1 \cdot \vec{B}_{\text{ext}}) - (\vec{\sigma}_1 \cdot \vec{r}_{G2})(\vec{r}_{12} \cdot \vec{B}_{\text{ext}}) \\ & + (\vec{r}_{21} \cdot \vec{r}_{G1})(\vec{\sigma}_2 \cdot \vec{B}_{\text{ext}}) - (\vec{\sigma}_2 \cdot \vec{r}_{G1})(\vec{r}_{21} \cdot \vec{B}_{\text{ext}})] \end{aligned}$$

A contribution from the nuclear dipolar field $\vec{A}_N(\vec{r}_i) = (\mu_0/4\pi)r_{Ni}^{-3}(\vec{\mu}_N \times \vec{r}_{Ni})$ yields the *spin–other orbit hyperfine correction*

$$\begin{aligned} \hat{H}_{12}^c(1c) = & -\frac{e^2}{4\pi\epsilon_0} \frac{e\hbar}{2m_0^2c^2} \frac{1}{r_{12}^3} \left(\frac{\mu_0}{4\pi}\right) \sum_N \left(\frac{1}{r_{N2}^3} \vec{\sigma}_1 \cdot \vec{r}_{12} \times \vec{\mu}_N \times \vec{r}_{N2} \right. \\ & \left. + \frac{1}{r_{N1}^3} \vec{\sigma}_2 \cdot \vec{r}_{21} \times \vec{\mu}_N \times \vec{r}_{N1} \right) = -\left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{m_0} \frac{1}{r_{12}^3} \\ & \sum_N \left(\frac{1}{r_{N2}^3} \left[(\vec{r}_{12} \cdot \vec{r}_{N2})(\vec{\mu}_N \cdot \vec{\sigma}_1) - (\vec{r}_{12} \cdot \vec{\mu}_N)(\vec{r}_{N2} \cdot \vec{\sigma}_1) \right] \right. \\ & \left. + \frac{1}{r_{N1}^3} \left[(\vec{r}_{21} \cdot \vec{r}_{N1})(\vec{\mu}_N \cdot \vec{\sigma}_2) - (\vec{r}_{21} \cdot \vec{\mu}_N)(\vec{r}_{N1} \cdot \vec{\sigma}_2) \right] \right) \end{aligned}$$

The next two terms are the *spin–spin dipolar interaction* term

$$\begin{aligned} \hat{H}_{12}^c(2) = & \frac{e^2}{4\pi\epsilon_0} \frac{\hbar^2}{4m_0^2c^2} \frac{1}{r_{12}^3} [(\vec{\sigma}_1 \cdot \vec{\sigma}_2) - 3r_{12}^{-2}(\vec{\sigma}_1 \cdot \vec{r}_{21})(\vec{\sigma}_2 \cdot \vec{r}_{21})] \\ = & \left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right)^2 \left[\frac{1}{r_{12}^3} (\vec{\sigma}_1 \cdot \vec{\sigma}_2) - \frac{3}{r_{12}^5} (\vec{\sigma}_1 \cdot \vec{r}_{21})(\vec{\sigma}_2 \cdot \vec{r}_{21}) \right] \end{aligned}$$

and the *spin–spin contact interaction* term

$$\begin{aligned} \hat{H}_{12}^c(3) = & -\frac{e^2}{4\pi\epsilon_0} \frac{\hbar^2}{4m_0^2c^2} \frac{8\pi}{3} (\vec{\sigma}_1 \cdot \vec{\sigma}_2) \delta(\vec{r}_{21}) \\ = & -\left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_0}\right)^2 \frac{8\pi}{3} (\vec{\sigma}_1 \cdot \vec{\sigma}_2) \delta(\vec{r}_{21}) \end{aligned}$$

The remaining terms $\hat{H}_{12}^c(4)$, $\hat{H}_{12}^c(5)$ and $\hat{H}_{12}^c(6)$ represent the *electron-electron orbital interaction*; these are of little interest since they are independent of both spins and magnetic field.

The two-electron Hamiltonian terms are collected in Table 4.5.

4.7 THE MAGNETOGYRIC FACTOR FOR THE ELECTRON

The g -factor of an elementary particle is introduced as a ratio of its magnetic moment $\vec{\mu}$ to its spin angular momentum $\vec{s}$, expressed in units of $(q/2m)$. For the electron, in terms of the Dirac theory

$$\vec{\mu}/\vec{s} = \left(-\frac{e\hbar}{2m_e} \vec{\sigma} \right) / \left(\frac{\hbar}{2} \vec{\sigma} \right) = 2 \left(-\frac{e}{2m_e} \right)$$

and thus

$$g_e = 2, \quad [\text{Dirac}]$$

However, this “theoretical” value differs slightly but significantly from the experimental determination

$$g_e = 2.002319315(\pm 7 \times 10^{-9}), \quad [\text{exptl}]$$

The “anomalous” contribution to the magnetic moment of an electron has been explained by the quantum electrodynamic theory. The additional contribution—the “radiative correction”—arises from the interaction of the electron–positron virtual pair emitted and absorbed by the real electron. A theoretical expression in terms of the fine structure constant α is

$$g_e = 2 + (\alpha/\pi) - 0.65696(\alpha/\pi)^2 + 1.49(\alpha/\pi)^3 + O((\alpha/\pi)^4)$$

Instead of

$$\vec{\sigma} = \frac{2}{\hbar} \vec{s}$$

we let

$$\vec{\sigma} = \frac{g_e}{\hbar} \vec{s}$$

TABLE 4.5

Nominal two-electron Hamiltonian terms

	Hamiltonian term	Meaning
$\hat{H}_{12}^a$	$\frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$	interelectron Coulomb repulsion
$\hat{H}_{12}^b(1)$	$-\left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{2m_0}\right)^2 4\pi\delta(\vec{r}_{21})$	electron Darwin term
$\hat{H}_{12}^b(2)$	$-\left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{2m_0}\right)^2 \frac{1}{\hbar} \frac{1}{r_{12}^3} (\vec{\sigma}_1 \cdot \vec{r}_{21} \times \vec{p}_1 + \vec{\sigma}_2 \cdot \vec{r}_{12} \times \vec{p}_2)$	electron-electron spin-orbit interaction
$\hat{H}_{12}^b(3a)$	$\left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{4m_0} \frac{1}{r_{12}^3}$ $[(\vec{\sigma}_1 \cdot \vec{r}_{G1})(\vec{r}_{21} \cdot \vec{B}_{\text{ext}}) - (\vec{r}_{21} \cdot \vec{r}_{G1})(\vec{\sigma}_1 \cdot \vec{B}_{\text{ext}})]$ $+ (\vec{\sigma}_2 \cdot \vec{r}_{G2})(\vec{r}_{12} \cdot \vec{B}_{\text{ext}}) - (\vec{r}_{12} \cdot \vec{r}_{G2})(\vec{\sigma}_2 \cdot \vec{B}_{\text{ext}})]$	electron-electron spin-orbit Zeeman gauge correction
$\hat{H}_{12}^b(3b)$	$\left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{2m_0} \frac{1}{r_{12}^3}$ $\sum_N \left[\frac{1}{r_{N1}^3} \left\{ (\vec{r}_{12} \cdot \vec{r}_{N1})(\vec{\mu}_N \cdot \vec{\sigma}_1) - (\vec{r}_{12} \cdot \vec{\mu}_N)(\vec{r}_{N1} \cdot \vec{\sigma}_1) \right\} \right.$ $\left. + \frac{1}{r_{N2}^3} \left\{ (\vec{r}_{21} \cdot \vec{r}_{N2})(\vec{\mu}_N \cdot \vec{\sigma}_2) - (\vec{r}_{21} \cdot \vec{\mu}_N)(\vec{r}_{N2} \cdot \vec{\sigma}_2) \right\} \right]$	electron-electron spin-orbit hyperfine correction
$\hat{H}_{12}^c(1a)$	$-\left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{2m_0}\right)^2 \frac{2}{\hbar} \frac{1}{r_{12}^3} [\vec{\sigma}_1 \cdot \vec{r}_{12} \times \vec{p}_2 + \vec{\sigma}_2 \cdot \vec{r}_{21} \times \vec{p}_1]$	spin-other orbit interaction
$\hat{H}_{12}^c(1b)$	$-\left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{2m_0} \frac{1}{r_{12}^3}$ $[(\vec{r}_{12} \cdot \vec{r}_{G2})(\vec{\sigma}_1 \cdot \vec{B}_{\text{ext}}) - (\vec{\sigma}_1 \cdot \vec{r}_{G2})(\vec{r}_{12} \cdot \vec{B}_{\text{ext}})]$ $+ (\vec{r}_{21} \cdot \vec{r}_{G1})(\vec{\sigma}_2 \cdot \vec{B}_{\text{ext}}) - (\vec{\sigma}_2 \cdot \vec{r}_{G1})(\vec{r}_{21} \cdot \vec{B}_{\text{ext}})]$	spin-other orbit Zeeman gauge correction
$\hat{H}_{12}^c(1c)$	$-\left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{e\hbar}{2m_0}\right) \frac{e^2}{m_0} \frac{1}{r_{12}^3}$ $\sum_N \left[\frac{1}{r_{N2}^3} \left\{ (\vec{r}_{12} \cdot \vec{r}_{N2})(\vec{\mu}_N \cdot \vec{\sigma}_1) - (\vec{r}_{12} \cdot \vec{\mu}_N)(\vec{r}_{N2} \cdot \vec{\sigma}_1) \right\} \right.$ $\left. + \frac{1}{r_{N1}^3} \left\{ (\vec{r}_{21} \cdot \vec{r}_{N1})(\vec{\mu}_N \cdot \vec{\sigma}_2) - (\vec{r}_{21} \cdot \vec{\mu}_N)(\vec{r}_{N1} \cdot \vec{\sigma}_2) \right\} \right]$	spin-other orbit hyperfine correction
$\hat{H}_{12}^c(2)$	$\left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{2m_0}\right)^2 \left[\frac{1}{r_{12}^3} (\vec{\sigma}_1 \cdot \vec{\sigma}_2) - \frac{3}{r_{12}^5} (\vec{\sigma}_1 \cdot \vec{r}_{21})(\vec{\sigma}_2 \cdot \vec{r}_{21}) \right]$	spin-spin dipolar interaction

TABLE 4.5

Nominal two-electron Hamiltonian terms (*contd.*)

Hamiltonian term	Meaning
$\hat{H}_{12}^c(3) \quad -\left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{2m_0}\right)^2 \frac{8\pi}{3} (\vec{\sigma}_1 \cdot \vec{\sigma}_2) \delta(\vec{r}_{21})$	spin-spin contact interaction

with

$$g_e = 2(1 + g_1)$$

where g_1 is a correction factor. We shall see later that the magnetogyric factor is different for the Zeeman interaction and the spin-orbit term.

For a consistent treatment an extended Dirac equation is considered

$$\{c\vec{\alpha} \cdot \vec{\pi} + \beta m_0 c^2 - e\Phi - E\}\Psi = \hat{G}\Psi$$

with the operator $\hat{G}$ expressing the effect of the radiative corrections

$$\hat{G} = -g_1 \frac{e\hbar}{2m_0 c} \begin{pmatrix} \vec{\sigma} \cdot \vec{B} & -i\vec{\sigma} \cdot \vec{E} \\ i\vec{\sigma} \cdot \vec{E} & -\vec{\sigma} \cdot \vec{B} \end{pmatrix} = \begin{pmatrix} \hat{G}_{uu} & \hat{G}_{ul} \\ \hat{G}_{lu} & \hat{G}_{ll} \end{pmatrix}$$

In the first-order perturbation theory there is

$$\hat{H}^0 = \hat{H}_D$$

$$\hat{H}' = -\hat{G}$$

and the correction term is

$$\begin{aligned} \langle \Psi^0 | \hat{H}' | \Psi^0 \rangle &= -\langle \Psi^0 | \hat{G} | \Psi^0 \rangle \\ &= -\left[\langle \Psi_u^0 | \hat{G}_{uu} | \Psi_u^0 \rangle + \langle \Psi_u^0 | \hat{G}_{ul} | \Psi_l^0 \rangle + \langle \Psi_l^0 | \hat{G}_{lu} | \Psi_u^0 \rangle \right. \\ &\quad \left. + \langle \Psi_l^0 | \hat{G}_{ll} | \Psi_l^0 \rangle \right] \end{aligned}$$

Using the resolvent operator $\hat{k}$ the lower-component spinor can be expressed in terms of the upper-component spinor, hence

$$\Psi_l^0 = \frac{1}{2m_0c} \hat{k}(\vec{\sigma} \cdot \vec{\pi}) \Psi_u^0$$

and consequently the correction term becomes

$$\begin{aligned} \langle \Psi^0 | \hat{H}' | \Psi^0 \rangle &= \left\langle \Psi_u^0 \left| g_1 \frac{e\hbar}{2m_0c} (\vec{\sigma} \cdot \vec{B}) \right| \Psi_u^0 \right\rangle \\ &+ \left\langle \Psi_u^0 \left| g_1 \frac{ie\hbar}{4m_0^2c^2} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}(\vec{\sigma} \cdot \vec{E}) - (\vec{\sigma} \cdot \vec{E}) \hat{k}(\vec{\sigma} \cdot \vec{\pi}) \right| \Psi_u^0 \right\rangle \\ &- \left\langle \Psi_u^0 \left| g_1 \frac{e\hbar}{8m_0^2c^3} (\vec{\sigma} \cdot \vec{\pi}) \hat{k}(\vec{\sigma} \cdot \vec{B}) \hat{k}(\vec{\sigma} \cdot \vec{\pi}) \right| \Psi_u^0 \right\rangle \end{aligned}$$

The first term

$$\hat{H}'(1) = g_1 \frac{e\hbar}{2m_0c} (\vec{\sigma} \cdot \vec{B})$$

can be split into a contribution from the external magnetic field, which provides a *Zeeman term correction*

$$\hat{H}'(1a) = g_1 \frac{e\hbar}{2m_0c} (\vec{\sigma} \cdot \vec{B}_{\text{ext}})$$

and a correction term from the internal dipolar field, which represents a *dipolar hyperfine term correction*

$$\begin{aligned} \hat{H}'_N(1a) &= g_1 \frac{e\hbar}{2m_0c} (\vec{\sigma} \cdot \vec{B}_N) \\ &= -g_1 \frac{e\hbar}{2m_0c} r_{Ne}^{-5} [r_{Ne}^2 (\vec{\sigma} \cdot \vec{\mu}_N) - 3(\vec{\sigma} \cdot \vec{r}_{Ne})(\vec{\mu}_N \cdot \vec{r}_{Ne})] \end{aligned}$$

The second term is rearranged as

$$\hat{H}'(2) = -2g_1 \frac{ie\hbar}{8m_0^2c^2} [(\vec{\sigma} \cdot \vec{E}) \hat{k}(\vec{\sigma} \cdot \vec{\pi}) - (\vec{\sigma} \cdot \vec{\pi}) \hat{k}(\vec{\sigma} \cdot \vec{E})]$$

and can be manipulated through the replacement of $\hat{k}$ by $\hat{k}_0$ with the additional commutator being neglected. The effect of this term is a correction to terms arising from $\hat{H}_1^{(1)}$: the Darwin term, the spin-orbit interaction term and the Fermi contact hyperfine term. In these terms the correction involves $2g_1$ instead of g_1 so that a different magnetogyric factor results

$$g' = 2(1 + 2g_1)$$

Thus the correct spin-orbit interaction term involves $\vec{\sigma} \rightarrow (g'/\hbar)\vec{s}$ and is

$$\hat{H}^{s-l} = \frac{\hbar e^2}{16\pi\epsilon_0 m_0^2 c^2} Z_N \hat{k}_0^2 r_{Ne}^{-3} (\vec{\sigma} \cdot \vec{l}_{Ne}) = \frac{e^2}{16\pi\epsilon_0 m_0^2 c^2} g' Z_N \hat{k}_0^2 r_{Ne}^{-3} (\vec{s} \cdot \vec{l}_{Ne})$$

4.8 MOLECULAR HAMILTONIAN TERMS

The molecular Hamiltonian terms resulting from the relativistic approach are collected in Table 4.6.

SUMMARY

1. The Dirac equation represents a proper relativistic form of the characteristic equation for energy. It is fulfilled for state vectors in a form of a four-component spinor. Since the upper two-component spinor dominates in the positive energy solutions for an electron, a decomposition of the Dirac equation is appropriate.
2. In the presence of the electromagnetic potential a new term appears in the quadratic form of the Dirac equation. This allows an introduction of the intrinsic magnetic moment of an electron, generated by its spin, which interacts with the external magnetic field.
3. The decoupling of the Dirac equation to the two-component form is a rather complicated process. It manipulates the resolvent operator which is transferred from the denominator to the numerator and then exposed to consecutive commutator relations in order to be shifted to the far right. Finally, a number of one-electron terms of the order $1/c^2$ is obtained; some of them have no classical analogy and cannot be derived from non-relativistic theories.
4. The Lorenz transformation requires some additional terms in the electron-electron interaction resulting in the Breit operator. The two-electron Breit Hamiltonian consists of the Dirac Hamiltonian for the individual electrons plus the Breit operator. The decoupling of the Breit equation to the upper-upper subspace of interest results in the appearance of several new Hamiltonian terms.
5. Slight modification of the electron g -factor is due to the radiative corrections introduced through quantum electrodynamics. The magnetogyric factor is different for the Zeeman interaction and the spin-orbit term.

TABLE 4.6
Hamiltonian terms

No.	Description	Origin	Operator	Usage
<i>(a) Schrödinger terms</i>				
1	kinetic energy of electrons	$\hat{T}_e, \hat{H}^{0b}(1)$	$-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2$	$\hat{H}_0$
2	kinetic energy of nuclei	$\hat{T}_N$	$-\sum_N \frac{\hbar^2}{2m_N} \nabla_N^2$	$\hat{H}_0$
3	interelectron Coulomb repulsion	$\hat{V}_{ee}, \hat{H}_{12}^a$	$\sum_i \sum_{j<i} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}}$	$\hat{H}_0$
4	electron–nuclear Coulomb attraction	$\hat{V}_{eN}, \hat{H}_N^{0a}(2)$	$-\sum_i \sum_N \frac{e^2}{4\pi\epsilon_0} Z_N \frac{1}{r_{Ni}}$	$\hat{H}_0$
5	internuclear Coulomb repulsion	$\hat{V}_{NN}$	$\sum_N \sum_{M<N} \frac{e^2}{4\pi\epsilon_0} Z_N Z_M \frac{1}{r_{NM}}$	$\hat{H}_0$
<i>(b) Relativistic corrections</i>				
6	electron kinetic energy correction	$\hat{H}^{1b}(1)$	$-\sum_i \frac{\hbar^4}{8m_e^3 c^2} \nabla_i^4$	$\hat{H}_0$ for heavy atoms
7	electron–nuclear Darwin term	$\hat{H}_N^{1a}(1)$	$\sum_i \sum_N \left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_e}\right)^2 2\pi Z_N \delta(\vec{r}_{Ni})$	$\hat{H}_0$ for heavy atoms
8	interelectron Darwin term	$\hat{H}_{12}^b(1)$	$-\sum_i \sum_{j<i} \left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_e}\right)^2 4\pi \delta(\vec{r}_{ji})$	neglected

9	interelectron orbital interaction	$\hat{H}_{12}^c(4)$	$\sum_i \sum_{j<i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 2\pi \left[\frac{1}{r_{ij}} \vec{\nabla}_i \cdot \vec{\nabla}_j + \frac{1}{r_{ij}^3} (\vec{r}_{ij} \cdot \vec{\nabla}_i)(\vec{r}_{ij} \cdot \vec{\nabla}_j) \right]$	neglected
10	interelectron orbital interaction	$\hat{H}_{12}^c(5)$	$\sum_i \sum_{j<i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 \frac{1}{r_{ij}^3} [(\vec{r}_{ji} \cdot \vec{\nabla}_i) - (\vec{r}_{ji} \cdot \vec{\nabla}_j)]$	neglected
11	interelectron orbital interaction	$\hat{H}_{12}^c(6)$	$-\sum_i \sum_{j<i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 4\pi \delta(\vec{r}_{ji}) [(\vec{r}_{ji} \cdot \vec{\nabla}_i) - (\vec{r}_{ji} \cdot \vec{\nabla}_j)]$	neglected
<i>(c) Terms depending on magnetic field $\vec{B}_{\text{ext}}$</i>				
12	diamagnetic term	$\hat{H}^{0b}(3a)$	$\sum_i \frac{e^2}{8m_e} [B_{\text{ext}}^2 r_{Gi}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Gi})^2]$	$\hat{H}_{200} \rightarrow \bar{k}^{\text{dia}}$
13	higher-order diamagnetic correction	$\hat{H}^{0b}(3a)$	$-\sum_i \frac{e^3}{16m_e^2 c^2} \hat{k}_0(r_i) \Phi_{\text{int}} [B_{\text{ext}}^2 r_{Gi}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Gi})^2]$	neglected
14	higher-order diamagnetic correction	$\hat{H}^{1b}(7a)$	$-\sum_i \frac{e^4}{128m_e^2 c^2} \hat{k}_0^3(r_i) [B_{\text{ext}}^2 r_{Gi}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Gi})^2]^2$	neglected
15	orbital Zeeman interaction	$\hat{H}^{0b}(2a)$	$-i \sum_i \left(\frac{e\hbar}{2m_e} \right) \vec{B}_{\text{ext}} \cdot (\vec{r}_{Gi} \times \vec{\nabla}_i)$	$\hat{H}_{100} \rightarrow \bar{k}^{\text{para}}, \bar{\sigma}_N^{\text{para}}, \bar{\Delta g}$
16	higher-order orbital Zeeman correction	$\hat{H}^{0b}(2a)$	$-\sum_i \frac{e^2}{8m_e^2 c^2} [\hat{k}_0(r_i) \Phi_{\text{int}} \vec{B}_{\text{ext}} \cdot (\vec{r}_{Gi} \times \vec{\nabla}_i) + \vec{B}_{\text{ext}} \cdot (\vec{r}_{Gi} \times \vec{\nabla}_i) \Phi_{\text{int}} \hat{k}_0(r_i)]$	neglected

(contd.)

TABLE 4.6
Hamiltonian terms (*contd.*)

No.	Description	Origin	Operator	Usage
17	orbital Zeeman–kinetic energy correction	$\hat{H}^{1b}(2a)$	$-i \sum_i \frac{e\hbar^3}{4m_e^3 c^2} [\hat{k}_0^3(r_i) \nabla_i^2 (\vec{r}_{Gi} \times \vec{\nabla}_i) \cdot \vec{B}_{\text{ext}}]$	neglected
<i>(d) Terms depending on electric field Φ</i>				
18	electron–external field interaction	$\hat{H}^{0a}(1)$	$-e\Phi_{\text{ext}}$	vanishes for $\Phi_{\text{ext}} = 0$
19	higher-order field correction	$\hat{H}^{1c}(1) + \hat{H}^{0b}(1^*)$	$-\sum_i \frac{e\hbar^2}{8m_e^2 c^2} [(\Phi - \Phi_{\text{int}}) \nabla_i^2 + \nabla_i^2 (\Phi - \Phi_{\text{int}})]$	vanishes for $\Phi_{\text{ext}} = 0$
20	higher-order field correction	$\hat{H}^{1c}(2) + \hat{H}^{0b}(2^*)$	$-i \sum_i \frac{e^2 \hbar}{8m_e^2 c^2} [(\Phi - \Phi_{\text{int}}) \vec{B}_{\text{ext}} \cdot (\vec{r}_{Gi} \times \vec{\nabla}_i) + \vec{B}_{\text{ext}} \cdot (\vec{r}_{Gi} \times \vec{\nabla}_i) (\Phi - \Phi_{\text{int}})]$	vanishes for $\Phi_{\text{ext}} = 0$
21	higher-order field correction	$\hat{H}^{1c}(3) + \hat{H}^{0b}(3^*)$	$\sum_i \frac{e^3}{16m_e^2 c^2} (\Phi - \Phi_{\text{int}}) [B_{\text{ext}}^2 r_{Gi}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Gi})^2]$	vanishes for $\Phi_{\text{ext}} = 0$
<i>(e) Terms depending on electron spin $\vec{s}_i$</i>				
22	spin–(own)orbit interaction	$\hat{H}_N^{1a}(3)$	$-i \sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 g' Z_N \hat{k}_0^2(\vec{r}_{Ni}) \frac{1}{r_{Ni}^3} \vec{s}_i \cdot (\vec{r}_{Ni} \times \vec{\nabla}_i)$	$\hat{H}_{001} \rightarrow \overline{\overline{\Delta g}}, \overline{\overline{D}}, \overline{\overline{T}}_N$
23	spin–other orbit interaction	$\hat{H}_{12}^c(1a)$	$i \sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 4 \frac{1}{r_{ij}^3} \vec{s}_i \cdot (\vec{r}_{ij} \times \vec{\nabla}_j)$	$\hat{H}_{001} \rightarrow \overline{\overline{\Delta g}}, \overline{\overline{D}}, \overline{\overline{T}}_N$
24	electron–electron spin–orbit interaction	$\hat{H}_{12}^b(2)$	$i \sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 g' \frac{1}{r_{ij}^3} \vec{s}_i \cdot (\vec{r}_{ji} \times \vec{\nabla}_i)$	$\hat{H}_{001} \rightarrow \overline{\overline{\Delta g}}, \overline{\overline{D}}, \overline{\overline{T}}_N$

25	spin–spin dipolar interaction	$\hat{H}_{12}^c(2)$	$\sum_i \sum_{j < i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 4 \left[\frac{1}{r_{ij}^3} (\vec{s}_i \cdot \vec{s}_j) - \frac{3}{r_{ij}^5} (\vec{s}_i \cdot \vec{r}_{ji})(\vec{s}_j \cdot \vec{r}_{ji}) \right]$	$\hat{H}_{002} \rightarrow \bar{\bar{D}}$
26	spin–spin contact interaction	$\hat{H}_{12}^c(3)$	$- \sum_i \sum_{j < i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 \frac{32\pi}{3} \delta(\vec{r}_{ji}) \vec{s}_i \cdot \vec{s}_j$	$\hat{H}_{002} \rightarrow \bar{\bar{D}}$
<i>(f) Terms depending on nuclear spin $\vec{I}_N$</i>				
27	internuclear spin–spin dipolar interaction		$\sum_N \sum_{M < N} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_p} \right)^2 g_N g_M \left[\frac{1}{r_{NM}^3} (\vec{I}_N \cdot \vec{I}_M) - \frac{3}{r_{NM}^5} (\vec{I}_N \cdot \vec{r}_{MN})(\vec{I}_M \cdot \vec{r}_{MN}) \right]$	$\hat{H}_{020} \rightarrow \bar{\bar{K}}_{NM}^{\text{dia}}$
28	nuclear quadrupole interaction	$\hat{H}^q$	$\sum_i \sum_N \frac{e^2}{4\pi\epsilon_0} \frac{Q_N}{2I_N(2I_N - 1)} \left[\frac{1}{r_{Ni}^3} \vec{I}_N^2 - \frac{3}{r_{Ni}^5} (\vec{I}_N \cdot \vec{r}_{Ni})^2 \right]$	$\hat{H}_{020} \rightarrow \bar{\bar{K}}_{NN}^{\text{dia}}$
29	orbital hyperfine interaction	$\hat{H}^{0b}(2b)$	$-i \sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right) \left(\frac{e\hbar}{2m_p} \right) 2g_N \hat{k}_0(r_{Ni}) \frac{1}{r_{Ni}^3} \vec{I}_N \cdot (\vec{r}_{Ni} \times \vec{\nabla}_i)$	$\hat{H}_{010} \rightarrow \bar{\bar{K}}_{NM}^{\text{para}}, \bar{\bar{\sigma}}_N^{\text{para}}$
30	orbital hyperfine correction	$\hat{H}^{1b}(2b)$	$i \sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right) \left(\frac{e\hbar}{2m_p} \right) \left(\frac{\hbar}{m_e c} \right)^2 g_N \hat{k}_0^3(r_{Ni}) \nabla_i^2 \frac{1}{r_{Ni}^3} \vec{I}_N \cdot (\vec{r}_{Ni} \times \vec{\nabla}_i)$	neglected
31	electron coupled nuclear spin–spin interaction	$\hat{H}_{NM}^{0b}(3c)$	$\sum_i \sum_N \sum_M \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e\hbar}{2m_p} \right)^2 \frac{e^2}{2m_e} g_N g_M \hat{k}_0(r_{Ni}) \frac{1}{r_{Ni}^3} \frac{1}{r_{Mi}^3} [(\vec{I}_N \cdot \vec{I}_M)(\vec{r}_{Ni} \cdot \vec{r}_{Mi}) - (\vec{I}_N \cdot \vec{r}_{Mi})(\vec{I}_M \cdot \vec{r}_{Ni})]$	$\hat{H}_{020} \rightarrow \bar{\bar{K}}_{NM}^{\text{dia}}$

TABLE 4.6
Hamiltonian terms (*contd.*)

No.	Description	Origin	Operator	Usage
<i>(g) Terms depending on electron spin and magnetic field</i>				
32	(electron spin) Zeeman term	$\hat{H}^{0b}(4a)$	$\sum_i \left(\frac{e\hbar}{2m_e} \right) g_e (\vec{s}_i \cdot \vec{B}_{\text{ext}})$	$\hat{H}_{101} \rightarrow g_e$
33	Zeeman–kinetic energy correction	$\hat{H}^{1b}(4a)$	$\sum_i \left(\frac{e\hbar}{2m_e} \right) \left(\frac{\hbar}{m_e c} \right)^2 \frac{g_e}{2} (\vec{s}_i \cdot \vec{B}_{\text{ext}}) \nabla_i^2$	$\hat{H}_{101} \rightarrow \overline{\overline{\Delta g}}$
34	spin–orbit Zeeman gauge correction	$\hat{H}_N^{1a}(5a)$	$\sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right) \frac{e^2}{4m_e} g' Z_N$ $\tilde{k}_0^2(r_{Ni}) \frac{1}{r_{Ni}^3} [(\vec{r}_{Ni} \cdot \vec{r}_{Gi})(\vec{s}_i \cdot \vec{B}_{\text{ext}}) - (\vec{s}_i \cdot \vec{r}_{Gi})(\vec{r}_{Ni} \cdot \vec{B}_{\text{ext}})]$	$\hat{H}_{101} \rightarrow \overline{\overline{\Delta g}}$
35	spin–other orbit Zeeman gauge correction	$\hat{H}_{12}^c(1b)$	$\sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right) \frac{e^2}{m_e} \frac{1}{r_{ij}^3} [(\vec{r}_{ji} \cdot \vec{r}_{Gj})(\vec{s}_i \cdot \vec{B}_{\text{ext}}) - (\vec{s}_i \cdot \vec{r}_{Gj})(\vec{r}_{ji} \cdot \vec{B}_{\text{ext}})]$	$\hat{H}_{101} \rightarrow \overline{\overline{\Delta g}}$
36	electron–electron spin–orbit Zeeman gauge correction	$\hat{H}_{12}^b(3a)$	$-\sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right) \frac{e^2}{4m_e} g'$ $\frac{1}{r_{ij}^3} [(\vec{r}_{ji} \cdot \vec{r}_{Gi})(\vec{s}_i \cdot \vec{B}_{\text{ext}}) - (\vec{s}_i \cdot \vec{r}_{Gi})(\vec{r}_{ji} \cdot \vec{B}_{\text{ext}})]$	$\hat{H}_{101} \rightarrow \overline{\overline{\Delta g}}$
<i>(h) Terms depending on nuclear spin and magnetic field</i>				
37	nuclear Zeeman term		$\sum_N \left(\frac{e\hbar}{2m_p} \right) g_N (\vec{I}_N \cdot \vec{B}_{\text{ext}})$	$\hat{H}_{110} \rightarrow g_N$

38	electron–nuclear Zeeman correction	$\hat{H}_N^{0b}$ (3b)	$\sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_p} \right) \frac{e^2}{2m_e} g_N$ $\hat{k}_0(r_{Ni}) \frac{1}{r_{Ni}^3} [(\vec{B}_{\text{ext}} \cdot \vec{I}_N)(\vec{r}_{Gi} \cdot \vec{r}_{Ni}) - (\vec{B}_{\text{ext}} \cdot \vec{r}_N)(\vec{r}_{Gi} \cdot \vec{I}_N)]$	$\hat{H}_{110} \rightarrow \bar{\sigma}_N^{\text{dia}}$
(i)	Terms depending on electron and nuclear spins			
39	dipolar hyperfine interaction	$\hat{H}^{0b}$ (4b)	$- \sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right) \left(\frac{e\hbar}{2m_p} \right) g_e g_N$ $\hat{k}_0(r_{Ni}) \left[\frac{1}{r_{Ni}^3} (\vec{s}_i \cdot \vec{I}_N) - \frac{3}{r_{Ni}^5} (\vec{s}_i \cdot \vec{r}_{Ni})(\vec{I}_N \cdot \vec{r}_{Ni}) \right]$	$\hat{H}_{011} \rightarrow \bar{T}_N, \bar{K}_{NM}^{\text{para}}$
40	Fermi contact hyperfine interaction	$\hat{H}_{NN}^{1a}$ (5b')	$\sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right) \left(\frac{e\hbar}{2m_p} \right) \frac{8\pi}{3} g' g_N \delta(r_{Ni}) (\vec{s}_i \cdot \vec{I}_N)$	$\hat{H}_{011} \rightarrow \bar{T}_N, \bar{K}_{NM}^{\text{para}}$
41	spin–orbit hyperfine correction	$\hat{H}^{1a}$ (5b)	$\sum_i \sum_N \sum_{M \neq N} \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e\hbar}{2m_e} \right) \left(\frac{e\hbar}{2m_p} \right) \frac{e^2}{2m_e} g' g_N Z_M$ $[\hat{k}_0(r_{Mi})]^2 \frac{1}{r_{Ni}^3} \frac{1}{r_{Mi}^3} [(\vec{r}_{Ni} \cdot \vec{r}_{Mi})(\vec{s}_i \cdot \vec{I}_N) - (\vec{s}_i \cdot \vec{r}_{Ni})(\vec{I}_N \cdot \vec{r}_{Mi})]$	$\hat{H}_{011} \rightarrow \bar{T}_N, \bar{K}_{NM}^{\text{para}}$
42	spin–other orbit hyperfine correction	$\hat{H}_{12}^c$ (1c)	$- \sum_i \sum_{j \neq i} \sum_N \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e\hbar}{2m_e} \right) \left(\frac{e\hbar}{2m_p} \right) \frac{e^2}{m_e} 2g_N \frac{1}{r_{ij}^3} \frac{1}{r_{Ni}^3}$ $[(\vec{r}_{ij} \cdot \vec{r}_{Nj})(\vec{I}_N \cdot \vec{s}_i) - (\vec{r}_{ij} \cdot \vec{I}_N)(\vec{r}_{Nj} \cdot \vec{s}_j)]$	$\hat{H}_{011} \rightarrow \bar{T}_N, \bar{K}_{NM}^{\text{para}}$

(contd.)

TABLE 4.6
Hamiltonian terms (*contd.*)

No.	Description	Origin	Operator	Usage
43	electron–electron spin–orbit hyperfine correction	$\hat{H}_{12}^b(3b)$	$\sum_i \sum_{j \neq i} \sum_N \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e\hbar}{2m_e} \right) \left(\frac{e\hbar}{2m_p} \right) \frac{e^2}{2m_e} g' g_N$ $\frac{1}{r_{ij}^3} \frac{1}{r_{Ni}^3} [(\vec{r}_{ij} \cdot \vec{r}_{Ni})(\vec{I}_N \cdot \vec{s}_i) - (\vec{r}_{ij} \cdot \vec{I}_N)(\vec{r}_{Ni} \cdot \vec{s}_i)]$	$\hat{H}_{011} \rightarrow \bar{T}_N, \bar{K}_{NM}^{\text{para}}$

The reduced resolvent operator originating in the partitioning method is $\hat{k}_0 = (1 + e\Phi_{\text{int}}/2m_e c)^{-1}$; the internal electrostatic field generated by nuclei is $\Phi_{\text{int}} = (e/4\pi\epsilon_0) \sum_N Z_N r_{Ni}^{-1}$; the magnetogyric Zeeman factor for electrons is $g_e = 2(1 + g_1)$; the magnetogyric spin–orbit factor for electrons is $g' = 2(1 + 2g_1)$; the magnetogyric factors for nuclei g_N are phenomenological constants. Notice that in SI units $\epsilon_0 \mu_0 c^2 = 1$; the Bohr magneton is $\mu_B = e\hbar/2m_e$; the nuclear magneton is $\mu_p = e\hbar/2m_p$. The position vectors are defined as $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i = -\vec{r}_{ji}$; terms including magnetic field contain $\vec{r}_{Gi} = \vec{r}_i - \vec{r}_G$ where $\vec{r}_G$ is the position of the arbitrarily chosen gauge origin. The electron spin $\vec{s}_i$ and nuclear spin $\vec{I}_N$ are given in units of $\hbar$. Indices i, j label electrons and N, M nuclei. The imaginary unit and the eventual minus sign are situated before summations.

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Evaluation of Magnetic Parameters

5.1 METHODS

When the energy of the system depends upon the magnetic field $\vec{B}$, electron spin $\vec{S}$ and nuclear spins $\vec{I}_N$, the set of magnetic parameters is covered by the second-rank tensors $\bar{\bar{k}}$, $\bar{\bar{D}}$, $\bar{\bar{\Delta g}}$, $\bar{\bar{\sigma}}_N$, $\bar{\bar{T}}_N$ and $\bar{\bar{K}}_{NM}$. These are the *reduced magnetic parameters*, interrelated with the observed (measured) quantities according to Table 5.1.

Each magnetic parameter is received as a second derivative of the total energy with respect to the pertinent variables [1]. The total energy can be viewed as an expectation value of the molecular Hamiltonian which includes all the interaction terms. Some of the Hamiltonian terms were constructed on the basis of non-relativistic quantum theory. It should be noticed, however, that the relativistic quantum theory brings new terms which are usually truncated at the cut-off of $1/c^2$.

There is one principal complication which arises from the fact that the electromagnetic vector potential is uncertain (invariant) with respect to gauge transformation. Consequently the magnetic parameters involving the derivatives with respect to $\vec{B}$ contain integrals which depend upon a choice of the gauge origin [2]. The gauge-dependent magnetic parameters are $\bar{\bar{k}}$, $\bar{\bar{\Delta g}}$ and $\bar{\bar{\sigma}}_N$. The remaining magnetic parameters ($\bar{\bar{D}}$, $\bar{\bar{T}}_N$ and $\bar{\bar{K}}_{NM}$) do not suffer such a complication.

To evaluate the magnetic parameters several methods have been developed (Table 5.2):

- (a) a molecular orbital method and a (sum-over-states) perturbation theory;
- (b) magnetic orbitals and a finite perturbation theory;
- (c) London atomic orbital (LAO) method, also known as the gauge invariant atomic orbitals (GIAO) method [3–6];
- (d) IGLO—Individual gauge for localized orbitals [7–11];
- (e) LORG—Localized origin gauge [12,13];
- (f) IGAIM—Individual gauges for atoms in molecules [14];
- (g) DOGON—Distributed origin gauge with origin at the nuclei [15];
- (h) CTOCD—Continuous transformation of origin of current density [16].

TABLE 5.1
Relationships between magnetic parameters

Meaning	Reduced parameter	Observed (measured) parameter ^a
magnetic susceptibility	$\bar{\kappa}$	$\bar{\chi} = N_A \mu_0 \bar{\kappa}$
magnetogyric tensor (<i>g</i> -factor)	$\bar{\Delta g}$	$\bar{g} = g_e \bar{1} + \bar{\Delta g}$
nuclear shielding tensor	$\bar{\sigma}_N$	$\bar{\gamma}_N = \hbar g_N \mu_p (\bar{1} - \bar{\sigma}_N)$
nuclear spin–spin coupling tensor (constant)	$\bar{K}_{MN}$	$\bar{J}_{MN} = (\hbar/2\pi) \gamma_M \gamma_N \bar{K}_{MN}$
electron–nuclear hyperfine tensor	$\bar{T}_N$	$\bar{I}_N = g_e \mu_B \gamma_N \hbar \bar{T}_N$

^a Magnetogyric ratio of nucleus *N* is $\gamma_N = g_N \mu_p / \hbar$.

TABLE 5.2
Comparison of methods evaluating magnetic parameters

Method	Perturbation theory	Gauge factors	Problems
molecular orbitals	SOS-PT	none	rough values of excitation energies, infinite sum (slow convergence), gauge variance
magnetic orbitals	FPT	none	complex MOs, gauge variance
GIAO	FPT	for each AO	new integrals of higher angular momentum, coupled Hartree–Fock equations, complex MOs
IGLO	FPT	for each LMO	coupled Hartree–Fock equations, complex MOs, complicated formulae
LORG IGAIm DOGON CTOCD	SOS-PT	for each LMO	diagonalisation of energy resolvent

5.1.1 Molecular orbital method and sum-over-states perturbation theory

A magnetic parameter in tensor form can be evaluated as a sum of two contributions: the first term expressed over the ground-state wave function and the second term involving transition moments between the ground-state and excited-state wave functions

$$\begin{aligned} \overline{X}^{\lambda_1 \lambda_2} &= \left(\frac{\partial^2 E(\lambda_1, \lambda_2)}{\partial \lambda_1 \partial \lambda_2} \right)_{\lambda_1 = \lambda_2 = 0} = \left\langle \Psi_0 \left| \frac{\partial^2 \hat{H}^{(\lambda_1, \lambda_2)}}{\partial \lambda_1 \partial \lambda_2} \right| \Psi_0 \right\rangle \\ &\quad - \sum_{K=1}^{\infty} \frac{1}{E_K - E_0} \left\langle \Psi_0 \left| \frac{\partial \hat{H}^{(\lambda_1)}}{\partial \lambda_1} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \frac{\partial \hat{H}^{(\lambda_2)}}{\partial \lambda_2} \right| \Psi_0 \right\rangle \end{aligned}$$

In the molecular orbital method the ground-state determinantal wave function $|\Psi_0\rangle = |\Psi^{(0,0,0)}\rangle$ is constructed from the set of occupied molecular spin-orbitals $\{\varphi_i\}$. Then the matrix elements of the one- and two-electron operators can be evaluated by utilising the Slater rules. The expectation value of a one-electron operator is

$$\left\langle \Psi_0 \left| \sum_i \hat{h}_i \right| \Psi_0 \right\rangle = \sum_o^{\text{occ}} \langle \varphi_o | \hat{h}_1 | \varphi_o \rangle$$

and that of a two-electron operator is

$$\left\langle \Psi_0 \left| \sum_i \sum_{j < i} \hat{h}_{ij} \right| \Psi_0 \right\rangle = \sum_o^{\text{occ}} \sum_{p < o}^{\text{occ}} \left[\langle \varphi_o \varphi_p | \hat{h}_{12} | \varphi_o \varphi_p \rangle - \langle \varphi_o \varphi_p | \hat{h}_{12} | \varphi_p \varphi_o \rangle \right]$$

Within the LCAO approximation, when the molecular orbitals are expanded over the basis set of atomic orbitals $|\chi_\mu\rangle$

$$|\phi_i\rangle = \sum_{\mu} C_{i\mu} |\chi_\mu\rangle$$

the relevant information is carried by the bond-order matrix $\mathbf{P}$ consisting of a contribution from α - and β -electrons, respectively

$$\mathbf{P} = \mathbf{P}^\alpha + \mathbf{P}^\beta$$

where

$$P_{\mu\nu}^\alpha = \sum_o^{\text{occ}} C_{o\mu}^{\alpha*} C_{ov}^\alpha$$

Then the expectation value of a one-electron spinless operator becomes

$$\left\langle \Psi_0 \left| \sum_i \hat{h}_i \right| \Psi_0 \right\rangle = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} (P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta) \langle \chi_\mu | \hat{h}_1 | \chi_\nu \rangle$$

and that of the two-electron operator is

$$\left\langle \Psi_0 \left| \sum_i \sum_{j < i} \hat{h}_{ij} \right| \Psi_0 \right\rangle = \frac{1}{2} \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} \sum_{\lambda}^{\text{AO}} \sum_{\sigma}^{\text{AO}} \left\langle \chi_{\mu} \chi_{\lambda} \left| \hat{h}_{12} \right| \chi_{\nu} \chi_{\sigma} \right\rangle \\ [(P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta})(P_{\lambda\sigma}^{\alpha} + P_{\lambda\sigma}^{\beta}) - P_{\mu\sigma}^{\alpha} P_{\lambda\nu}^{\alpha} - P_{\mu\sigma}^{\beta} P_{\lambda\nu}^{\beta}]$$

The sum-over-states perturbation theory (SOS-PT) requires an evaluation of matrix elements between the ground and monoexcited electron configurations and again the Slater rules are helpful

$$\left\langle \Psi_0 \left| \sum_i \hat{h}_i \right| \Psi_K \right\rangle = \left\langle \varphi_o \left| \hat{h}_1 \right| \varphi_u \right\rangle$$

where the index o (occupied) and u (unoccupied) identifies the different spin-orbitals between the ground and the monoexcited $|\Psi_K\rangle = |\Psi_o^u\rangle$ configurations. The above reduction is true when the wave function for an excited state is single-determinantal. However, this is not the case for monoexcited configurations which require a linear combination of two determinantal functions in order to maintain a proper symmetry

$$|\Psi_K\rangle = |\Psi_o^u\rangle = \frac{1}{\sqrt{2}} (|\phi_1 \bar{\phi}_1 \dots \phi_o \bar{\phi}_u \dots| - |\phi_1 \bar{\phi}_1 \dots \bar{\phi}_o \phi_u \dots|) \\ = \frac{1}{\sqrt{2}} (|\phi_1 \bar{\phi}_1 \dots \phi_o \bar{\phi}_u \dots| + |\phi_1 \bar{\phi}_1 \dots \phi_u \bar{\phi}_o \dots|)$$

Consequently

$$\left\langle \Psi_0 \left| \sum_i \hat{h}_i \right| \Psi_o^u \right\rangle = \frac{1}{\sqrt{2}} (\langle \phi_o | \hat{h}_1 | \phi_u \rangle + \langle \phi_u | \hat{h}_1 | \phi_o \rangle) = \sqrt{2} \langle \phi_o | \hat{h}_1 | \phi_u \rangle$$

Then the perturbation formula involving one-electron operators is expanded as

$$R^{\lambda_1 \lambda_2} = \sum_K \frac{1}{E_K - E_0} \left\langle \Psi_0 \left| \sum_i \hat{h}_i^{(\lambda_1)} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \sum_i \hat{h}_i^{(\lambda_2)} \right| \Psi_0 \right\rangle \\ = 2 \sum_o^{\text{occ}} \sum_u^{\text{un}} \frac{1}{\Delta E_o^u} \langle \phi_o | \hat{h}_1^{(\lambda_2)} | \phi_u \rangle \langle \phi_u | \hat{h}_1^{(\lambda_2)} | \phi_o \rangle$$

where ΔE_o^u is an excitation energy within the molecular orbital method. For example, the singlet excitation energy from the ground singlet state is expressed as

$$^1\Delta E_o^u = \varepsilon_u - \varepsilon_o - J_{ou} + 2K_{ou}$$

where ε_o (ε_u) are energies of occupied (unoccupied) molecular orbitals; J_{ou} (K_{ou}) are the Coulomb (exchange) integrals over pertinent molecular orbitals. Some formulae for excitation energies are collected in Table 5.3.

The evaluation of the excitation energies for the purpose of SOS-PT is crucial since accurate values need large basis sets and the inclusion of correlation effects.

A more general problem arises from the fact that the usual wave functions do not guarantee gauge invariance: the result may depend on the position of the molecule in the Cartesian frame. This behaviour originates in the fact that the magnetic field modifies the momenta. For example, the magnetic field applied in the z -direction twists the orbitals around the z -axis in the imaginary xy -plane. For an atom far from the z -axis the rotation of the orbitals can be accommodated by using basis set functions having high angular momenta. The use of very large basis sets guarantees an approximate gauge invariance. In the limit of a complete basis set the result is a gauge invariant [2].

5.1.2 Random phase approximation

The central problem of the sum-over-states perturbation theory lies in the evaluation of the energy resolvent which includes the inverse of excitation energies and transition moments of the one-electron operators

$$R^{\lambda_1\lambda_2} = \sum_{K=1}^{\infty} \frac{1}{E_K - E_0} \left[\vec{e}^{(\lambda_1)} \times \left\langle \Psi_0 \left| \vec{h}^{(\lambda_1)} \right| \Psi_K \right\rangle \right] \cdot \left[\vec{e}^{(\lambda_2)} \times \left\langle \Psi_K \left| \vec{h}^{(\lambda_2)} \right| \Psi_0 \right\rangle \right]$$

TABLE 5.3

Excitation energies in the MO method^a

States	RHF formula	LHP formula
$^1\Delta E_o^u$	$\varepsilon_u - \varepsilon_o - J_{ou} + 2K_{ou}$	
$^2\Delta E_o^u$	$\varepsilon_u - \varepsilon_o - J_{ou} + 2K_{os} + 2K_{us}$	$\varepsilon_u - \varepsilon_o - J_{ou} + 2K_{ou}$
$^2\Delta E_s^u$	$\varepsilon_u - \varepsilon_s - J_{su} + \frac{3}{2}K_{su} + \frac{1}{2}J_{ss}$	$\varepsilon_u - \varepsilon_s - J_{su} + \frac{1}{2}K_{su} + \frac{1}{2}J_{ss}$
$^2\Delta E_o^s$	$\varepsilon_s - \varepsilon_o - J_{os} + \frac{3}{2}K_{os} + \frac{1}{2}J_{ss}$	$\varepsilon_s - \varepsilon_o - J_{os} + \frac{1}{2}K_{os} + \frac{1}{2}J_{ss}$

^aDesignation of molecular orbitals: o —doubly occupied, s —singly occupied, u —unoccupied [17].

Here $\vec{e}^{(\lambda_1)}$ and $\vec{e}^{(\lambda_2)}$ are unit vectors along the directions of the magnetic field (the applied magnetic field or the internal magnetic field generated by nuclear magnetic moments and the electronic magnetic moment, respectively); $\hat{h}^{(\lambda_1)}$ and $\hat{h}^{(\lambda_2)}$ are the corresponding one-electron operators. Within the philosophy of the *random phase approximation* (RPA) the transition moments of a real Hermitian one-electron operator can be expressed in the form

$$M_{0K} = \langle \Psi_0 | \hat{h}_{\text{Re}} | \Psi_K \rangle = \sum_o^{\text{occ}} \sum_u^{\text{un}} \langle \Psi_0 | \hat{h}_{\text{Re}} | \Psi_o^u \rangle (S_K)_o^u$$

where $|\Psi_o^u\rangle$ is a configuration (determinantal) function generated by electron excitation from an occupied into an unoccupied molecular orbital. Analogously, the transition moments of a purely imaginary Hermitian one-electron operator are

$$M_{0K} = \langle \Psi_0 | \hat{h}_{\text{Im}} | \Psi_K \rangle = \sum_o^{\text{occ}} \sum_u^{\text{un}} \langle \Psi_0 | \hat{h}_{\text{Im}} | \Psi_o^u \rangle (T_K)_o^u$$

The amplitudes $(S_K)_o^u$ and $(T_K)_o^u$ are determined from the coupled sets of linear RPA equations

$$\sum_o^{\text{occ}} \sum_u^{\text{un}} (A + B)_{po}^{vu} (S_K)_o^u = \omega_K (T_K)_p^v$$

and

$$\sum_o^{\text{occ}} \sum_u^{\text{un}} (A - B)_{po}^{vu} (T_K)_o^u = \omega_K (S_K)_p^v$$

where the matrix elements just introduced

$$A_{po}^{vu} = \langle \Psi_p^v | \hat{H}_0 - E_0 | \Psi_o^u \rangle$$

$$B_{po}^{vu} = \langle \Psi_{po}^{vu} | \hat{H}_0 | \Psi_0 \rangle$$

involve monoexcitation energies and biexcitation energies. Here $|\Psi_{op}^{uv}\rangle$ is a doubly excited configurational wave function and ω_K is the eigenvalue for the transition energy $(E_K - E_0)$; $\hat{H}_0$ is the unperturbed molecular Hamiltonian, E_0 is the Hartree-Fock ground-state energy. The amplitudes fulfil the orthonormality relation

$$\sum_o^{\text{occ}} \sum_u^{\text{un}} (S_K)_o^u (T_L)_o^u = \delta_{KL}$$

and closure relation

$$\sum_K (S_K)_o^u (T_K)_p^v = \delta_{op} \delta_{uv}$$

The above equations can be combined to yield the inverse energy relations

$$\sum_K (S_K)_o^u \omega_K^{-1} (S_K)_p^v = ([A + B]^{-1})_{op}^{uv}$$

$$\sum_K (T_K)_o^u \omega_K^{-1} (T_K)_p^v = ([A - B]^{-1})_{op}^{uv}$$

The elements of the inverse matrix $(\mathbf{A} - \mathbf{B})^{-1}$, which will be required later, can be obtained by diagonalisation of the Hermitian matrix $(\mathbf{A} - \mathbf{B})$

$$\mathbf{U}^+ (\mathbf{A} - \mathbf{B}) \mathbf{U} = \boldsymbol{\omega}$$

yielding the eigenvalues $\boldsymbol{\omega}$ and eigenvectors $\mathbf{U}$, so that one gets

$$([A - B]^{-1})_{op}^{uv} = \sum_K (U_K)_o^v \omega_K^{-1} (U_K)_p^v$$

When the one-electron operators are spin free, only the spin-singlet configuration functions contribute and hence the matrix elements to be evaluated are

$$(A - B)_{op}^{uv} = F_{uv} \delta_{op} - F_{op} \delta_{uv} + \langle uo | \hat{g}_{12} | pv \rangle - \langle vo | \hat{g}_{12} | up \rangle$$

and

$$(A + B)_{op}^{uv} = F_{uv} \delta_{op} - F_{op} \delta_{uv} + 4 \langle up | \hat{g}_{12} | ov \rangle - \langle uo | \hat{g}_{12} | pv \rangle - \langle vo | \hat{g}_{12} | up \rangle$$

where F_{op} (F_{uv}) are the matrix elements of the Fock operator over occupied (unoccupied) molecular orbitals.

Using the above expressions, the energy resolvent involving the purely imaginary one-electron operators adopts the form of

$$\begin{aligned}
R^{\lambda_1 \lambda_2} &= \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \sum_{K=1}^{\infty} \frac{1}{E_K - E_0} \left[\tilde{e}^{(\lambda_1)} \times \left\langle \Psi_0 \left| \tilde{h}^{(\lambda_1)} \right| \Psi_o^u \right\rangle (T_K)_o^u \right] \\
&\quad \cdot \left[\tilde{e}^{(\lambda_2)} \times \left\langle \Psi_p^v \left| \tilde{h}^{(\lambda_2)} \right| \Psi_0 \right\rangle (T_K)_p^v \right] \\
&= \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}^{(\lambda_1)} \times \left\langle \Psi_0 \left| \tilde{h}^{(\lambda_1)} \right| \Psi_o^u \right\rangle \right] \\
&\quad \cdot \left[\tilde{e}^{(\lambda_2)} \times \left\langle \Psi_p^v \left| \tilde{h}^{(\lambda_2)} \right| \Psi_0 \right\rangle \right] \left\{ \sum_{K=1}^{\infty} (T_K)_o^u \frac{1}{E_K - E_0} (T_K)_p^v \right\}
\end{aligned}$$

and using the identity

$$\sum_{K=1}^{\infty} (T_K)_o^u \frac{1}{E_K - E_0} (T_K)_p^v = \sum_{K=1}^{\infty} (T_K)_o^u \omega_K^{-1} (T_K)_p^v = ([A - B]^{-1})_{op}^{uv}$$

the formula can be simplified to

$$\begin{aligned}
R^{\lambda_1 \lambda_2} &= \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}^{(\lambda_1)} \times \left\langle \Psi_0 \left| \tilde{h}^{(\lambda_1)} \right| \Psi_o^u \right\rangle \right] \\
&\quad \cdot \left[\tilde{e}^{(\lambda_2)} \times \left\langle \Psi_p^v \left| \tilde{h}^{(\lambda_2)} \right| \Psi_0 \right\rangle \right] ([A - B]^{-1})_{op}^{uv}
\end{aligned}$$

For a closed-shell system the matrix elements of spin-free one-electron operators are reduced to

$$\left\langle \Psi_0 \left| \tilde{h}^{(\lambda_1)} \right| \Psi_o^u \right\rangle = \sqrt{2} \left\langle \phi_o \left| \tilde{h}_1^{(\lambda_1)} \right| \phi_u \right\rangle$$

and hence the resolvent in terms of molecular orbitals becomes

$$\begin{aligned}
R^{\lambda_1 \lambda_2} &= 2 \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}^{(\lambda_1)} \times \left\langle \phi_o \left| \tilde{h}_1^{(\lambda_1)} \right| \phi_u \right\rangle \right] \\
&\quad \cdot \left[\tilde{e}^{(\lambda_2)} \times \left\langle \phi_v \left| \tilde{h}_1^{(\lambda_2)} \right| \phi_p \right\rangle \right] ([A - B]^{-1})_{op}^{uv}
\end{aligned}$$

5.1.3 Finite perturbation theory

We seek a solution to the perturbed Schrödinger equation owing to the presence of an external magnetic field

$$\hat{H}(\vec{B})\Psi(\vec{B}) = E(\vec{B})\Psi(\vec{B})$$

with the Hamiltonian in the form suitable for an application of the finite perturbation theory

$$\hat{H}(\lambda) = \hat{H}(\lambda_1, \lambda_2, \dots) = \hat{H}^0 + \lambda_1 \hat{H}_1 + \lambda_2 \hat{H}_2 + \dots$$

A second-order property (magnetic parameter) is given as a derivative of the total energy

$$\overline{\overline{X}}^{\lambda_1 \lambda_2} = \left(\frac{\partial^2 E}{\partial \lambda_1 \partial \lambda_2} \right)_{\lambda_1 = \lambda_2 = 0}$$

According to the Hellman–Feynmann theorem it holds true that

$$\frac{\partial E(\lambda)}{\partial \lambda_1} = \left\langle \Psi(\lambda) \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda_1} \right| \Psi(\lambda) \right\rangle = \left\langle \Psi(\lambda) \left| \hat{H}_1 \right| \Psi(\lambda) \right\rangle$$

This is true not only for the exact wave function but also for the wave function in the molecular orbital method (i.e. molecular orbitals satisfying the Brillouin theorem). Then

$$\overline{\overline{X}} = \left[\frac{\partial \left\langle \Psi(\lambda) \left| \hat{H}_1 \right| \Psi(\lambda) \right\rangle}{\partial \lambda_2} \right]_{\lambda=0} = \left[\frac{\partial \left\langle \Psi(\lambda_2) \left| \hat{H}_1 \right| \Psi(\lambda_2) \right\rangle}{\partial \lambda_2} \right]_{\lambda_2=0}$$

For the calculation of a second-order property the wave function $\Psi(\lambda_2)$ should be determined first by utilising a Hamiltonian of the form

$$\hat{H}(\lambda_2) = \hat{H}^0 + \lambda_2 \hat{H}_2$$

Then the first derivative of the expectation value of $\hat{H}_1$ over the perturbed wave function $\Psi(\lambda_2)$ is evaluated by a numerical method for $\lambda_2 = 0$. The set of magnetic parameters is expressed as the sum of the first-order (diamagnetic) and second-order (paramagnetic) contributions [1]

$$\begin{aligned} -\frac{1}{2} \kappa_{ab} &= \left[\frac{\partial \left\langle \Psi(B_b) \left| \hat{H}_a^{(1,0,0)} + B_b \hat{H}_{ab}^{(2,0,0)} \right| \Psi(B_b) \right\rangle}{\partial B_b} \right]_{B=0} \\ &= \left\langle \Psi(0) \left| \hat{H}_{ab}^{(2,0,0)} \right| \Psi(0) \right\rangle + \left[\frac{\partial \left\langle \Psi(B_b) \left| \hat{H}_a^{(1,0,0)} \right| \Psi(B_b) \right\rangle}{\partial B_b} \right]_{B=0} \end{aligned}$$

$$\begin{aligned}
\sigma_{Nab} &= \left[\frac{\partial \langle \Psi(B_b) | \hat{H}_{Na}^{(0,1,0)} + B_b \hat{H}_{Nab}^{(1,1,0)} | \Psi(B_b) \rangle}{\partial B_b} \right]_{B=0} \\
&= \langle \Psi(0) | \hat{H}_{Nab}^{(1,1,0)} | \Psi(0) \rangle + \left[\frac{\partial \langle \Psi(B_b) | \hat{H}_{Na}^{(0,1,0)} | \Psi(B_b) \rangle}{\partial B_b} \right]_{B=0} \\
S_a \Delta g_{ab} &= \left[\frac{\partial \langle \Psi(B_b) | \hat{H}_a^{(0,0,1)} + B_b \hat{H}_{ab}^{(1,0,1)} | \Psi(B_b) \rangle}{\partial B_b} \right]_{B=0} \\
&= \langle \Psi(0) | \hat{H}_{ab}^{(1,0,1)} | \Psi(0) \rangle + \left[\frac{\partial \langle \Psi(B_b) | \hat{H}_a^{(0,0,1)} | \Psi(B_b) \rangle}{\partial B_b} \right]_{B=0} \\
S_a T_{Nab} &= \left[\frac{\partial \langle \Psi(\mu_{Nb}) | \hat{H}_{Na}^{(0,0,1)} + \mu_{Nb} \hat{H}_{Nab}^{(0,1,1)} | \Psi(\mu_{Nb}) \rangle}{\partial \mu_{Nb}} \right]_{\mu_N=0} \\
&= \langle \Psi(0) | \hat{H}_{Nab}^{(0,1,1)} | \Psi(0) \rangle + \left[\frac{\partial \langle \Psi(\mu_{Nb}) | \hat{H}_{Na}^{(0,0,1)} | \Psi(\mu_{Nb}) \rangle}{\partial \mu_{Nb}} \right]_{\mu_N=0} \\
K_{MNab} &= \left[\frac{\partial \langle \Psi(\mu_{Mb}) | \hat{H}_{Na}^{(0,1,0)} + \hat{H}_{Nab}^{(0,1,1)} + \mu_{Na} \hat{H}_{MNab}^{(0,2,0)} | \Psi(\mu_{Mb}) \rangle}{\partial \mu_{Mb}} \right]_{\mu_N=\mu_M=0} \\
&= \langle \Psi(0) | \hat{H}_{MNab}^{(0,2,0)} | \Psi(0) \rangle \\
&\quad + \left[\frac{\partial \langle \Psi(\mu_{Mb}) | \hat{H}_{Na}^{(0,1,1)} + \hat{H}_{Nab}^{(0,1,1)} | \Psi(\mu_{Mb}) \rangle}{\partial \mu_{Mb}} \right]_{\mu_M=0} \\
-\frac{1}{2} S_a D_{ab} S_b &= \left[\frac{\partial \langle \Psi(\mu_{eb}) | \hat{H}_a^{(0,0,1)} + \mu_{eb} \hat{H}_{ab}^{(0,0,2)} | \Psi(\mu_{eb}) \rangle}{\partial \mu_{eb}} \right]_{\mu_e=0} \\
&= \langle \Psi(0) | \hat{H}_{ab}^{(0,0,2)} | \Psi(0) \rangle + \left[\frac{\partial \langle \Psi(\mu_{eb}) | \hat{H}_a^{(0,0,1)} | \Psi(\mu_{eb}) \rangle}{\partial \mu_{eb}} \right]_{\mu_e=0}
\end{aligned}$$

Although the problem of the accurate calculation of excitation energies and an infinite sum has been removed, it should be mentioned that the problem of

gauge variance still remains in the finite perturbation theory with the fixed basis set.

5.1.4 Magnetic orbitals

For the first group of magnetic parameters $\bar{\kappa}$, $\overline{\Delta g}$ and $\bar{\sigma}_N$, depending explicitly upon the magnetic field, we need a wave function $|\Psi(B)\rangle$ correct to the first order in the magnetic field. The Hamiltonian to be used for its derivation adopts the form of

$$\hat{H}(B_a) = \hat{H}^{(0,0,0)} + B_a \hat{H}_a^{(1,0,0)}$$

Because the perturbation includes the imaginary unit

$$\hat{H}_a^{(1,0,0)} = -i\mu_B \sum_i (\vec{r}_{Gi} \times \vec{\nabla}_i)_a$$

the entire Hamiltonian and the wave function (molecular orbitals) become complex in the presence of the magnetic field. The LCAO expansion includes field-dependent LCAO coefficients but a fixed (real) basis set of atomic orbitals

$$\phi_i^{(B)} = \sum_{\mu}^{\text{AO}} C_{i\mu}^{(B)} \chi_{\mu}$$

The LCAO coefficients, correct to the first order in the magnetic field, can be written in the form

$$C_{a,i\mu}^{(B)} = C_{i\mu}^{(0)} + iB_a C_{a,i\mu}^{(1)}$$

and consequently the charge-density matrix (hereafter for a closed-shell system) also becomes complex

$$P_{a,\mu\nu}^{(B)} = P_{\mu\nu}^{(0)} + iB_a P_{a,\mu\nu}^{(1)}$$

with the zero-field charge-density matrix

$$P_{\mu\nu}^{(0)} = 2 \sum_i^{\text{occ}} C_{i\mu}^{(0)} C_{i\nu}^{(0)}$$

and its first-order field correction

$$P_{a,\mu\nu}^{(1)} = 2 \sum_i^{\text{occ}} (C_{i\mu}^{(0)} C_{a,i\nu}^{(1)} - C_{a,i\mu}^{(1)} C_{i\nu}^{(0)})$$

The LCAO coefficients are determined by solving the modified Roothaan equations [3]

$$\sum_{\mu}^{\text{AO}} (F_{a,\mu\nu}^{(B)} - \varepsilon_{a,j}^{(B)} S_{\mu\nu}) C_{a,j\nu}^{(B)} = 0$$

with the orthonormality constraint

$$\sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} C_{a,i\mu}^{(B)*} S_{\mu\nu} C_{a,j\nu}^{(B)} = \delta_{ij}$$

for each molecular orbital, where the dependence on the magnetic field is indicated explicitly. The Fock matrix elements are

$$F_{a,\mu\nu}^{(B)} = H_{a,\mu\nu}^{(B)} + G_{a,\mu\nu}^{(B)}$$

with the matrix element of the one-electron operator including the usual one-electron core part and the magnetic perturbation

$$H_{a,\mu\nu}^{(B)} = \left\langle \chi_{\mu} \left| \frac{1}{2m_e} (-i\hbar \vec{\nabla}_1)^2 - \frac{e^2}{4\pi\epsilon_0} \sum_N \frac{Z_N}{r_{N1}} \right| \chi_{\nu} \right\rangle + iB_a \left\langle \chi_{\mu} \left| \hat{H}_a^{(1,0,0)} \right| \chi_{\nu} \right\rangle$$

and the two-electron part

$$G_{a,\mu\nu}^{(B)} = \sum_{\lambda}^{\text{AO}} \sum_{\sigma}^{\text{AO}} P_{a,\lambda\sigma}^{(B)} \left[\langle \mu\lambda | \hat{g}_{12} | \nu\sigma \rangle - \frac{1}{2} \langle \mu\lambda | \hat{g}_{12} | \sigma\nu \rangle \right]$$

containing the usual two-electron integrals but field-dependent (complex) charge-density matrix. The set of modified Roothaan equations is to be solved by an iterative procedure. The result of the SCF procedure is carried out by zero-order and first-order (in the magnetic field) charge-density matrices. These are used to express the magnetic parameters, viz.

$$X_{ab}^{\lambda_1\lambda_2} = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} (P_{\mu\nu}^{(0)} H_{ab,\mu\nu}^{(\dots\lambda_1\dots\lambda_2\dots)} + P_{a,\mu\nu}^{(1)} H_{b,\mu\nu}^{(\dots\lambda_2\dots)})$$

with properly selected (including sign and a constant factor) one-electron operators and their matrix elements evaluated in the basis set of (fixed) atomic orbitals. Thus

$$\kappa_{ab} = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} (P_{\mu\nu}^{(0)} H_{ab,\mu\nu}^{(2,0,0)} + P_{a,\mu\nu}^{(1)} H_{b,\mu\nu}^{(1,0,0)})$$

$$\Delta g_{ab} = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} (P_{\mu\nu}^{(0)} H_{ab,\mu\nu}^{(1,0,1)} + P_{a,\mu\nu}^{(1)} H_{b,\mu\nu}^{(0,0,1)})$$

$$\sigma_{Nab} = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} (P_{\mu\nu}^{(0)} H_{Nab,\mu\nu}^{(1,1,0)} + P_{a,\mu\nu}^{(1)} H_{Nb,\mu\nu}^{(0,1,0)})$$

5.1.5 GIAO method

The GIAO method has roots in the old idea of London who introduced field-dependent gauge-invariant atomic orbitals. These are constructed from real atomic orbitals multiplied by a field-dependent phase factor

$$\chi_{\mu_M}^{(B)} = \exp\left(-\frac{ie}{\hbar} \vec{A}_M \cdot \vec{r}_{Gi}\right) \chi_{\mu_M} = \exp\left(-\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{r}_{GM} \cdot \vec{r}_{Gi}\right) \chi_{\mu_M}$$

where $\vec{r}_{GM} = \vec{r}_M - \vec{r}_G$ is the distance vector from the arbitrary gauge origin G to the nucleus M on which the atomic orbital χ_{μ_M} is located. (The term “gauge-invariant atomic orbitals” is an unfortunate phrase since, in fact, these orbitals include a phase factor which depends on the gauge.) Thus each atomic orbital has its own local gauge origin identified by its nuclear position [3–6].

Within the LCAO approximation it is assumed that

$$\phi_i^{(B)} = \sum_{\mu}^{\text{AO}} C_{i\mu}^{(B)} \chi_{\mu}^{(B)}$$

so that the LCAO coefficients are also field dependent.

The general aspect of gauge invariance is that the addition of the gradient of an arbitrary function $\Lambda(\vec{r})$ to the vector potential $\vec{A}$ leaves the magnetic field $\vec{B} = \vec{\nabla} \times \vec{A}$ unaffected. Hence the vector potential transforms as

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \vec{\nabla}\Lambda(\vec{r})$$

For example, the translation of a position vector $\vec{r}$ by a constant vector $\vec{d}$

$$\vec{r} \rightarrow \vec{r}' = \vec{d} + \vec{r}$$

is represented by the gauge transformation

$$A = \vec{A} \cdot \vec{r} = \frac{1}{2}(\vec{B} \times \vec{d}) \cdot \vec{r}$$

Each atomic orbital transforms as

$$\begin{aligned} \chi_{\mu_M}^{(B)} &\rightarrow \chi_{\mu_M}'^{(B)} = \exp\left(-\frac{ie}{\hbar} A\right) \chi_{\mu_M}^{(B)} \\ &= \exp\left(-\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{d} \cdot \vec{r}\right) \exp\left(-\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{r}_{GM} \cdot \vec{r}_{Gi}\right) \chi_{\mu_M} \end{aligned}$$

and molecular orbitals obey the transformation relationship

$$\phi_i^{(B)} \rightarrow \phi_i'^{(B)} = \exp\left(-\frac{ie}{\hbar} A\right) \phi_i^{(B)} = \exp\left(-\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{d} \cdot \vec{r}\right) \phi_i^{(B)}$$

The molecular orbitals satisfy the Brillouin condition which states that the matrix elements of the Fock operator between occupied and unoccupied molecular orbitals vanish

$$F_{ou} = 0$$

The Fock matrix for a closed-shell system is defined as

$$F_{ij} = \langle i | \hat{h}_1 | j \rangle + \sum_k^{\text{occ}} [2\langle ik | \hat{g}_{12} | jk \rangle - \langle ik | \hat{g}_{12} | kj \rangle]$$

and for optimum canonical molecular orbitals it is diagonal

$$F_{ij} = \varepsilon_i \delta_{ij}$$

The Brillouin condition, rewritten into the AO basis, is

$$\sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} C_{o\mu}^{(B)*} F_{\mu\nu}^{(B)} C_{u\nu}^{(B)} = 0$$

and it should be satisfied also for transformed orbitals

$$\sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} C_{o\mu}'^{(B)*} F_{\mu\nu}'^{(B)} C_{u\nu}'^{(B)} = 0$$

The expression for the Fock operator is

$$F'_{\mu_M \nu_N}^{(B)} = \exp\left(\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{d} \cdot \vec{r}\right) \exp\left(\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{r}_{GM} \cdot \vec{r}_{Gi}\right) F_{\mu_M \nu_N}^{(B)} \\ \exp\left(-\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{d} \cdot \vec{r}\right) \exp\left(-\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{r}_{GN} \cdot \vec{r}_{Gi}\right)$$

so that we get

$$\sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} C_{o\mu}^{(B)*} \exp\left(\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{r}_{GM} \cdot \vec{r}_{Gi}\right) F_{\mu\nu}^{(B)} \\ \exp\left(-\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{r}_{GN} \cdot \vec{r}_{Gi}\right) C_{uv}^{(B)} = 0$$

which implies

$$C_{uv}^{(B)} = \exp\left(\frac{ie}{\hbar} \frac{1}{2} \vec{B} \times \vec{r}_{GN} \cdot \vec{r}_{Gi}\right) C_{uv}^{(B)}$$

The one-electron operator transforms as

$$\hat{h}_1^{(B)} \rightarrow \hat{h}_1^{(B)} = \exp\left(-\frac{ie}{\hbar} \Lambda\right) \hat{h}_1^{(B)} \exp\left(\frac{ie}{\hbar} \Lambda\right)$$

The LCAO coefficients satisfy the modified Roothaan equations

$$\sum_{\mu}^{\text{AO}} (F_{a,\mu\nu}^{(B)} - \varepsilon_{a,j}^{(B)} S_{a,\mu\nu}^{(B)}) C_{a,j\nu}^{(B)} = 0$$

with the orthonormality constraint

$$\sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} C_{a,i\mu}^{(B)*} S_{a,\mu\nu}^{(B)} C_{a,j\nu}^{(B)} = \delta_{ij}$$

for each molecular orbital, where the dependence on the a th component of the magnetic field is indicated explicitly. However, since the atomic orbitals $\chi_{\mu}^{(B)}$ depend upon the magnetic field, there are some differences with respect to the standard self-consistent field theory. The Fock matrix elements are given by

$$F_{a,\mu\nu}^{(B)} = h_{a,\mu\nu}^{(B)} + G_{a,\mu\nu}^{(B)}$$

with the matrix element of the one-electron operator

$$h_{a,\mu\nu}^{(B)} = \left\langle \chi_{a,\mu}^{(B)} \left| \frac{1}{2m_e} [-i\hbar \vec{\nabla}_1 + e\vec{A}_a(\vec{r})]^2 - \frac{e^2}{4\pi\epsilon_0} \sum_N \frac{Z_N}{r_{N1}} \right| \chi_{a,\nu}^{(B)} \right\rangle$$

and the two-electron part

$$\begin{aligned} G_{a,\mu\nu}^{(B)} &= \sum_{\lambda}^{\text{AO}} \sum_{\sigma}^{\text{AO}} P_{a,\lambda\sigma}^{(B)} \left[\langle \mu\lambda | \hat{g}_{12} | \nu\sigma \rangle_a^{(B)} - \frac{1}{2} \langle \mu\lambda | \hat{g}_{12} | \sigma\nu \rangle_a^{(B)} \right] \\ &= \sum_{\lambda}^{\text{AO}} \sum_{\sigma}^{\text{AO}} P_{a,\lambda\sigma}^{(B)} G_{a,\mu\lambda\nu\sigma}^{(B)} \end{aligned}$$

The charge-density matrix becomes

$$P_{a,\mu\nu}^{(B)} = 2 \sum_i^{\text{occ}} C_{a,i\mu}^{(B)} C_{a,i\nu}^{(B)}$$

and the total electronic energy is given by the formula

$$E(B) = \sum_a^{x,y,z} \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} P_{a,\mu\nu}^{(B)} \left(h_{a,\mu\nu}^{(B)} + \frac{1}{2} G_{a,\mu\nu}^{(B)} \right)$$

Now the derivatives according to the field are obtained as follows. Differentiating the energy expression with respect to the B_a component we obtain

$$E_a^{(1)} = \left[\frac{\partial E(B)}{\partial B_a} \right] = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} P_{a,\mu\nu}^{(1)} \left(h_{\mu\nu}^{(0)} + \frac{1}{2} G_{\mu\nu}^{(0)} \right) + P_{\mu\nu}^{(0)} \left(h_{a,\mu\nu}^{(1)} + \frac{1}{2} G_{a,\mu\lambda\nu\sigma}^{(1)} \right)$$

where the superscripts denote the degree of differentiation. Differentiating the orthonormality constraint one gets

$$\sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} C_{a,i\mu}^{(1)*} S_{\mu\nu}^{(0)} C_{j\nu}^{(0)} + C_{i\mu}^{(0)*} S_{a,\mu\nu}^{(1)} C_{j\nu}^{(0)} + C_{i\mu}^{(0)*} S_{\mu\nu}^{(0)} C_{a,j\nu}^{(1)} = 0$$

and finally, differentiating the charge density matrix, we have

$$P_{a,\mu\nu}^{(1)} = \left[\frac{\partial P_{a,\mu\nu}^{(B)}}{\partial B_a} \right] = 2 \sum_i^{\text{occ}} \left(\frac{\partial C_{a,i\mu}^{(B)*}}{\partial B_a} C_{i\nu}^{(B)} + C_{i\mu}^{(B)*} \frac{\partial C_{a,i\nu}^{(B)}}{\partial B_a} \right)$$

These conditions can be combined to get

$$E_a^{(1)} = \sum_i \sum_{\mu} \sum_{\nu} \text{AO} \text{AO} C_{i\mu}^{(0)*} \left(2h_{a,\mu\nu}^{(1)} + \sum_{\lambda} \sum_{\sigma} \text{AO} \text{AO} P_{\mu\nu}^{(0)} G_{a,\mu\lambda\nu\sigma}^{(1)} - 2S_{a,\mu\nu}^{(1)} \varepsilon_i^{(0)} \right) C_{i\nu}^{(0)}$$

An important finding is that the first derivative of the energy contains only the zero-order LCAO coefficients and the zero-order orbital energies. Therefore a second-order property

$$\begin{aligned} X_{ab} &= \left(\frac{\partial E_a^{(1)}}{\partial \lambda_b} \right) \\ &= \sum_i \sum_{\mu} \sum_{\nu} \text{AO} \text{AO} \left\{ C_{b,i\mu}^{(1)*} \left[2h_{a,\mu\nu}^{(1)} + \sum_{\lambda} \sum_{\sigma} \text{AO} \text{AO} P_{\mu\nu}^{(0)} G_{a,\mu\lambda\nu\sigma}^{(1)} - 2S_{a,\mu\nu}^{(1)} \varepsilon_i^{(0)} \right] C_{i\nu}^{(0)} \right. \\ &\quad + C_{i\mu}^{(0)*} \left[2h_{ab,\mu\nu}^{(2)} + \sum_{\lambda} \sum_{\sigma} \text{AO} \text{AO} \left(P_{b,\mu\nu}^{(1)} G_{a,\mu\lambda\nu\sigma}^{(1)} + P_{\mu\nu}^{(0)} G_{ab,\mu\lambda\nu\sigma}^{(2)} \right) \right. \\ &\quad \left. \left. - 2S_{ab,\mu\nu}^{(2)} \varepsilon_i^{(0)} - 2S_{a,\mu\nu}^{(1)} \varepsilon_{b,i}^{(1)} \right] C_{i\nu}^{(0)} \right. \\ &\quad \left. + C_{i\mu}^{(0)*} \left[2h_{a,\mu\nu}^{(1)} + \sum_{\lambda} \sum_{\sigma} \text{AO} \text{AO} P_{\mu\nu}^{(0)} G_{a,\mu\lambda\nu\sigma}^{(1)} - 2S_{a,\mu\nu}^{(1)} \varepsilon_i^{(0)} \right] C_{b,i\nu}^{(1)} \right\} \end{aligned}$$

requires only the first derivatives of these quantities. The first-order LCAO coefficients $C_{a,i\mu}^{(1)}$ are determined on the basis of equations resulting from the expansion of the modified Roothaan equations. The expansion is

$$[(\mathbf{F}^{(0)} + i\mathbf{B}\mathbf{F}^{(1)}) - \mathbf{e}^{(0)}(\mathbf{S}^{(0)} + i\mathbf{B}\mathbf{S}^{(1)})](\mathbf{C}^{(0)} + i\mathbf{B}\mathbf{C}^{(1)}) = \mathbf{0}$$

(the eigenvalues of a Hermitian matrix should be real) and the separation of orders of B yields the first-order equations—*coupled Hartree–Fock* (CHF) perturbation equations

$$[\mathbf{F}^{(0)} - \mathbf{e}^{(0)}\mathbf{S}^{(0)}]\mathbf{C}^{(1)} - [\mathbf{F}^{(1)} - \mathbf{e}^{(0)}\mathbf{S}^{(1)}]\mathbf{C}^{(0)} = \mathbf{0}$$

The first-order Fock matrix is

$$F_{a,\mu\nu}^{(1)} = h_{a,\mu\nu}^{(1)} + \sum_{\lambda} \sum_{\sigma} \text{AO} \text{AO} \left[P_{\lambda\sigma}^{(0)} G_{a,\mu\lambda\nu\sigma}^{(1)} + P_{a,\lambda\sigma}^{(1)} G_{\mu\lambda\nu\sigma}^{(0)} \right]$$

The LCAO coefficients for the i th molecular orbital can be arranged into a column vector $\mathbf{c}_i$ and the CHF equations can be rewritten as

$$\mathbf{c}_i^{(1)} = \sum_o^{\text{occ}} \left[-\frac{1}{2} \mathbf{c}_o^{(0)+} \mathbf{S}^{(1)} \mathbf{c}_i^{(0)} \right] \mathbf{c}_o^{(0)} - \sum_u^{\text{un}} \frac{1}{\varepsilon_u^{(0)} - \varepsilon_o^{(0)}} \left[\mathbf{c}_u^{(0)+} (\mathbf{F}^{(1)} - \varepsilon_i^{(0)} \mathbf{S}^{(1)}) \mathbf{c}_i^{(0)} \right] \mathbf{c}_u^{(0)}$$

These equations should be solved by an iterative procedure since the Fock matrix $\mathbf{F}^{(1)}$ depends upon the LCAO coefficients through the charge-density matrix.

In an alternative formulation, the first-order charge-density matrix is the subject of determination through the CHF equations [18]

$$\mathbf{P}^{(1)} = \frac{1}{2} \mathbf{P}^{(0)+} \mathbf{S}^{(1)} \mathbf{P}^{(0)} - \sum_o^{\text{occ}} \sum_u^{\text{un}} \frac{1}{\varepsilon_u^{(0)} - \varepsilon_o^{(0)}} \left[\mathbf{c}_o^{(0)+} (\mathbf{F}^{(1)} - \varepsilon_o^{(0)} \mathbf{S}^{(1)}) \mathbf{c}_u^{(0)} \right] \left[\mathbf{c}_o^{(0)} \mathbf{c}_u^{(0)+} - \mathbf{c}_u^{(0)} \mathbf{c}_o^{(0)+} \right]$$

and again an iterative procedure is necessary to solve them. The magnetic parameter is expressed as

$$X_{ab} = \text{Tr}\{\mathbf{P}^0 \mathbf{H}_{ab}^{(\lambda_1 \lambda_2)}\} + \text{Tr}\{\mathbf{P}_a^{(\lambda_1)} \mathbf{H}_b^{(\lambda_2)}\}$$

where $\mathbf{P}_a^{(\lambda_1)}$ is the first derivative of the charge-density matrix with respect to the variable (e.g. the magnetic field component) λ_1 . Hence the formulae for gauge-dependent magnetic parameters

$$\kappa_{ab} = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} (P_{\mu\nu}^{(0)} H_{ab,\mu\nu}''^{(2,0,0)} + P_{a,\mu\nu}^{(1)} H_{b,\mu\nu}'^{(1,0,0)})$$

$$\Delta g_{ab} = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} (P_{\mu\nu}^{(0)} H_{ab,\mu\nu}''^{(1,0,1)} + P_{a,\mu\nu}^{(1)} H_{b,\mu\nu}'^{(0,0,1)})$$

$$\sigma_{Nab} = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} (P_{\mu\nu}^{(0)} H_{Nab,\mu\nu}''^{(1,1,0)} + P_{a,\mu\nu}^{(1)} H_{Nb,\mu\nu}'^{(0,1,0)})$$

are formally identical with those for the fixed basis set, but the matrix elements of the Hamiltonian terms now adopt a different meaning (a more complex form). In their derivation let us consider first the one-electron Hamiltonian in the presence of an external electromagnetic potential

$$\begin{aligned}
h_{\mu\nu}^{(B)} &= \left\langle \chi_{\mu}^{(B)} \left| \frac{1}{2m_e} [-i\hbar\vec{\nabla}_1 + e\vec{A}(\vec{r}_{G1})]^2 + V_{eN} \right| \chi_{\nu}^{(B)} \right\rangle \\
&= \left\langle \Gamma_{\mu\nu} \chi_{\mu} \left| \frac{1}{2m_e} [-i\hbar\vec{\nabla}_1 + e\vec{A}(\vec{r}_{G1})]^2 + V_{eN} \right| \chi_{\nu} \right\rangle \\
&= \left\langle \Gamma_{\mu\nu} \chi_{\mu} \left| \hat{h}^{(0)} + \frac{e}{2m_e} \vec{B} \cdot \vec{l}_{G1} + \frac{e^2}{8m_e} [B^2(\vec{r}_{G1})^2 - (\vec{B} \cdot \vec{r}_{G1})^2] \right| \chi_{\nu} \right\rangle
\end{aligned}$$

where $\vec{r}_{G1}$ is the position vector of the electron (1) relative to some arbitrary origin (G). The above one-electron Hamiltonian, in addition to the Schrödinger term $\hat{h}^{(0)}$, includes the Zeeman interaction and the diamagnetic term. The gauge factor

$$\begin{aligned}
\Gamma_{\mu\nu} &= \exp\left(-\frac{ie}{\hbar} \vec{A}_M \cdot \vec{r}_{G1}\right)^* \exp\left(-\frac{ie}{\hbar} \vec{A}_N \cdot \vec{r}_{G1}\right) \\
&= \exp\left(\frac{ie}{\hbar} (\vec{A}_M \cdot \vec{r}_{G1} - \vec{A}_N \cdot \vec{r}_{G1})\right)
\end{aligned}$$

contains the vector potential $\vec{A}_N = (1/2)\vec{B} \times \vec{r}_{GN}$ at the nuclear position $\vec{r}_{GN} = \vec{r}_N - \vec{r}_G$ of the atomic orbital $\chi_{\nu N}$. It can be expanded as

$$\begin{aligned}
\Gamma_{\mu\nu} &= 1 + \frac{ie}{\hbar} (\vec{A}_M \cdot \vec{r}_{G1} - \vec{A}_N \cdot \vec{r}_{G1}) + \dots \\
&= 1 + \frac{ie}{2\hbar} \vec{B} \times (\vec{r}_{GM} \cdot \vec{r}_{G1} - \vec{r}_{GN} \cdot \vec{r}_{G1}) + \dots \\
&= 1 + \frac{ie}{2\hbar} \vec{B} \cdot (\vec{r}_{GM} \times \vec{r}_{G1} - \vec{r}_{GN} \times \vec{r}_{G1}) + \dots
\end{aligned}$$

The positions of the gauge origin (G), the atoms (M, N) and the electron (1) are interrelated through the vector relationships

$$\vec{r}_{G1} = \vec{r}_{GM} + \vec{r}_{M1}$$

$$\vec{r}_{NM} = \vec{r}_{GM} - \vec{r}_{GN}$$

By substituting into the gauge factor we get

$$\begin{aligned}
(\vec{r}_{GM} \times \vec{r}_{G1} - \vec{r}_{GN} \times \vec{r}_{G1}) &= (\vec{r}_{GM} - \vec{r}_{GN}) \times (\vec{r}_{GM} + \vec{r}_{M1}) \\
&= \vec{r}_{GM} \times \vec{r}_{GM} - \vec{r}_{GN} \times \vec{r}_{GM} + (\vec{r}_{GM} - \vec{r}_{GN}) \times \vec{r}_{M1} \\
&= \vec{r}_{GM} \times \vec{r}_{GN} + \vec{r}_{NM} \times \vec{r}_{M1}
\end{aligned}$$

where the following identity was exploited

$$\vec{r}_{GM} \times \vec{r}_{GM} = 0$$

It is useful to introduce the vector quantities

$$\vec{Q}_{\mu\nu}^{MN} = \vec{r}_{GM} \times \vec{r}_{GN}$$

and

$$\vec{T}_{\mu\nu}^{MN} = \vec{r}_{NM} \times \vec{r}_{Mi}$$

in terms of which the gauge factor is expressed as

$$\begin{aligned} \Gamma_{\mu\nu} &= 1 + \frac{ie}{2\hbar} \vec{B} \cdot (\vec{Q}_{\mu\nu}^{MN} + \vec{T}_{\mu\nu}^{MN}) + \frac{1}{2} \left[\frac{ie}{2\hbar} \vec{B} \cdot (\vec{Q}_{\mu\nu}^{MN} + \vec{T}_{\mu\nu}^{MN}) \right]^2 + \dots \\ &= 1 + \vec{B} \cdot \vec{R}_{\mu\nu}^{MN} + \frac{1}{2} (\vec{B} \cdot \vec{R}_{\mu\nu}^{MN})^2 + \dots \end{aligned}$$

with the substitution

$$\vec{R}_{\mu\nu}^{MN} = \frac{ie}{2\hbar} (\vec{Q}_{\mu\nu}^{MN} + \vec{T}_{\mu\nu}^{MN})$$

Then the matrix elements of the one-electron Hamiltonian in the presence of the magnetic field become

$$\begin{aligned} h_{\mu\nu}^{(B)} &= \left\langle \left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu}^{MN} + \frac{1}{2} (\vec{B} \cdot \vec{R}_{\mu\nu}^{MN})^2 \right\} \chi_{\mu} \right. \\ &\quad \left. \left| \hat{h}^{(0)} + \frac{e}{2m_e} \vec{B} \cdot \vec{l}_{G1} + \frac{e^2}{8m_e} \left[B^2 (\vec{r}_{G1})^2 - (\vec{B} \cdot \vec{r}_{G1})^2 \right] \right| \chi_{\nu} \right\rangle \end{aligned}$$

and the first derivative according to the magnetic field component B_a is

$$\begin{aligned} \frac{\partial h_{\mu\nu}^{(B)}}{\partial B_a} &= \left\langle \left\{ R_{a,\mu\nu}^{MN} + (\vec{B} \cdot \vec{R}_{\mu\nu}^{MN}) R_{a,\mu\nu}^{MN} \right\} \chi_{\mu} \right| \hat{h}^{(0)} + \frac{e}{2m_e} \vec{B} \cdot \vec{l}_{G1} + \frac{e^2}{8m_e} \\ &\quad \left[B^2 (\vec{r}_{G1})^2 - (\vec{B} \cdot \vec{r}_{G1})^2 \right] \chi_{\nu} \rangle + \left\langle \left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu}^{MN} + \frac{1}{2} (\vec{B} \cdot \vec{R}_{\mu\nu}^{MN})^2 \right\} \chi_{\mu} \right. \\ &\quad \left. \left| \frac{e}{2m_e} \hat{l}_{G1a} + \frac{\partial}{\partial B_a} \frac{e^2}{8m_e} \left[B^2 (\vec{r}_{G1})^2 - (\vec{B} \cdot \vec{r}_{G1})^2 \right] \right| \chi_{\nu} \right\rangle \end{aligned}$$

In the zero field we arrive at the expression for the (complex) first-order correction

$$\begin{aligned}
 H_{a,\mu\nu}^{(1,0,0)} &\equiv h_{a,\mu\nu}^{(1)} = \left(\frac{\partial h_{\mu\nu}^{(B)}}{\partial B_a} \right)_{B=0} \\
 &= \left\langle \left\{ R_{a,\mu\nu}^{MN} \right\} \chi_\mu \left| \hat{h}^{(0)} \right| \chi_\nu \right\rangle + \frac{e}{2m_e} \left\langle \chi_\mu \left| \hat{l}_{G1a} \right| \chi_\nu \right\rangle \\
 &= \left\langle \left\{ \frac{ie}{2\hbar} (Q_{a,\mu\nu}^{MN} + T_{a,\mu\nu}^{MN}) \right\} \chi_\mu \left| \hat{h}^{(0)} \right| \chi_\nu \right\rangle + \frac{e}{2m_e} \left\langle \chi_\mu \left| \hat{l}_{G1a} \right| \chi_\nu \right\rangle \\
 &= i \left[\frac{e}{2\hbar} Q_{a,\mu\nu}^{MN} \left\langle \chi_\mu \left| \hat{h}^{(0)} \right| \chi_\nu \right\rangle + \frac{e}{2\hbar} \left\langle T_{a,\mu\nu}^{MN} \chi_\mu \left| \hat{h}^{(0)} \right| \chi_\nu \right\rangle \right. \\
 &\quad \left. - \left(\frac{e\hbar}{2m_e} \right) \left\langle \chi_\mu \left| (\vec{r}_{G1} \times \vec{\nabla}_1)_a \right| \chi_\nu \right\rangle \right]
 \end{aligned}$$

which can be compared with the fixed basis set case when

$$H_{a,\mu\nu}^{(1,0,0)} = \frac{e}{2m_e} \left\langle \chi_\mu \left| \hat{l}_{G1a} \right| \chi_\nu \right\rangle = -i \left(\frac{e\hbar}{2m_e} \right) \left\langle \chi_\mu \left| (\vec{r}_{G1} \times \vec{\nabla}_1)_a \right| \chi_\nu \right\rangle$$

We can conclude that the GIAO expression involves the integrals over the fixed basis set

$$h_{\mu\nu}^{(0)} = \left\langle \chi_\mu \left| \hat{h}^{(0)} \right| \chi_\nu \right\rangle$$

and

$$L_{\mu\nu}^{(0)} = \left\langle \chi_\mu \left| \hat{l}_{G1a} \right| \chi_\nu \right\rangle$$

but, in addition, also the integrals with an increased angular momentum for the bra-vector

$$\langle \chi_{\sigma_M} | = \langle T_{a,\mu\nu}^{MN} \chi_\mu |$$

i.e.

$$h_{\sigma\nu}^{(0)} = \left\langle T_{a,\mu\nu}^{MN} \chi_\mu \left| \hat{h}^{(0)} \right| \chi_\nu \right\rangle$$

The second derivative of the one-electron integrals is calculated as

$$\begin{aligned}
 H''_{ab,\mu\nu}(2,0,0) &\equiv h_{ab,\mu\nu}^{(2)} = \left(\frac{\partial^2 h_{\mu\nu}^{(B)}}{\partial B_a \partial B_b} \right)_{B=0} \\
 &= \frac{\partial}{\partial B_a} \left\langle \left\{ R_{b,\mu\nu}^{MN} + (\vec{B} \cdot \vec{R}_{\mu\nu}^{MN}) R_{b,\mu\nu}^{MN} \right\} \chi_\mu \right| \hat{h}^{(0)} \\
 &\quad + \frac{e}{2m_e} \vec{B} \cdot \vec{l}_{G1} + \frac{e^2}{8m_e} \left[B^2 (\vec{r}_{G1})^2 - (\vec{B} \cdot \vec{r}_{G1})^2 \right] \chi_\nu \Bigg\rangle_{B=0} \\
 &\quad + \frac{\partial}{\partial B_a} \left\langle \left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu}^{MN} + \frac{1}{2} (\vec{B} \cdot \vec{R}_{\mu\nu}^{MN})^2 \right\} \chi_\mu \right| \frac{e}{2m_e} \hat{l}_{G1b} \\
 &\quad + \frac{\partial}{\partial B_b} \frac{e^2}{8m_e} \left[B^2 (\vec{r}_{G1})^2 - (\vec{B} \cdot \vec{r}_{G1})^2 \right] \chi_\nu \Bigg\rangle_{B=0}
 \end{aligned}$$

and we arrive at the expression

$$\begin{aligned}
 H''_{ab,\mu\nu}(2,0,0) &= \left\langle \left\{ R_{a,\mu\nu}^{MN} R_{b,\mu\nu}^{MN} \right\} \chi_\mu \right| \hat{h}^{(0)} \chi_\nu \Big\rangle + \left\langle \left\{ R_{b,\mu\nu}^{MN} \right\} \chi_\mu \right| \frac{e}{2m_e} \hat{l}_{G1a} \chi_\nu \Big\rangle \\
 &\quad + \frac{e^2}{4m_e} \langle \chi_\mu | [(\vec{r}_{G1})^2 \delta_{ab} - r_{G1a} r_{G1b}] | \chi_\nu \rangle \\
 &= -\frac{e^2}{4\hbar^2} \left[Q_{a,\mu\nu}^{MN} Q_{b,\mu\nu}^{MN} \langle \chi_\mu | \hat{h}^{(0)} | \chi_\nu \rangle + Q_{a,\mu\nu}^{MN} \langle T_{b,\mu\nu}^{MN} \chi_\mu | \hat{h}^{(0)} | \chi_\nu \rangle \right. \\
 &\quad \left. + Q_{b,\mu\nu}^{MN} \langle T_{a,\mu\nu}^{MN} \chi_\mu | \hat{h}^{(0)} | \chi_\nu \rangle + \langle T_{a,\mu\nu}^{MN} T_{b,\mu\nu}^{MN} \chi_\mu | \hat{h}^{(0)} | \chi_\nu \rangle \right] \\
 &\quad + \frac{ie}{2\hbar 2m_e} \left[Q_{b,\mu\nu}^{MN} \langle \chi_\mu | \hat{l}_{G1a} | \chi_\nu \rangle + \langle T_{b,\mu\nu}^{MN} \chi_\mu | \hat{l}_{G1a} | \chi_\nu \rangle \right] \\
 &\quad + \frac{e^2}{4m_e} \langle \chi_\mu | [(\vec{r}_{G1})^2 \delta_{ab} - r_{G1a} r_{G1b}] | \chi_\nu \rangle
 \end{aligned}$$

which can be compared with the fixed basis set result

$$H''_{ab,\mu\nu}(2,0,0) = \frac{e^2}{4m_e} \langle \chi_\mu | [(\vec{r}_{G1})^2 \delta_{ab} - r_{G1a} r_{G1b}] | \chi_\nu \rangle$$

We can see that, in addition, we have integrals involving increased angular momenta for the bra-vector.

A similar procedure yields the one-electron integrals for the GIAO evaluation of the nuclear shielding tensor [3–6]

$$H_{Na,\mu\nu}^{(0,1,0)} = \left(\frac{\partial h_{\mu\nu}^{(B,\mu_N)}}{\partial \mu_{Na}} \right)_{\mu_N=0, B=0}$$

$$H_{Nab,\mu\nu}^{\prime(1,1,0)} = \left(\frac{\partial^2 h_{\mu\nu}^{(B,\mu_N)}}{\partial B_a \partial \mu_{Nb}} \right)_{\mu_N=0, B=0}$$

The matrix elements of the one-electron Hamiltonian are

$$\begin{aligned} h_{\mu\nu}^{(B,\mu_N)} &= \left\langle \chi_{\mu}^{(B)} \left| \hat{h}^{(0)} + \frac{e}{m_e} [\vec{A} \cdot \vec{p}_1 + \vec{A}_N \cdot \vec{p}_1] \right. \right. \\ &\quad \left. \left. + \frac{e^2}{2m_e} [\vec{A}^2 + 2\vec{A} \cdot \vec{A}_N + A_N^2] \right| \chi_{\nu}^{(B)} \right\rangle \\ &= \left\langle \Gamma_{\mu\nu} \chi_{\mu} \left| \hat{h}^{(0)} + \hat{H}_{100} + \hat{H}_{010} + \hat{H}_{110} + \hat{H}_{200} + \hat{H}_{020} \right| \chi_{\nu} \right\rangle \end{aligned}$$

with the relevant Hamiltonian terms being the orbital hyperfine interaction

$$\hat{H}_{010} = \frac{\mu_0}{4\pi} \frac{e}{m_e} r_{N1}^{-3} \vec{\mu}_N \cdot \vec{l}_{N1}$$

and the electron–nuclear Zeeman correction

$$\hat{H}_{110} = \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} r_{N1}^{-3} [(\vec{B} \cdot \vec{\mu}_N)(\vec{r}_{G1} \cdot \vec{r}_{N1}) - (\vec{B} \cdot \vec{r}_{N1})(\vec{r}_{G1} \cdot \vec{\mu}_N)]$$

The first derivative is

$$\begin{aligned} &\frac{\partial}{\partial \mu_{Na}} \left\langle \left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu}^{MN} \right\} \chi_{\mu} \left| \hat{h}^{(0)} + \hat{H}_{010} + \hat{H}_{110} \right| \chi_{\nu} \right\rangle \\ &= \left\langle \left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu}^{MN} \right\} \chi_{\mu} \left| \frac{\mu_0}{4\pi} \frac{e}{m_e} r_{N1}^{-3} \hat{l}_{N1a} \right. \right. \\ &\quad \left. \left. + \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} r_{N1}^{-3} [B_a(\vec{r}_{G1} \cdot \vec{r}_{N1}) - (\vec{B} \cdot \vec{r}_{N1})r_{G1a}] \right| \chi_{\nu} \right\rangle \end{aligned}$$

and thus

$$H_{Na,\mu\nu}^{(0,1,0)} = \frac{\mu_0}{4\pi} \frac{e}{m_e} \left\langle \chi_\mu \left| r_{N1}^{-3} \hat{l}_{N1a} \right| \chi_\nu \right\rangle$$

$$H_{Nab,\mu\nu}^{(1,1,0)} = \frac{\mu_0}{4\pi} \frac{e}{m_e} \left\langle R_{a,\mu\nu}^{MN} \chi_\mu \left| r_{N1}^{-3} \hat{l}_{N1b} \right| \chi_\nu \right\rangle$$

$$+ \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} \left\langle \chi_\mu \left| r_{N1}^{-3} [(\vec{r}_{G1} \cdot \vec{r}_{N1}) \delta_{ab} - r_{N1a} r_{G1b}] \right| \chi_\nu \right\rangle$$

These expressions differ from the fixed basis set result only in the first term of $H_{Nab,\mu\nu}^{(1,1,0)}$ which enters the paramagnetic contribution.

Finally, the GIAO evaluation of the $\overline{\Delta g}$ tensor requires the derivatives

$$H_{a,\mu\nu}^{(0,0,1)} = \left(\frac{\partial h_{\mu\nu}^{(B,\mu_e)}}{\partial \mu_{ea}} \right)_{\mu_e=0, B=0}$$

$$H_{ab,\mu\nu}^{(1,0,1)} = \left(\frac{\partial^2 h_{\mu\nu}^{(B,\mu_e)}}{\partial B_a \partial \mu_{eb}} \right)_{\mu_e=0, B=0}$$

with the matrix elements of the one-electron Hamiltonian

$$h_{\mu\nu}^{(B,\mu_N)} = \left\langle \Gamma_{\mu\nu} \chi_\mu \left| \hat{h}^{(0)} + \hat{H}_{100} + \hat{H}_{001} + \hat{H}_{101} + \hat{H}_{200} + \hat{H}_{002} \right| \chi_\nu \right\rangle$$

and the relevant Hamiltonian terms including the spin-(own)orbit interaction

$$\hat{H}_{001} = -\frac{\mu_0}{4\pi} \frac{e}{2m_e} \left(\sum_N Z_N r_{N1}^{-3} \vec{l}_{N1} \cdot \vec{\mu}_e \right)$$

and the spin-orbit Zeeman gauge correction

$$\hat{H}_{101} = \frac{\mu_0}{4\pi} \frac{e^2}{4m_e} \left(\sum_N Z_N r_{N1}^{-3} [(\vec{r}_{Ni} \cdot \vec{r}_{Gi})(\vec{\mu}_e \cdot \vec{B}) - (\vec{\mu}_e \cdot \vec{r}_{Gi})(\vec{r}_{Ni} \cdot \vec{B})] \right)$$

The first derivative is

$$\begin{aligned}
& \frac{\partial}{\partial \mu_{ea}} \left\langle \left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu}^{MN} \right\} \chi_\mu \left| \hat{h}^{(0)} + \hat{H}_{001} + \hat{H}_{101} \right| \chi_\nu \right\rangle \\
&= \left\langle \left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu}^{MN} \right\} \chi_\mu \left| -\frac{\mu_0}{4\pi} \frac{e}{2m_e} \left(\sum_N Z_N r_{N1}^{-3} \hat{l}_{N1a} \right) \right. \right. \\
&\quad \left. \left. + \frac{\mu_0}{4\pi} \frac{e^2}{4m_e} \left(\sum_N Z_N r_{N1}^{-3} \left[(\vec{r}_{Ni} \cdot \vec{r}_{Gi}) B_a - r_{Gia} (\vec{r}_{Ni} \cdot \vec{B}) \right] \right) \right| \chi_\nu \right\rangle
\end{aligned}$$

yielding

$$\begin{aligned}
H_{a,\mu\nu}^{(0,0,1)} &= -\frac{\mu_0}{4\pi} \frac{e}{2m_e} \left\langle \chi_\mu \left| \left(\sum_N Z_N r_{N1}^{-3} \hat{l}_{N1a} \right) \right| \chi_\nu \right\rangle \\
H_{ab,\mu\nu}^{\prime\prime(1,0,1)} &= \left\langle R_{a,\mu\nu}^{MN} \chi_\mu \left| -\frac{\mu_0}{4\pi} \frac{e}{2m_e} \left(\sum_N Z_N r_{N1}^{-3} \hat{l}_{N1b} \right) \right| \chi_\nu \right\rangle \\
&\quad + \left\langle \chi_\mu \left| \frac{\mu_0}{4\pi} \frac{e^2}{4m_e} \left(\sum_N Z_N r_{N1}^{-3} \left[(\vec{r}_{Ni} \cdot \vec{r}_{Gi}) \delta_{ab} - r_{Gib} r_{Nia} \right] \right) \right| \chi_\nu \right\rangle
\end{aligned}$$

These expressions again differ from the fixed basis set result only in the first term of $H_{ab,\mu\nu}^{\prime\prime(1,0,1)}$ which enters the paramagnetic contribution.

In evaluating the first-order correction to two-electron integrals (entering the first-order Fock matrix) we can again use the expansion of the gauge factor

$$\begin{aligned}
\langle \mu\lambda | \hat{g}_{12} | \nu\sigma \rangle^{(B)} &= (\chi_\mu \chi_\nu | \chi_\lambda \chi_\sigma)^{(B)} \\
&= (\Gamma_{\mu\nu} \chi_\mu \chi_\nu | \Gamma_{\lambda\sigma} \chi_\lambda \chi_\sigma) \\
&= \left(\left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu} \right\} \chi_\mu \chi_\nu \left| \left\{ 1 + \vec{B} \cdot \vec{R}_{\lambda\sigma} \right\} \chi_\lambda \chi_\sigma \right. \right)
\end{aligned}$$

and the first derivative becomes

$$\begin{aligned}
\langle \mu\lambda | \hat{g}_{12} | \nu\sigma \rangle_a^{(1)} &= \left(\{ R_{a,\mu\nu} \} \chi_\mu \chi_\nu \left| \left\{ 1 + \vec{B} \cdot \vec{R}_{\lambda\sigma} \right\} \chi_\lambda \chi_\sigma \right. \right) \\
&\quad + \left(\left\{ 1 + \vec{B} \cdot \vec{R}_{\mu\nu} \right\} \chi_\mu \chi_\nu \left| \{ R_{a,\lambda\sigma} \} \chi_\lambda \chi_\sigma \right. \right) \Big|_{B=0} \\
&= (\{ R_{a,\mu\nu} \} \chi_\mu \chi_\nu | \chi_\lambda \chi_\sigma) + (\chi_\mu \chi_\nu | \{ R_{a,\lambda\sigma} \} \chi_\lambda \chi_\sigma) \\
&= \frac{ie}{2\hbar} [(\mathcal{Q}_{a,\mu\nu} + \mathcal{Q}_{a,\lambda\sigma})(\chi_\mu \chi_\nu | \chi_\lambda \chi_\sigma) + (T_{a,\mu\nu} \chi_\mu \chi_\nu | \chi_\lambda \chi_\sigma) \\
&\quad + (\chi_\mu \chi_\nu | T_{a,\lambda\sigma} \chi_\lambda \chi_\sigma)]
\end{aligned}$$

At the end of this subsection let us notice that the GIAO concept has also been implemented in the density functional theory [19]; this theory can be compared with SOS-PT implementation in the DFT [20].

5.1.6 IGLO method

The IGLO method is based on the assumption that each *localised molecular orbital* is multiplied by a gauge factor [7–11]. This is the principal difference with respect to the GIAO method. The main advantage of this choice is that one needs only the original two-electron integrals in the fixed basis set as opposed to the GIAO method where two-electron integrals over the modified basis set (with increasing angular momenta) are necessary. Since the localised molecular orbitals are not too different from being spherical in shape, the local paramagnetic contributions are rather small, so that errors in them affect the final result only slightly.

The IGLO method starts with the MO-LCAO-SCF calculation which produces the conventional (canonical) molecular orbitals $\{\phi_i\}$. These satisfy Hartree-Fock equations written in the form

$$(1 - \hat{P}^{(0)})\hat{F}^{(0)}\phi_i^{(0)} = 0$$

where $\hat{F}^{(0)}$ is the Fock operator in the absence of the magnetic field, and $\hat{P}^{(0)}$ is the projection operator onto the space spanned by the (doubly) occupied MOs $\phi_i^{(0)}$

$$\hat{P}^{(0)} = \sum_i^{\text{occ}} |\phi_i^{(0)}\rangle\langle\phi_i^{(0)}|$$

In the next step the set of canonical molecular orbitals is transformed to the set of localised molecular orbitals according to the criterion of Boys [21]. This means that the following functional is maximised

$$D = \sum_i^{\text{occ}} \langle \phi_i \phi_i | r_{12}^2 | \phi_i \phi_i \rangle$$

(These facilities belong to a standard equipment of *ab initio* programs in the Gaussian basis set.) The localisation is applied separately for the set of inner shells (K, L, . . .) and the valence MOs. For multiple bonds the localisation leads to “banana bonds” [22].

When the magnetic perturbation is on, each (localised) molecular orbital can be written in the form of an expansion

$$\phi_i^{(B)} = \phi_i^{(0)} + i\phi_i^{(1)} + \dots$$

and similarly we expand

$$\hat{P}^{(B)} = \hat{P}^{(0)} + i\hat{P}^{(1)} + \dots$$

$$\hat{F}^{(B)} = \hat{F}^{(0)} + i\hat{F}^{(1)} + \dots$$

$$\hat{h}^{(B)} = \hat{h}^{(0)} + i\hat{h}^{(1)} + \hat{h}^{(2)} + \dots$$

$$E^{(B)} = E^{(0)} + iE^{(1)} + E^{(2)} + \dots$$

The first-order perturbation correction to the molecular orbitals $\phi_i^{(1)}$ satisfies the coupled Hartree–Fock equations written in the form

$$[(1 - \hat{P}^{(0)})\hat{F}^{(1)} - \hat{P}^{(1)}\hat{F}^{(0)}]\phi_i^{(0)} + (1 - \hat{P}^{(0)})\hat{F}^{(0)}\phi_i^{(1)} = 0$$

where the projection operator is defined as

$$\hat{P}^{(1)} = \sum_i^{\text{occ}} \left[|\phi_i^{(1)}\rangle\langle\phi_i^{(0)}| - |\phi_i^{(0)}\rangle\langle\phi_i^{(1)}| \right]$$

In these equations the first-order Fock operator is given as

$$\hat{F}^{(1)} = \hat{h}^{(1)} - \sum_i^{\text{occ}} \hat{K}_i^{(1)}$$

where there is an exchange correction term. The first-order perturbation operator corresponding to the external magnetic field is the electron Zeeman term

$$i\hat{h}^{(1)} = \frac{e}{2m_e}(\vec{B} \cdot \vec{l}_{G1})$$

and the second-order contribution contains the diamagnetic term

$$\hat{h}^{(2)} = \frac{e^2}{8m_e}(\vec{B} \times \vec{r}_{G1})^2$$

The energy increments become

$$E^{(1)} = 2 \sum_i^{\text{occ}} \langle \phi_i^{(0)} | \hat{h}^{(1)} | \phi_i^{(0)} \rangle = 0$$

$$E^{(2)} = 2 \sum_i^{\text{occ}} \langle \phi_i^{(0)} | \hat{h}^{(2)} | \phi_i^{(0)} \rangle - 2 \sum_i^{\text{occ}} \langle \phi_i^{(0)} | \hat{h}^{(1)} | \phi_i^{(1)} \rangle$$

Modified, gauge-dependent (localised) molecular orbitals are introduced through

$$\psi_i^{(B)} = \exp(-iA_i)\phi_i^{(B)}$$

where the gauge factor occurs

$$A_i = \frac{e}{2\hbar} (\vec{r}_{Gi} \times \vec{B}) \cdot \vec{r}_{Gi}$$

with the choice of the reference point $\vec{r}_{Gi}$ as the centre of gravity of the localised molecular orbital $\phi_i^{(0)}$. The above gauge transformation is an example of the unitary transformation which can be applied to the molecular Hamiltonian. The use of the Hausdorff formula yields

$$\hat{H}^{(i)} = \exp(-\lambda A_i) \hat{H} \exp(\lambda A_i) = \hat{H} + \lambda [\hat{H}, A_i] + \frac{1}{2} \lambda^2 [[\hat{H}, A_i], A_i] + \dots$$

Now we can see that the change of the gauge origin corresponds to a unitary transformation of the Hamiltonian. Although the wave function is affected by the unitary transformation, the eigenvalues remain unchanged and the Schrödinger equation is solved exactly.

Considering first the simplest case of the perturbation expansion

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1 + \lambda^2 \hat{H}_2$$

and a similar one for the transformed Hamiltonian

$$\begin{aligned} \hat{H}^{(i)} &= \hat{H}_0 + \lambda \hat{H}_1^{(i)} + \lambda^2 \hat{H}_2^{(i)} \\ &= \hat{H}_0 + \lambda \left\{ \hat{H}_1 + \lambda [\hat{H}_1, A_i] + \frac{1}{2} \lambda^2 [[\hat{H}_1, A_i], A_i] \right\} \\ &\quad + \lambda^2 \left\{ \hat{H}_2 + \lambda [\hat{H}_2, A_i] + \frac{1}{2} \lambda^2 [[\hat{H}_2, A_i], A_i] \right\} \end{aligned}$$

after collecting powers of λ one gets

$$\hat{H}_1^{(i)} = \hat{H}_1 + [\hat{H}_0, A_i]$$

$$\hat{H}_2^{(i)} = \hat{H}_2 + [\hat{H}_1, A_i] + \frac{1}{2}[[\hat{H}_0, A_i], A_i]$$

For a more complex perturbation expansion (involving the magnetic field and the nuclear magnetic moments)

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_{10} + \lambda^2 \hat{H}_{20} + \mu \hat{H}_{01} + \lambda \mu \hat{H}_{11} + \mu^2 \hat{H}_{02}$$

the transformed Hamiltonian terms become

$$\hat{H}_{10}^{(i)} = \hat{H}_{10} + [\hat{H}_0, A_i]$$

$$\hat{H}_{20}^{(i)} = \hat{H}_{20} + [\hat{H}_{10}, A_i] + \frac{1}{2}[[\hat{H}_0, A_i], A_i]$$

$$\hat{H}_{11}^{(i)} = \hat{H}_{11} + [\hat{H}_{01}, A_i]$$

$$\hat{H}_{01}^{(i)} = \hat{H}_{01} + [\hat{H}_0, A_i]$$

$$\hat{H}_{02}^{(i)} = \hat{H}_{02} + [\hat{H}_{01}, A_i] + \frac{1}{2}[[\hat{H}_0, A_i], A_i]$$

(The last two terms are gauge independent and there is no need to deal with them.)

For the most complex perturbation expansion including the magnetic field, nuclear magnetic moments and the electronic magnetic moment

$$\begin{aligned} \hat{H} = & \hat{H}_0 + \lambda \hat{H}_{100} + \lambda^2 \hat{H}_{200} + \mu \hat{H}_{010} + \lambda \mu \hat{H}_{110} + \mu^2 \hat{H}_{020} \\ & + \nu \hat{H}_{001} + \lambda \nu \hat{H}_{101} + \mu \nu \hat{H}_{011} + \nu^2 \hat{H}_{002} \end{aligned}$$

we need

$$\hat{H}_{100}^{(i)} = \hat{H}_{100} + [\hat{H}_0, A_i]$$

$$\hat{H}_{200}^{(i)} = \hat{H}_{200} + [\hat{H}_{100}, A_i] + \frac{1}{2}[[\hat{H}_0, A_i], A_i]$$

$$\hat{H}_{110}^{(i)} = \hat{H}_{110} + [\hat{H}_{010}, A_i]$$

$$\hat{H}_{101}^{(i)} = \hat{H}_{101} + [\hat{H}_{001}, A_i]$$

By substituting for the individual unperturbed operators we obtain the expressions

$$[\hat{H}_0, A_i] = \frac{e}{2m_e} (\vec{B} \times \vec{r}_{Gi}) \cdot \vec{p}$$

$$\frac{1}{2} [[\hat{H}_0, A_i], A_i] = \frac{e^2}{8m_e} (\vec{B} \times \vec{r}_{Gi})^2$$

$$[\hat{H}_{100}, A_i] = \frac{e^2}{4m_e} (\vec{B} \times \vec{r}_{G1})(\vec{B} \times \vec{r}_{Gi})$$

$$[\hat{H}_{010}, A_i] = \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} r_{N1}^{-3} (\vec{B} \times \vec{r}_{Gi})(\vec{\mu}_N \times \vec{r}_{N1})$$

$$[\hat{H}_{001}, A_i] = \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} \sum_N Z_N r_{N1}^{-3} (\vec{B} \times \vec{r}_{Gi})(\vec{\mu}_e \times \vec{r}_{N1})$$

so that the (gauge, unitary) transformation of the one-electron Hamiltonian terms is complete.

The gauge-transformed molecular orbitals are again written in the form of an expansion

$$\psi_i^{(B)} = \psi_i^{(0)} + i\psi_i^{(1)} + \dots$$

and it holds true that

$$\psi_i^{(0)} = \phi_i^{(0)}$$

The first-order correction $\psi_i^{(1)}$ satisfies the (gauge) modified coupled Hartree–Fock equations

$$[(1 - \hat{P}^{(0)})\tilde{F}_i^{(1)} - \tilde{P}_i^{(1)}\hat{F}^{(0)}]\psi_i^{(0)} + (1 - \hat{P}^{(0)})\hat{F}^{(0)}\psi_i^{(1)} = 0$$

with new definitions of the first-order Fock operator and the first-order projection operator. These are

$$\tilde{P}_i^{(B)} = P^{(0)} + i\tilde{P}_i^{(1)} + \dots$$

$$\tilde{P}_i^{(1)} = \sum_k^{\text{occ}} \left\{ \left| \phi_k^{(1)} \right\rangle \left\langle \phi_k^{(0)} \right| - \left| \phi_k^{(0)} \right\rangle \left\langle \phi_k^{(1)} \right| + \left[\left| \phi_k^{(1)} \right\rangle \left\langle \phi_k^{(0)} \right|, (A_i - A_k) \right] \right\}$$

$$\tilde{F}_i^{(B)} = F^{(0)} + i\tilde{F}_i^{(1)} + \dots$$

$$\tilde{F}_i^{(1)} = \tilde{h}_i^{(1)} - \sum_k^{\text{occ}} \left\{ \tilde{K}_k^{(1)} + [\tilde{K}_k^{(0)}, (A_k - A_i)] \right\}$$

The exchange operator $\tilde{K}_k^{(1)}$ is defined through its matrix elements

$$\langle a | \tilde{K}_i^{(1)} | b \rangle \equiv \langle a \psi_i^{(1)} | \hat{g}_{12} | \psi_i^{(0)} b \rangle - \langle a \psi_i^{(0)} | \hat{g}_{12} | \psi_i^{(1)} b \rangle$$

The above modified coupled Hartree–Fock equations for $\psi_i^{(1)}$ should be solved through an iterative procedure. Once they are determined, the second-order energy appears as a sum of four contributions

$$E_2 = E_2^{\text{dia}} + E_2^{\text{para}} + E_2^{\text{ex}} + E_2^{\text{res}}$$

with the *diamagnetic term*

$$E_2^{\text{dia}} = 2 \sum_i^{\text{occ}} \langle \psi_i^{(0)} | \tilde{h}_i^{(2)} | \psi_i^{(0)} \rangle$$

the *paramagnetic term*

$$\begin{aligned} E_2^{\text{para}} = & -2 \sum_i^{\text{occ}} \sum_j^{\text{occ}} \langle \psi_i^{(0)} | \tilde{h}_i^{(1)} | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | (A_j - A_i) | \psi_i^{(0)} \rangle \\ & - 2 \sum_i^{\text{occ}} \langle \psi_i^{(0)} | \tilde{h}_i^{(1)} (1 - \hat{P}^{(0)}) | \psi_i^{(1)} \rangle \end{aligned}$$

the *exchange correction term*

$$\begin{aligned}
E_2^{\text{ex}} = & \frac{1}{2} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \left\langle \psi_i^{(0)} \left| [\tilde{K}_j^{(0)}, (A_i - A_j)], (A_i - A_j) \right| \psi_i^{(0)} \right\rangle \\
& + 2 \sum_i^{\text{occ}} \sum_j^{\text{occ}} \left\langle \psi_i^{(0)} \left| [\tilde{K}_j^{(0)}, (A_i - A_j)] (1 - \hat{P}^{(0)}) \right| \psi_i^{(1)} \right\rangle \\
& + \sum_i^{\text{occ}} \sum_j^{\text{occ}} \sum_k^{\text{occ}} \left\langle \psi_i^{(0)} \left| 2[\tilde{K}_k^{(0)}, (A_k - A_i)] - \tilde{K}_k^{(1)} \right| \psi_j^{(0)} \right\rangle \\
& \left\langle \psi_j^{(0)} | (A_i - A_j) | \psi_i^{(0)} \right\rangle
\end{aligned}$$

and the *resonance correction term* involving the off-diagonal matrix elements of the unperturbed Fock operator

$$\begin{aligned}
E_2^{\text{res}} = & 2 \sum_i^{\text{occ}} \sum_j^{\text{occ}} \left\langle \psi_j^{(0)} \left| \hat{F}^{(0)} \right| \psi_i^{(0)} \right\rangle \left\langle \psi_i^{(0)} \left| (A_j - A_i) (1 - \hat{P}^{(0)}) \right| \psi_j^{(1)} \right\rangle \\
& + \sum_i^{\text{occ}} \sum_j^{\text{occ}} \left\langle \psi_j^{(0)} \left| \hat{F}^{(0)} \right| \psi_i^{(0)} \right\rangle \left\langle \psi_i^{(0)} \left| (A_j - A_i)^2 \right| \psi_j^{(0)} \right\rangle \\
& + 2 \sum_i^{\text{occ}} \sum_j^{\text{occ}} \sum_k^{\text{occ}} \left\langle \psi_j^{(0)} \left| \hat{F}^{(0)} \right| \psi_i^{(0)} \right\rangle \left\langle \psi_i^{(0)} \left| (A_j - A_i) \right| \psi_k^{(0)} \right\rangle \\
& \left\langle \psi_k^{(0)} \left| (A_k - A_j) \right| \psi_j^{(0)} \right\rangle
\end{aligned}$$

The expression for the magnetic susceptibility tensor components is

$$\kappa_{ab} = \sum_{i=1}^n \left[\left\langle \psi_i^{(0)} \left| \tilde{H}_{ab,i}^{(2,0,0)} \right| \psi_i^{(0)} \right\rangle - \left\langle \psi_i^{(0)} \left| \tilde{H}_{a,i}^{(1,0,0)} \right| \psi_{b,i}^{(1)} \right\rangle \right]$$

The expression for the nuclear shielding tensor components is

$$\sigma_{Nab} = 2 \sum_{i=1}^n \left[\left\langle \psi_i^{(0)} \left| \tilde{H}_{Nab,i}^{(1,1,0)} \right| \psi_i^{(0)} \right\rangle - 2 \left\langle \psi_i^{(0)} \left| \tilde{H}_{Na,i}^{(0,1,0)} \right| \psi_{b,i}^{(1)} \right\rangle \right]$$

and it can be decomposed into the diamagnetic term

$$\sigma_{Nab}^{\text{dia}} = 2 \sum_{i=1}^n \left\langle \psi_i^{(0)} \left| \tilde{H}_{Nab,i}^{(1,1,0)} \right| \psi_i^{(0)} \right\rangle$$

and the paramagnetic term

$$\begin{aligned}\sigma_{Nab}^{\text{para}} = & -4 \sum_{i=1}^n \left\langle \psi_i^{(0)} \left| \tilde{H}_{Na,i}^{(0,1,0)} (1 - \hat{P}^{(0)}) \right| \psi_{b,i}^{(1)} \right\rangle \\ & - 4 \sum_{i=1}^n \sum_{j=1}^n \left\langle \psi_i^{(0)} \left| \tilde{H}_{Na,i}^{(0,1,0)} \right| \psi_j^{(0)} \right\rangle \left\langle \psi_i^{(0)} \left| (\Lambda_{bj} - \Lambda_{b,i}) \right| \psi_j^{(0)} \right\rangle\end{aligned}$$

Finally, the $\overline{\overline{\Delta g}}$ tensor components are expressed as

$$\Delta g_{ab} = 2 \sum_{i=1}^n \left[\left\langle \psi_i^{(0)} \left| \tilde{H}_{ab,i}^{(1,0,1)} \right| \psi_i^{(0)} \right\rangle - 2 \left\langle \psi_i^{(0)} \left| \tilde{H}_{Na,i}^{(0,0,1)} \right| \psi_{b,i}^{(1)} \right\rangle \right]$$

5.1.7 LORG method

This is a variant of the sum-over-states perturbation theory which applies the random phase approximation (RPA) to deal effectively with the paramagnetic contribution. A localised orbital scheme is utilised to ascribe the local gauge origins [12,13]. Complex (gauge-dependent) orbitals are not introduced.

In SOS-PT a magnetic parameter can be expressed as the sum of two contributions: the diamagnetic term involving only the ground-state wave function, and the paramagnetic term containing the resolvent operator

$$\begin{aligned}\overline{\overline{X}}^{\lambda_1 \lambda_2} = & \left(\frac{\partial^2 E(\lambda_1, \lambda_2)}{\partial \lambda_1 \partial \lambda_2} \right)_{\lambda_1=\lambda_2=0} = \left\langle \Psi_0 \left| \frac{\partial^2 \hat{H}(\lambda_1, \lambda_2)}{\partial \lambda_1 \partial \lambda_2} \right| \Psi_0 \right\rangle \\ & - \sum_{K=1}^{\infty} \frac{1}{E_K - E_0} \left\langle \Psi_0 \left| \frac{\partial \hat{H}(\lambda_1)}{\partial \lambda_1} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \frac{\partial \hat{H}(\lambda_2)}{\partial \lambda_2} \right| \Psi_0 \right\rangle\end{aligned}$$

We have already found out that within the RPA the resolvent operator can be expressed as

$$\begin{aligned}R_{ab}^{\lambda_1 \lambda_2} = & \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}_a^{(\lambda_1)} \cdot \left\langle \Psi_0 \left| \tilde{h}^{(\lambda_1)} \right| \Psi_o^u \right\rangle \right] \left[\tilde{e}_b^{(\lambda_1)} \cdot \left\langle \Psi_p^v \left| \tilde{h}^{(\lambda_2)} \right| \Psi_0 \right\rangle \right] \\ & ([A - B]^{-1})_{op}^{uv}\end{aligned}$$

For a closed shell system and spin-free one-electron operators this reduces to the form where integrals over MOs occur

$$R_{ab}^{\lambda_1 \lambda_2} = 2 \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}_a^{(\lambda_1)} \cdot \langle \phi_o | \tilde{h}_1^{(\lambda_1)} | \phi_u \rangle \right] \left[\tilde{e}_b^{(\lambda_2)} \cdot \langle \phi_v | \tilde{h}_1^{(\lambda_2)} | \phi_p \rangle \right] \\ ([A - B]^{-1})_{op}^{uv}$$

Normally the second parameter is the magnetic field, $\lambda_2 = B$, and the gauge-dependent one-electron Hamiltonian

$$\tilde{e}^{(B)} \cdot \tilde{h}^{(B)} = \frac{e}{2m_e} \sum_i \tilde{e}^{(B)} \cdot \vec{r}_{Gi} \times \vec{p}_i = \frac{e}{2m_e} \sum_i \tilde{e}^{(B)} \cdot \vec{l}_{Gi}$$

is the orbital Zeeman term containing the orbital angular momentum $\vec{l}_{Gi} = \vec{r}_{Gi} \times \vec{p}_i$.

The LORG method assumes that each occupied molecular orbital is localised (e.g. using the Boys criterion), and an origin vector $\vec{r}_{No} = \vec{r}_o - \vec{r}_N$ relative to the magnetic nucleus is associated with each localised orbital (ϕ_o) so that it holds true that

$$\vec{r}_{Gi} \equiv \vec{r}_i - \vec{r}_G = (\vec{r}_i - \vec{r}_{No}) + (\vec{r}_{No} - \vec{r}_G) = \vec{r}_{oi} + \vec{r}_{Go}$$

(A modified vector notation is used relative to the original paper [12].) Then the electron angular momentum can be expressed as

$$\vec{l}_{Gi} = \vec{r}_{oi} \times \vec{p}_i + \vec{r}_{Go} \times \vec{p}_i = \vec{l}_{oi} + \vec{r}_{Go} \times \vec{p}_i$$

and the resolvent relaxes to

$$R_{ab}^{\lambda B} = \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}_a^{(\lambda)} \cdot \langle \Psi_0 | \tilde{h}^{(\lambda)} | \Psi_o^u \rangle \right] \left[\tilde{e}_b^{(B)} \cdot \langle \Psi_p^v | \tilde{h}^{(B)} | \Psi_0 \rangle \right] \\ ([A - B]^{-1})_{op}^{uv} \\ = \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}_a^{(\lambda)} \cdot \langle \Psi_0 | \tilde{h}^{(\lambda)} | \Psi_o^u \rangle \right] \\ \left[\tilde{e}_b^{(B)} \cdot \left\langle \Psi_p^v \left| \frac{e}{2m_e} \sum_i (\vec{l}_{oi} + \vec{r}_{Go} \times \vec{p}_i) \right| \Psi_0 \right\rangle \right] ([A - B]^{-1})_{op}^{uv} \\ = R_{ab}^{\lambda B}(1) + R_{ab}^{\lambda B}(2)$$

The first term does not contain references to the gauge origin

$$R_{ab}^{\lambda B}(1) = \frac{e}{2m_e} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\vec{e}_a^{(\lambda)} \cdot \langle \Psi_0 | \vec{h}^{(\lambda)} | \Psi_o^u \rangle \right] \\ \left[\vec{e}_b^{(B)} \cdot \left\langle \Psi_p^v \left| \sum_i \vec{l}_{oi} \right| \Psi_0 \right\rangle \right] ([A - B]^{-1})_{op}^{uv}$$

and when the singlet determinantal wave functions are expressed through molecular orbitals one gets

$$R_{ab}^{\lambda B}(1) = \frac{e}{2m_e} 2 \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\vec{e}_a^{(\lambda)} \cdot \langle \phi_o | \vec{h}_1^{(\lambda)} | \phi_u \rangle \right] \left[\vec{e}_b^{(B)} \cdot \langle \phi_v | \vec{l}_{o1} | \phi_p \rangle \right] \\ ([A - B]^{-1})_{op}^{uv}$$

The second term, containing information about the gauge origin, can be heavily simplified. For this purpose we can use the property that the transition moment obeys [23]

$$\sum_o^{\text{occ}} \sum_u^{\text{un}} \langle \Psi_0 | \vec{p} | \Psi_o^u \rangle ([A - B]^{-1})_{op}^{uv} = -i \frac{m_e}{\hbar} \langle \Psi_0 | \vec{r} | \Psi_p^v \rangle$$

which implies the RPA *hypervirial relation*

$$\sum_o^{\text{occ}} \sum_u^{\text{un}} \langle \Psi_0 | \vec{p} | \Psi_o^u \rangle (T_K)_o^u = -i\omega_K \frac{m_e}{\hbar} \sum_o^{\text{occ}} \sum_u^{\text{un}} \langle \Psi_0 | \vec{r} | \Psi_o^u \rangle (S_K)_o^u$$

or alternatively

$$\sum_p^{\text{occ}} \sum_v^{\text{un}} \langle \Psi_p^v | \vec{p} | \Psi_0 \rangle (T_K)_p^v = i\omega_K \frac{m_e}{\hbar} \sum_p^{\text{occ}} \sum_v^{\text{un}} \langle \Psi_p^v | \vec{r} | \Psi_0 \rangle (S_K)_p^v$$

Using this formula, the following replacement holds true

$$R_{ab}^{\lambda B}(2) = \frac{e}{2\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\vec{e}_a^{(\lambda)} \cdot \langle \Psi_0 | \vec{h}^{(\lambda)} | \Psi_o^u \rangle \right] \\ \left[\vec{e}_b^{(B)} \cdot \left\langle \Psi_p^v \left| \vec{r}_{Go} \times \sum_i \vec{p}_i \right| \Psi_0 \right\rangle \right] \left\{ \sum_{K=1}^{\infty} (T_K)_o^u \omega_K^{-1} (T_K)_p^v \right\}$$

$$= i \frac{e}{2\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}_a^{(\lambda)} \cdot \left\langle \Psi_0 \left| \tilde{h}^{(\lambda)} \right| \Psi_o^u \right\rangle \right] \\ \left[\tilde{e}_b^{(B)} \cdot \left\langle \Psi_p^v \left| \tilde{r}_{Go} \times \sum_i \tilde{r}_{Ni} \right| \Psi_0 \right\rangle \right] \left\{ \sum_{K=1}^{\infty} (T_K)_o^u (S_K)_p^v \right\}$$

and, because of the closure relationship, this is simplified to

$$R_{ab}^{\lambda B}(2) = \frac{ie}{2\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \\ \left[\tilde{e}_a^{(\lambda)} \cdot \left\langle \Psi_0 \left| \tilde{h}^{(\lambda)} \right| \Psi_o^u \right\rangle \right] \left[\tilde{e}_b^{(B)} \cdot \left\langle \Psi_p^v \left| \tilde{r}_{Go} \times \sum_i \tilde{r}_{Ni} \right| \Psi_0 \right\rangle \right] \delta_{op} \delta_{uv}$$

In terms of molecular orbitals for a closed shell system it becomes

$$R_{ab}^{\lambda B}(2) = \frac{ie}{\hbar} \sum_o^{\text{occ}} \sum_u^{\text{un}} \left[\tilde{e}_a^{(\lambda)} \cdot \left\langle \phi_o \left| \tilde{h}_1^{(\lambda)} \right| \phi_u \right\rangle \right] \left[\tilde{e}_b^{(B)} \cdot \tilde{r}_{Go} \times \left\langle \phi_u \left| \tilde{r}_{N1} \right| \phi_o \right\rangle \right]$$

A further manipulation utilises the completeness relation for molecular orbitals

$$\sum_u^{\text{un}} |\phi_u\rangle\langle\phi_u| = 1 - \sum_p^{\text{occ}} |\phi_p\rangle\langle\phi_p|$$

to yield

$$R_{ab}^{\lambda B}(2) = \frac{ie}{\hbar} \sum_o^{\text{occ}} \left\langle \phi_o \left| \left[\tilde{e}_a^{(\lambda)} \cdot \tilde{h}_1^{(\lambda)} \right] \left[\tilde{e}_b^{(B)} \cdot \tilde{r}_{Go} \times \tilde{r}_{N1} \right] \right| \phi_o \right\rangle \\ - \frac{ie}{\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\tilde{e}_a^{(\lambda)} \cdot \left\langle \phi_o \left| \tilde{h}_1^{(\lambda)} \right| \phi_p \right\rangle \right] \left[\tilde{e}_b^{(B)} \cdot \tilde{r}_{Go} \times \left\langle \phi_p \left| \tilde{r}_{N1} \right| \phi_o \right\rangle \right]$$

The second resolvent is constructed in the way that the operators are interchanged as follows

$$Q_{ab}^{\lambda B}(1) = \frac{e}{m_e} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} \left[\tilde{e}_b^{(B)} \cdot \left\langle \phi_o \left| \tilde{l}_{o1} \right| \phi_u \right\rangle \right] \left[\tilde{e}_a^{(\lambda)} \cdot \left\langle \phi_v \left| \tilde{h}_1^{(\lambda)} \right| \phi_p \right\rangle \right] \\ ([A - B]^{-1})_{op}^{uv}$$

and

$$\begin{aligned} Q_{ab}^{\lambda B}(2) = & -\frac{ie}{\hbar} \sum_o^{\text{occ}} \left\langle \phi_o \left| \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right] \left[\vec{e}_a^{(\lambda)} \cdot \vec{h}_1^{(\lambda)} \right] \right| \phi_o \right\rangle \\ & + \frac{ie}{\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \langle \phi_o | \vec{r}_{N1} | \phi_p \rangle \right] \left[\vec{e}_a^{(\lambda)} \cdot \langle \phi_p | \vec{h}_1^{(\lambda)} | \phi_o \rangle \right] \end{aligned}$$

Let us deal with the nuclear shielding tensor. This is a sum of two terms. The diamagnetic term is

$$\begin{aligned} \sigma_{Nab}^{\text{dia}} = & \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} \left\langle \Psi_0 \left| \sum_i r_{Ni}^{-3} (\vec{e}_a^{(\mu_N)} \times \vec{r}_{Ni}) \cdot (\vec{e}_b^{(B)} \times \vec{r}_{Gi}) \right| \Psi_0 \right\rangle \\ = & \frac{\mu_0}{4\pi} \frac{e^2}{2m_e} 2 \sum_o^{\text{occ}} \left\langle \phi_o \left| r_{N1}^{-3} (\vec{e}_a^{(\mu_N)} \times \vec{r}_{N1}) \cdot (\vec{e}_b^{(B)} \times \vec{r}_{G1}) \right| \phi_o \right\rangle \end{aligned}$$

This can be decomposed, using individual gauge origins, by using a substitution $\vec{r}_{G1} = \vec{r}_{o1} + \vec{r}_{Go}$ so that

$$\begin{aligned} \sigma_{Nab}^{\text{dia}} = & \frac{\mu_0}{4\pi} \frac{e^2}{m_e} \sum_o^{\text{occ}} \left\langle \phi_o \left| r_{N1}^{-3} (\vec{e}_a^{(\mu_N)} \times \vec{r}_{N1}) \cdot (\vec{e}_b^{(B)} \times [\vec{r}_{o1} + \vec{r}_{Go}]) \right| \phi_o \right\rangle \\ = & \frac{\mu_0}{4\pi} \frac{e^2}{m_e} \sum_o^{\text{occ}} \left\langle \phi_o \left| r_{N1}^{-3} (\vec{e}_a^{(\mu_N)} \times \vec{r}_{N1}) \cdot (\vec{e}_b^{(B)} \times \vec{r}_{o1}) \right| \phi_o \right\rangle \\ & + \frac{\mu_0}{4\pi} \frac{e^2}{m_e} \sum_o^{\text{occ}} \left\langle \phi_o \left| r_{N1}^{-3} (\vec{e}_a^{(\mu_N)} \times \vec{r}_{N1}) \right| \phi_o \right\rangle \cdot (\vec{e}_b^{(B)} \times \vec{r}_{Go}) \\ = & \sigma_{Nab}^{\text{dia}}(1) + \sigma_{Nab}^{\text{dia}}(2) \end{aligned}$$

with

$$\sigma_{Nab}^{\text{dia}}(1) = \frac{\mu_0}{4\pi} \frac{e^2}{m_e} \sum_o^{\text{occ}} \left\langle \phi_o \left| r_{N1}^{-3} [\vec{r}_{o1} \cdot \vec{r}_{N1} \delta_{ab} - (\vec{e}_a^{(\mu_N)} \cdot \vec{r}_{o1})(\vec{e}_b^{(B)} \cdot \vec{r}_{N1})] \right| \phi_o \right\rangle$$

The reference to the gauge origin (G) is now present in the second term $\sigma_{Nab}^{\text{dia}}(2)$

$$\sigma_{Nab}^{\text{dia}}(2) = \frac{\mu_0}{4\pi} \frac{e^2}{m_e} \sum_o^{\text{occ}} \left\langle \phi_o \left| r_{N1}^{-3} (\vec{e}_a^{(\mu_N)} \times \vec{r}_{N1}) \right| \phi_o \right\rangle \cdot (\vec{e}_b^{(B)} \times \vec{r}_{Go})$$

The paramagnetic term is

$$\sigma_{Nab}^{\text{para}} = -(R_{Nab}^{\mu_N, B} + Q_{Nab}^{\mu_N, B}) = \sigma_{Nab}^{\text{para}}(1) + \sigma_{Nab}^{\text{para}}(2)$$

with

$$\begin{aligned}\sigma_{Nab}^{\text{para}}(1) &= -[R_{Nab}^{\mu_N, B}(1) + Q_{Nab}^{\mu_N, B}(1)] \\ &= -2 \frac{e}{m_e} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \sum_u^{\text{un}} \sum_v^{\text{un}} [\vec{e}_a^{(\lambda)} \cdot \langle \phi_o | \vec{h}_1^{(\lambda)} | \phi_u \rangle] [\vec{e}_b^{(B)} \cdot \langle \phi_v | \vec{l}_{o1} | \phi_p \rangle] \\ &\quad ([A - B]^{-1})_{op}^{uv}\end{aligned}$$

and

$$\begin{aligned}\sigma_{Nab}^{\text{para}}(2) &= -[R_{Nab}^{\mu_N, B}(2) + Q_{Nab}^{\mu_N, B}(2)] \\ &= -\frac{ie}{\hbar} \sum_o^{\text{occ}} \left\langle \phi_o \left| \left[\vec{e}_a^{(\lambda)} \cdot \vec{h}_1^{(\lambda)} \right] \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right] \right. \right. \\ &\quad \left. \left. + \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right] \left[\vec{e}_a^{(\lambda)} \cdot \vec{h}_1^{(\lambda)} \right] \right| \phi_o \right\rangle \\ &\quad + \frac{ie}{\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\vec{e}_a^{(\lambda)} \cdot \langle \phi_o | \vec{h}_1^{(\lambda)} | \phi_p \rangle \right] \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \langle \phi_p | \vec{r}_{N1} | \phi_o \rangle \right] \\ &\quad - \frac{ie}{\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \langle \phi_o | \vec{r}_{N1} | \phi_p \rangle \right] \left[\vec{e}_a^{(\lambda)} \cdot \langle \phi_p | \vec{h}_1^{(\lambda)} | \phi_o \rangle \right]\end{aligned}$$

The gauge-dependent terms can be combined to yield

$$\begin{aligned}\sigma_{Nab}^{\text{gauge}} &= \sigma_{Nab}^{\text{dia}}(2) + \sigma_{Nab}^{\text{para}}(2) = \frac{\mu_0}{4\pi} \frac{e^2}{m_e} \sum_o^{\text{occ}} \left\langle \phi_o \left| \vec{r}_{N1}^{-3} (\vec{e}_a^{(\mu_N)} \times \vec{r}_{N1}) \right| \phi_o \right\rangle \\ &\quad \cdot (\vec{e}_b^{(B)} \times \vec{r}_{Go}) - \frac{ie}{\hbar} \sum_o^{\text{occ}} \left\langle \phi_o \left| \left[\vec{e}_a^{(\mu_N)} \cdot \vec{h}_1^{(\mu_N)} \right] \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right] \right. \right. \\ &\quad \left. \left. - \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right] \left[\vec{e}_a^{(\mu_N)} \cdot \vec{h}_1^{(\mu_N)} \right] \right| \phi_o \right\rangle \\ &\quad + \frac{ie}{\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\vec{e}_a^{(\mu_N)} \cdot \langle \phi_o | \vec{h}_1^{(\mu_N)} | \phi_p \rangle \right] \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \langle \phi_p | \vec{r}_{N1} | \phi_o \rangle \right] \\ &\quad - \frac{ie}{\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \langle \phi_o | \vec{r}_{N1} | \phi_p \rangle \right] \left[\vec{e}_a^{(\mu_N)} \cdot \langle \phi_p | \vec{h}_1^{(\mu_N)} | \phi_o \rangle \right]\end{aligned}$$

and, after insertion for the (complex) operator of the orbital hyperfine correction, we obtain

$$\begin{aligned}
\sigma_{Nab}^{\text{gauge}} = & \frac{\mu_0}{4\pi} \frac{e^2}{m_e} \sum_o^{\text{occ}} \left\langle \phi_o \left| r_{N1}^{-3} (\vec{e}_a^{(\mu_N)} \times \vec{r}_{N1}) \right| \phi_o \right\rangle \cdot (\vec{e}_b^{(B)} \times \vec{r}_{Go}) \\
& - \frac{\mu_0}{4\pi} \frac{e}{m_e} \frac{ie}{\hbar} \sum_o^{\text{occ}} \left\langle \phi_o \left| \left[\vec{e}_a^{(\mu_N)} \cdot r_{N1}^{-3} \vec{l}_{N1} \right] \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right] \right. \right. \\
& \left. \left. - \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right] \left[\vec{e}_a^{(\mu_N)} \cdot r_{N1}^{-3} \vec{l}_{N1} \right] \right| \phi_o \right\rangle + \frac{\mu_0}{4\pi} \frac{e}{m_e} 2 \frac{ie}{\hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \\
& \left[\vec{e}_a^{(\mu_N)} \cdot \left\langle \phi_o \left| r_{N1}^{-3} \vec{l}_{N1} \right| \phi_p \right\rangle \right] \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \langle \phi_p | \vec{r}_{N1} | \phi_o \rangle \right]
\end{aligned}$$

The second sum contains a commutator which can be simplified using the identity fulfilled for the angular momentum

$$[\vec{e} \cdot \vec{l}, \vec{r}] = -i\hbar(\vec{e} \times \vec{r})$$

Hence

$$\begin{aligned}
& \left\langle \phi_o \left| \left(\vec{e}_a^{(\mu_N)} \cdot r_{N1}^{-3} \vec{l}_{N1} \right) \left(\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right) \right. \right. \\
& \quad \left. \left. - \left(\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \vec{r}_{N1} \right) \left(\vec{e}_a^{(\mu_N)} \cdot r_{N1}^{-3} \vec{l}_{N1} \right) \right| \phi_o \right\rangle \\
& = \left\langle \phi_o \left| \left(\vec{e}_a^{(\mu_N)} \cdot r_{N1}^{-3} \vec{l}_{N1} \right) \left(\vec{e}_b^{(B)} \times \vec{r}_{Go} \cdot \vec{r}_{N1} \right) \right. \right. \\
& \quad \left. \left. - \left(\vec{e}_b^{(B)} \times \vec{r}_{Go} \cdot \vec{r}_{N1} \right) \left(\vec{e}_a^{(\mu_N)} \cdot r_{N1}^{-3} \vec{l}_{N1} \right) \right| \phi_o \right\rangle \\
& = \left(\vec{e}_b^{(B)} \times \vec{r}_{Go} \right) \cdot \left\langle \phi_o \left| \left[\left(\vec{e}_a^{(\mu_N)} \cdot r_{N1}^{-3} \vec{l}_{N1} \right), \vec{r}_{N1} \right] \right| \phi_o \right\rangle \\
& = -i\hbar \left(\vec{e}_b^{(B)} \times \vec{r}_{Go} \right) \cdot \left\langle \phi_o \left| \vec{e}_a^{(\mu_N)} \times r_{N1}^{-3} \vec{r}_{N1} \right| \phi_o \right\rangle
\end{aligned}$$

Because of the exact cancellation of this term and the first term, the only surviving residuum is

$$\sigma_{Nab}^{\text{gauge}} = 2i \frac{\mu_0}{4\pi} \frac{e^2}{m_e \hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\vec{e}_a^{(\mu_N)} \cdot \left\langle \phi_o \left| r_{N1}^{-3} \vec{l}_{N1} \right| \phi_p \right\rangle \right] \left[\vec{e}_b^{(B)} \cdot \vec{r}_{Go} \times \langle \phi_p | \vec{r}_{N1} | \phi_o \rangle \right]$$

and, since the indices o and p both run over all occupied orbitals, it can be rewritten in the final form

$$\sigma_{Nab}^{\text{gauge}} = i \frac{\mu_0}{4\pi} \frac{e^2}{m_e \hbar} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\vec{e}_a^{(\mu_N)} \cdot \left\langle \phi_o \left| r_{N1}^{-3} \vec{l}_{N1} \right| \phi_p \right\rangle \right] \\ \left[\vec{e}_b^{(B)} \cdot (\vec{r}_{No} - \vec{r}_{Np}) \times \langle \phi_p | \vec{r}_{N1} | \phi_o \rangle \right]$$

This expression is free of the gauge origin. The formula for the total nuclear shielding tensor is

$$\sigma_{Nab} = \sigma_{Nab}^{\text{dia}}(1) + \sigma_{Nab}^{\text{gauge}} + \sigma_{Nab}^{\text{para}}(1)$$

where the middle contribution can be formally included in either the diamagnetic or the paramagnetic term.

5.1.8 Current density

An alternative approach to evaluating the magnetic properties is based on the concept of current density [15,24,25]. The electronic current density is an expectation value of the current operator, the product of the observables for the electron density and velocity

$$\vec{J}(\vec{r}) = -\frac{e}{m_e} \{ \vec{\pi} P_1(\vec{r}; \vec{r}') \}_{\vec{r}'=\vec{r}}$$

The operator for the linear momentum of an electron

$$\vec{\pi}_i = \vec{p}_i + e\vec{A}(\vec{r}_i)$$

includes a perturbing vector potential $\vec{A}$. The (probability) density function (“density matrix”) is defined with the help of the n -electron wave function $\Psi(\vec{X}_1, \dots, \vec{X}_n)$, with the space and spin coordinates $\vec{X}_i = \{\vec{r}_i, s_i\}$, as follows [26]

$$P_1(\vec{r}; \vec{r}') = n \int \dots \int [\Psi(\vec{r}, \vec{X}_2, \dots, \vec{X}_n) \Psi^*(\vec{r}', \vec{X}_2', \dots, \vec{X}_n')] d\vec{X}_2 \vec{X}_n$$

The contributions to the vector potential

$$\vec{A} = \vec{A}_B + \sum_N \vec{A}_N$$

may have two sources:

(a) space-uniform, time-independent magnetic field $\vec{B}$

$$\vec{A}_B = \frac{1}{2} \vec{B} \times (\vec{r} - \vec{G})$$

where $\vec{G}$ stands for an arbitrarily chosen gauge origin;

(b) contributions from the nuclear magnetic moments

$$\vec{A}_N = \frac{\mu_0}{4\pi} \vec{\mu}_N \times \frac{\vec{r} - \vec{r}_N}{|\vec{r} - \vec{r}_N|^3}$$

The energy of interaction between the field $\vec{A}$ and the electrons of a molecule, flowing with current density $\vec{J}$, is

$$E = - \int \vec{A} \cdot \vec{J} dV$$

For an external magnetic field we have the expression

$$E = - \int \vec{A}_B \cdot \vec{J}_B dV = - \frac{1}{2} \int (\vec{B} \times \vec{r}) \cdot \vec{J}_B dV = - \vec{B} \cdot \left[\frac{1}{2} \int (\vec{r} \times \vec{J}_B) dV \right]$$

which has the form of the magnetic field interacting with a magnetic moment.

The n -electron wave function can be written in the form of a perturbation expansion

$$|\Psi\rangle = |\Psi^{(0)}\rangle + \vec{B} \cdot |\vec{\Psi}^{(1,0,0)}\rangle + \vec{\mu}_N \cdot |\vec{\Psi}_N^{(0,1,0)}\rangle + \dots$$

and, in terms of the Rayleigh–Schrödinger perturbation theory, the first-order electronic wave function in the presence of a magnetic field becomes expressed as

$$|\vec{\Psi}^{(1,0,0)}\rangle \equiv |\vec{\Psi}_B\rangle = - \frac{e}{2\hbar m_e} \sum_{K \neq 0} \frac{\langle K | \vec{L} | 0 \rangle}{E_K - E_0} |K\rangle$$

At the same time the electronic current density can be expanded in powers of the magnetic induction

$$\vec{J} = \vec{J}^{(0)} + \vec{B} \cdot \vec{J}^{(1)} + \dots$$

where, for the diamagnetic molecules, $\vec{J}^{(0)} = \vec{0}$ holds true. The first-order term can be partitioned into a diamagnetic and a paramagnetic contribution, respectively, hence

$$\vec{B} \cdot \vec{J}^{(1)} \equiv \vec{J}_B^{(1)} = \vec{J}_B^{\text{dia}} + \vec{J}_B^{\text{para}}$$

with

$$\begin{aligned}\vec{J}_B^{\text{dia}} &= -\frac{e^2}{2m_e}(\vec{B} \times \vec{r})P_1(\vec{r}; \vec{r}) \\ \vec{J}_B^{\text{para}} &= -\frac{e}{m_e}n \int \dots \int \{[\vec{B} \cdot \vec{\Psi}_B^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_n)]\vec{p}\Psi^{(0)}(\vec{r}, \vec{r}_2, \dots, \vec{r}_n) \\ &\quad + \Psi^{(0)}(\vec{r}, \vec{r}_2, \dots, \vec{r}_n)\vec{p}[\vec{B} \cdot \Psi_B(\vec{r}, \vec{r}_2, \dots, \vec{r}_n)]\}d\vec{r}_2 \dots d\vec{r}_n \\ &= i\hbar\frac{e}{m_e}n \int \dots \int \{[\vec{B} \cdot \vec{\Psi}_B^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_n)]\vec{\nabla}\Psi^{(0)}(\vec{r}, \vec{r}_2, \dots, \vec{r}_n) \\ &\quad + \Psi^{(0)}(\vec{r}, \vec{r}_2, \dots, \vec{r}_n)\vec{\nabla}[\vec{B} \cdot \Psi_B(\vec{r}, \vec{r}_2, \dots, \vec{r}_n)]\}d\vec{r}_2 \dots d\vec{r}_n\end{aligned}$$

For a field applied along the a th Cartesian axis, the induced current density can be rewritten in the form

$$\begin{aligned}\vec{J}_a^{(1)}(\vec{r}) &= -\frac{e}{m_e}\sum_{i=1}^n \left[e\langle \Psi^{(0)} | \delta(\vec{r}_i - \vec{r}) \vec{A}_i | \Psi^{(0)} \rangle \right. \\ &\quad \left. + \langle \Psi^{(0)} | \delta(\vec{r}_i - \vec{r}) \vec{p}_i | \Psi_a^{(1)} \rangle + \langle \Psi_a^{(1)} | \delta(\vec{r}_i - \vec{r}) \vec{p}_i | \Psi^{(0)} \rangle \right]\end{aligned}$$

where $|\Psi_a^{(1)}\rangle$ is the corresponding first-order correction to the wave function.

The *magnetisability density* (magnetic susceptibility density), $\bar{\chi}(\vec{r})$, is defined through

$$\bar{\chi}(\vec{r}) \cdot \vec{B} = \frac{1}{2} \vec{r} \times \vec{J}^{(1)}(\vec{r})$$

and its a th component, resulting from the current induced by a field applied in the b th direction, is

$$\chi_{ab}(\vec{r}) = \frac{1}{2B} \{\vec{r} \times \vec{J}_b^{(1)}(\vec{r})\}_a$$

Finally the (reduced) magnetic susceptibility tensor is

$$\bar{\kappa} \cdot \vec{B} = \frac{1}{2} \int [\vec{r} \times \vec{J}^{(1)}(\vec{r})] d\vec{r}$$

and its components are obtained by integrating the magnetisability density over a region of space

$$\kappa_{ab} = \int \chi_{ab}(\vec{r}) d\vec{r}$$

Let us introduce a second-rank current density tensor, $\bar{\bar{j}}_B$, through the relationship

$$\vec{J}_B(\vec{r}) = \bar{\bar{j}}_B(\vec{r}) \cdot \vec{B}$$

Then the components of the magnetic susceptibility tensor are expressed as

$$\kappa_{ad} = \frac{1}{2} \varepsilon_{abc} \int r_b j_{B,cd}(\vec{r}) d\vec{r}$$

and the nuclear magnetic shielding tensor is

$$\sigma_{N,ad} = -\varepsilon_{abc} \int \frac{r_b - r_{N,b}}{|\vec{r} - \vec{r}_N|^3} j_{B,cd}(\vec{r}) d\vec{r}$$

where ε_{abc} is the Levi-Civita antisymmetric third-rank tensor.

The current density is an observable which can be visualised for a molecule through oriented contour lines. Usually the applied field is perpendicular to the plane of the paper, and points inward. Clockwise circulation corresponds to a diamagnetic current since it induces an internal magnetic field pointing against the applied field [27].

5.2 MAGNETIC SUSCEPTIBILITY

The (reduced) magnetic susceptibility tensor appears in the energy term

$$E_{200} = -\frac{1}{2} \vec{B} \cdot \bar{\bar{\kappa}} \cdot \vec{B}$$

and can be written as consisting of two contributions: the diamagnetic and paramagnetic terms. Both these quantities are temperature-independent contributions. The temperature dependence of the observed magnetic susceptibility will be analysed in the next chapter.

5.2.1 Diamagnetic term

The components of the diamagnetic term are expressed through

$$\kappa_{ab}^{\text{dia}} = - \left(\frac{\partial^2 \langle \Psi^{(0,0,0)} | \hat{H}_{\text{mg}} | \Psi^{(0,0,0)} \rangle}{\partial B_a \partial B_b} \right)_0$$

with the dominating Hamiltonian term

$$\hat{H}_{\text{mg}}(12) = \sum_i \frac{e^2}{8m_e} [B_{\text{ext}}^2 r_{Gi}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Gi})^2]$$

(The number in the magnetic Hamiltonian indicates an ordering number of the Hamiltonian term according to Table 4.6.) When the derivatives are completed one gets

$$\kappa_{ab}^{\text{dia}} = -2 \langle \Psi^{(0,0,0)} | \hat{H}_{ab}^{(2,0,0)} | \Psi^{(0,0,0)} \rangle$$

with

$$\hat{H}_{ab}^{(2,0,0)} = \frac{e^2}{8m_e} \sum_i (r_{Gi}^2 \delta_{ab} - r_{Gia} r_{Gib})$$

However, there are also higher-order diamagnetic corrections to $\hat{H}_{\text{mg}}$ as they result from the partitioning of the Dirac equation

$$\hat{H}_{\text{mg}}(13) = - \sum_i \frac{e^3}{16m_e^2 c^2} \hat{k}_0(r_i) \Phi_{\text{int}} [B_{\text{ext}}^2 r_{Gi}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Gi})^2]$$

$$\hat{H}_{\text{mg}}(14) = - \sum_i \frac{e^4}{128m_e^3 c^2} \hat{k}_0^3(r_i) [B_{\text{ext}}^2 r_{Gi}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Gi})^2]^2$$

$$\hat{H}_{\text{mg}}(21) = \sum_i \frac{e^3}{16m_e^2 c^2} (\Phi - \Phi_{\text{int}}) [B_{\text{ext}}^2 r_{Gi}^2 - (\vec{B}_{\text{ext}} \cdot \vec{r}_{Gi})^2]$$

These are expected to be negligibly small because of the coefficient $1/c^2$.

The dominant diamagnetic Hamiltonian term is a simple one-electron operator and its expectation value, when the ground-state determinantal wave function is constructed from the set of occupied molecular spin-orbitals, is

$$\langle \Psi_0 | \hat{H}_{ab}^{(2,0,0)} | \Psi_0 \rangle = \sum_i^{\text{occ}} \langle \phi_i | \hat{h}_1 | \phi_i \rangle = \frac{e^2}{8m_e} \sum_i^{\text{occ}} \langle \phi_i | (r_{G1}^2 \delta_{ab} - r_{G1a} r_{G1b}) | \phi_i \rangle$$

After introducing the LCAO approximation, with the bond-order matrix $\mathbf{P}$ as a result of the SCF procedure, we get

$$\langle \Psi_0 | \hat{H}_{ab}^{(2,0,0)} | \Psi_0 \rangle = \frac{e^2}{8m_e} \sum_{\mu} \sum_{\nu}^{\text{AO}} P_{\mu\nu} \langle \chi_{\mu} | (r_{G1}^2 \delta_{ab} - r_{G1a} r_{G1b}) | \chi_{\nu} \rangle$$

The integrals over atomic orbitals include second-order momenta for all combinations of the Cartesian coordinates, i.e. x^2, xy, xz, y^2, yz and z^2 , which can be arranged into six symmetric matrices

$$M_{ab,\mu\nu} = \langle \chi_{\mu} | r_{G1a} r_{G1b} | \chi_{\nu} \rangle$$

The position vector of the electron is measured relative to the common gauge origin. When the gauge origin is altered, different κ_{ab}^{dia} values are obtained. The gauge origin (G), the positions of the atoms (M) and electrons (l) are interrelated by the vector formula

$$\vec{r}_{G1} = \vec{r}_{GM} + \vec{r}_{M1}$$

Substitution into the momentum integrals yields

$$\begin{aligned} M_{ab,\mu\nu} &= \langle \chi_{\mu}^M | (r_{GMa} + r_{M1a})(r_{GMb} + r_{M1b}) | \chi_{\nu}^N \rangle \\ &= r_{GMa} r_{GMb} \langle \chi_{\mu} | \chi_{\nu} \rangle + r_{GMa} \langle \chi_{\mu} | r_{M1b} | \chi_{\nu} \rangle + r_{GMb} \langle \chi_{\mu} | r_{M1a} | \chi_{\nu} \rangle \\ &\quad + \langle \chi_{\mu} | r_{M1a} r_{M1b} | \chi_{\nu} \rangle \end{aligned}$$

We can conclude that, in addition to the second-order momenta (quadrupole integrals), also the first-order momenta (dipole integrals) and zero-order momenta (overlap integrals), each referring to the position of the atom M in the bra-vector $\langle \chi_{\mu}^M |$, are necessary.

5.2.2 Atomic calculations

In a free atom, however, the situation is much simpler: owing to the spherical symmetry only a scalar component is relevant and it is gauge invariant since the position of the nucleus refers to the natural gauge origin. The magnetic susceptibility reduces to

$$\begin{aligned} \kappa_{aa}^{\text{dia}} &= -2 \langle \Psi_0 | \hat{H}_{aa}^{(2,0,0)} | \Psi_0 \rangle = -\frac{e^2}{4m_e} \sum_{\mu}^{\text{occ}} P_{\mu\mu} \langle \chi_{\mu} | (r_{G1}^2 - r_{G1a}^2) | \chi_{\mu} \rangle \\ &= -\frac{e^2}{6m_e} \sum_{\mu}^{\text{occ}} P_{\mu\mu} \langle \chi_{\mu} | r_{N1}^2 | \chi_{\mu} \rangle \end{aligned}$$

Some atomic calculations of magnetic susceptibilities based on the analytical Hartree–Fock functions were collected in [28] and are presented in Table 5.4.

For heavy atoms, however, it is generally accepted that relativistic corrections are essential. The most important relativistic Hamiltonian terms appear to be the mass–velocity correction, the spin–orbit coupling and the Darwin

TABLE 5.4

Calculated diamagnetic susceptibilities $-\chi^{\text{dia}}$ ($10^{-12} \text{ m}^3 \text{ mol}^{-1}$) for neutral and charged atomic systems in ground states^a

Atom	A ⁺	A	A [−]
He		23.9	
Li	8.8	186.0	875.9
Be	65.3	172.2	
B	79.2	158.3	395.8
C	80.4	137.0	261.4
N	76.7	120.6	222.4
O	72.9	111.8	187.2
F	70.4	101.8	158.3
Ne	67.9	93.0	
Na	64.1	270.2	983.9
Mg	140.7	295.3	
Al	173.4	333.0	738.9
Si	201.1	321.7	542.9
P	208.6	301.6	485.1
S	207.3	290.3	428.5
Cl	206.1	275.2	380.8
Ar	201.1	258.9	
K	194.8	510.2	1588.4
Ca	311.6	563.0	
Sc	228.7	529.0	1108.4
Ti	222.4	500.1	1083.2
V	216.1	473.8	1034.2
Cr	207.3	378.2	987.7
Mn	204.8	428.5	919.9
Fe	199.8	410.0	878.4
Co	194.8	392.1	826.9
Ni	189.8	377.0	483.8
Cu	184.7	330.5	755.2
Zn	224.9	348.1	
Ga	251.3	407.2	834.4
Ge	287.8	414.7	643.4
As	304.1	408.4	609.5
Se	310.4	410.0	569.3
Br	317.9	403.4	530.3
Kr	319.2	393.3	

^aBased on analytical Hartree–Fock functions.

term. The effect of these corrections is that the atomic orbitals primarily exhibit a contraction (stabilisation). However, the increased screening of the atomic nucleus by contracted *s*- and *p*-orbitals reduces the effective potential acting on the high-angular momentum *d*- and *f*-orbitals which exhibit an indirect expansion (destabilisation). The quantitative effect can be dramatic. For example, for the platinum atom the *5d*–*6s* energy gap drops from a value of 7.1 eV to a *5d*_{5/2}–*6s*_{1/2} gap of 3.0 eV only. It may be interesting to perform monitoring of relativistic effects on the diamagnetic susceptibilities of heavy atoms. Table 5.5 summarizes the results of numerical Dirac–Fock calculations [29] for the atoms of Cu, Ag and Au [30]. The non-relativistic limit was obtained by substituting the velocity of light by a very high number.

It can be seen that the contributions of valence orbitals to the total second momentum $\langle r^2 \rangle$ are essential; the inner shells contribute insignificantly. For example, within the series of Cu, Ag and Au atoms the contributions of valence *ns*_{1/2} orbitals are 40, 44 and 18% and those of (*n* – 1)*d*_{3/2} plus (*n* – 1)*d*_{5/2} are 43, 37 and 50% of the total, respectively. The reduced contribution of the *6s*_{1/2} orbital for the Au atom has roots in the relativistic contraction of this orbital, as is seen from the comparison with the non-relativistic limit.

5.2.3 Additive schemes

For evaluating the ground-state properties the canonical (delocalised) molecular orbitals can be replaced by a set of localised molecular orbitals having amplitudes limited by the region of chemical bonds (or lone pairs). Such orbitals are, to a good approximation, transferable from one molecule to another one having a similar chemical structure. In this equivalent representation the diamagnetic susceptibility is given by contributions over the set of chemical bonds and atomic contributions embracing inner shells

$$\kappa^{\text{dia}} = \sum_s^{\text{inner shells}} \kappa_s + \sum_i^{\text{bonds}} \kappa_i + \sum_{\lambda}^{\text{constituents}} \kappa_{\lambda} = \sum_A^{\text{atoms}} \kappa_A + \sum_{\lambda}^{\text{constituents}} \kappa_{\lambda}$$

Also, corrections to special constituents such as multiple bonds, lone pairs, rings, atoms in special positions, groups of atoms etc. can be introduced. The above expression is a basis for the successful empirical calculations of diamagnetic susceptibilities on the basis of constitutive increments. The best known and the most widely used scheme refers to the *Pascal method* [31], although some other schemes are available [32]. A set of Pascal constants is collected in Appendix 4.

The absolute values of diamagnetic susceptibilities for atoms increase with an increasing number of electrons, i.e.

TABLE 5.5

Dirac-Fock (rel) and Hartree-Fock (non-rel) calculations of the second moments $\langle r^2 \rangle$ (a.u.)^a

	Cu(rel)	Ag(rel)	Au(rel)	Cu(non-rel)	Ag(non-rel)	Au(non-rel)
1s	3.6522723D - 03	1.3078625D - 03	3.9328426D - 04	3.7477441D - 03	1.4033771D - 03	4.9082143D - 04
2s-	6.4593509D - 02	2.1337559D - 02	5.9334501D - 03	6.6499365D - 02	2.3127006D - 02	7.6296101D - 03
2p-	5.1090005D - 02	1.6027320D - 02	4.2128563D - 03	5.2747438D - 02	1.7555314D - 02	5.6406622D - 03
2p+	5.2599218D - 02	1.7341837D - 02	5.3969712D - 03	5.2747438D - 02	1.7555314D - 02	5.6406622D - 03
3s	5.8714866D - 01	1.5347895D - 01	3.8435354D - 02	6.0346323D - 01	1.6389502D - 01	4.7107582D - 02
3p-	6.5834431D - 01	1.4947118D - 01	3.5150402D - 02	6.7831922D - 01	1.5989360D - 01	4.3481425D - 02
3p+	6.7636408D - 01	1.5813233D - 01	4.1511927D - 02	6.7831921D - 01	1.5989360D - 01	4.3481425D - 02
3d-	1.3354042D + 00	1.3964179D - 01	3.1952770D - 02	1.3351154D + 00	1.4086822D - 01	3.3597434D - 02
3d+	1.3689351D + 00	1.4230603D - 01	3.3689101D - 02	1.3351156D + 00	1.4086822D - 01	3.3597434D - 02
4s	1.2551941D + 01	9.5854934D - 01	1.8693050D - 01	1.3084424D + 01	1.0199366D + 00	2.2478649D - 01
4p-		1.1233482D + 00	1.9118739D - 01		1.1998436D + 00	2.3104266D - 01
4p+		1.1916315D + 00	2.2218408D - 01		1.1998436D + 00	2.3104266D - 01
4d-		2.3291399D + 00	2.3524859D - 01		2.3136404D + 00	2.4371274D - 01
4d+		2.4270970D + 00	2.4658195D - 01		2.3136405D + 00	2.4371274D - 01
4f-			2.9258798D - 01			2.8139680D - 01
4f+			3.0054348D - 01			2.8139680D - 01
5s		2.8439844D + 01	9.9848645D - 01		3.3301608D + 01	1.2128083D + 00
5p-			1.1785275D + 00			1.4509816D + 00
5p+			1.4078171D + 00			1.4509816D + 00
5d-			2.8203784D + 00			2.8339942D + 00
5d+			3.1521519D + 00			2.8339941D + 00
6s			1.0864545D + 01			1.5891205D + 01
sum	31.753	64.047	59.955	32.169	68.527	64.316
χ /SI	-316.02×10^{-12}	-637.43×10^{-12}	-596.70×10^{-12}	-320.16×10^{-12}	-682.02×10^{-12}	-640.11×10^{-12}

^aThe diamagnetic susceptibility of an atom is $\chi^{\text{dia}} = -C\langle r^2 \rangle_{\text{a.u.}}$ with the constant factor $C = (N_A \mu_0 e^2 a_0^2 / 6m_e) = 9.9526 \times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$.

- (a) within the group (column) of the periodic table,
- (b) with the decreasing oxidation number of the atom.

Within the period (row) of the periodic table they alter only slightly and irregularly.

A rough estimate of the diamagnetic contribution is possible on the basis of the empirical formula

$$\chi_{\text{dia}}/10^{-12} \text{ m}^3 \text{ mol}^{-1} \approx -5 M_r (\text{g mol}^{-1})$$

where M_r is the molar mass.

5.2.4 Paramagnetic term

The (temperature-independent) paramagnetic susceptibility tensor is given by the perturbation formula

$$-\frac{1}{2}\kappa_{ab}^{\text{para}} = -\sum_K \frac{1}{E_K - E_0} \langle \Psi_0 | \hat{H}_a^{(1,0,0)} | \Psi_K \rangle \langle \Psi_K | \hat{H}_b^{(1,0,0)} | \Psi_0 \rangle$$

with the one-electron (orbital) Zeeman operator

$$\hat{H}_a^{(1,0,0)} = \frac{\mu_B}{\hbar} \sum_i \hat{l}_{Gia} = \sum_i \hat{h}_i^{(a)}$$

This is summed up in the equivalent terms

$$\hat{h}_1^{(a)} = \mu_B \hat{l}_{G1a}$$

where the angular momentum operator $\hat{l}_{G1a}$ is given in units of $\hbar$. Then the expansion into the molecular orbitals yields the result

$$\begin{aligned} -\frac{1}{2}\kappa_{ab}^{\text{para}} &= -\sum_o^{\text{occ}} \sum_u^{\text{un}} \frac{1}{\Delta E_o^u} \langle \phi_o | \hat{h}_1^{(a)} | \phi_u \rangle \langle \phi_u | \hat{h}_1^{(b)} | \phi_o \rangle \\ &= -\mu_B^2 \sum_o^{\text{occ}} \sum_u^{\text{un}} \frac{1}{\Delta E_o^u} \langle \phi_o | \hat{l}_{G1a} | \phi_u \rangle \langle \phi_u | \hat{l}_{G1b} | \phi_o \rangle \end{aligned}$$

After the LCAO approximation

$$\langle \phi_o | \hat{l}_{G1a} | \phi_u \rangle = \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} C_{o\mu}^* C_{u\nu} \langle \chi_{\mu} | \hat{l}_{G1a} | \chi_{\nu} \rangle$$

the integrals over atomic orbitals include three matrices with the elements

$$L_{a,\mu\nu} = \langle \chi_\mu^M | \hat{1}_{G1a} | \chi_\nu^N \rangle$$

The angular momentum operator, expressed in terms of the position of atoms relative to the gauge origin and electrons relative to the atom, becomes

$$\begin{aligned} L_{a,\mu\nu} &= -i \langle \chi_\mu^M | \left[(\vec{r}_{GN} + \vec{r}_{N1}) \times \vec{\nabla}_1 \right]_a | \chi_\nu^N \rangle \\ &= -i \left[\vec{r}_{GN} \times \langle \chi_\mu^M | \vec{\nabla}_1 | \chi_\nu^N \rangle \right]_a + \langle \chi_\mu^M | \hat{1}_{N1a} | \chi_\nu^N \rangle \end{aligned}$$

In evaluating the first term we need the matrix elements of the linear momentum

$$p_{a,\mu\nu} = \langle \chi_\mu^M | \nabla_{1a} | \chi_\nu^N \rangle$$

The second term is evaluable easily since the operator $\hat{1}_{G1a}$ acts only on the angular momentum functions irrespective of the radial part of the atomic orbitals. For this purpose the following formulae are applicable

$$\begin{aligned} \hat{1}_x |l, m\rangle &= \frac{1}{2} \left[\sqrt{(l-m)(l+m+1)} |l, m+1\rangle \right. \\ &\quad \left. + \sqrt{(l-m+1)(l+m)} |l, m-1\rangle \right] \\ \hat{1}_y |l, m\rangle &= \frac{1}{2i} \left[\sqrt{(l-m)(l+m+1)} |l, m+1\rangle \right. \\ &\quad \left. - \sqrt{(l-m+1)(l+m)} |l, m-1\rangle \right] \\ \hat{1}_z |l, m\rangle &= m |l, m\rangle \end{aligned}$$

The action of angular momenta operators on the basis set of real angular functions (which are linear combinations of the spherical harmonics $|l, m\rangle$) is summarised in Table 5.6. The matrix element $\langle \chi_\mu^M | \hat{1}_{N1a} | \chi_\nu^N \rangle$ is given by a number λ_ν^N multiplied by the overlap integral for a shifted ket-vector

$$\langle \chi_\mu^M | \hat{1}_{N1a} | \chi_\nu^N \rangle = \lambda_\nu^N \langle \chi_\mu^M | \chi_\sigma^N \rangle$$

Let us introduce a A -tensor through the following formula

$$A_{ab} = - \sum_K \frac{1}{E_K - E_0} \left\langle \Psi_0 \left| \sum_i \hat{1}_{G1a} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \sum_i \hat{1}_{G1b} \right| \Psi_0 \right\rangle$$

TABLE 5.6
Effect of the angular momenta operators

Real function	Operator $\hat{L}_x$	$\hat{L}_y$	$\hat{L}_z$
s	0	0	0
p_z	$-ip_y$	ip_x	0
p_x	0	$-ip_z$	ip_y
p_y	ip_z	0	$-ip_x$
d_{z2}	$-i\sqrt{3}d_{yz}$	$i\sqrt{3}d_{xz}$	0
d_{xz}	$-id_{xy}$	$-i\sqrt{3}d_{z2} + id_{x2-y2}$	id_{yz}
d_{yz}	$id_{x2-y2} + i\sqrt{3}d_{z2}$	id_{xy}	$-id_{xz}$
d_{x2-y2}	$-id_{yz}$	$-id_{xz}$	$2id_{xy}$
d_{xy}	id_{xz}	$-id_{yz}$	$-2id_{x2-y2}$

Then the reduced paramagnetic susceptibility tensor becomes expressed as

$$\kappa_{ab}^{\text{para}} = -2\mu_B^2 A_{ab}$$

and the observable paramagnetic susceptibility tensor is

$$\chi_{ab}^{\text{para}} = -2N_A\mu_0\mu_B^2 A_{ab}$$

Its average value is termed the *temperature-independent paramagnetism* (TIP) and reads

$$\chi_{\text{TIP}} = -\frac{2}{3}N_A\mu_0\mu_B^2(A_{xx} + A_{yy} + A_{zz})$$

The values of TIP are dominated by the excitation energies. The TIP value is small when the excitation energies are high; it becomes larger with decreasing excitation energies for some transition metal complexes (Table 5.7).

5.2.5 Hand calculations

A simplified calculation of the TIP is possible on the basis of crystal field theory. The diagonal components of the A -tensor, restricted to only the first excitation, are

$$A_{aa} = -\frac{\left\langle \Psi_0 \left| \sum_i \hat{L}_{Gia} \right| \Psi_1 \right\rangle \left\langle \Psi_1 \left| \sum_i \hat{L}_{Gia} \right| \Psi_0 \right\rangle}{E_1 - E_0}$$

and the wave functions include the ground and the first excited terms.

TABLE 5.7

Estimated values of temperature-independent paramagnetism

Ion	First excitation energy	$\Delta E/hc$ (cm ⁻¹) [33] ^a	χ_{TIP} (10 ⁻⁹ m ³ mol ⁻¹) [34]
Cr ³⁺	high-spin 6-O _h (⁴ T _{2g}) high-spin 4-T _d (⁴ T ₁)	14 000–22 000	0.63
Mn ²⁺	high-spin 6-O _h (⁴ T ₁ *)	19 000–21 000	
Fe ³⁺	high-spin 6-O _h (⁴ T ₁ *)	12 000–15 000	7.90
Fe ²⁺	high-spin 6-O _h (⁵ E _g) high-spin 4-T _d (⁵ T ₂) low-spin 6-O _h (¹ T ₁)	7000–10 000 4000–6000 19 000–30 000	
Co ³⁺	low-spin 6-O _h (¹ T ₁)	13 000–22 000	1.25
Co ²⁺	high-spin 6-O _h (⁴ T _{1g}) low-spin 4-D _{4h} high-spin 4-T _d (⁴ T ₁)	6500–9000 4000–6000 5000–7000	5.65
Ni ²⁺	high-spin 6-O _h (³ E _g) low-spin 4-D _{4h}	8000–12 000 15 000–18 000	3.77
Cu ²⁺	6-D _{4h}	11 000–17 000	0.75

^aSpin-conserving transitions (except those marked *); 6-O_h(⁵E_g) means a hexacoordinate octahedral complex, an excitation from the ground state ⁵T_{2g} (not indicated) to E_g.

For a hexacoordinate Cu²⁺ complex adopting the geometry of an elongated bipyramid (D_{4h} symmetry) the individual term functions can be replaced by the corresponding *d*-orbitals. Hence, according to Table 5.6, we have

$$|^2B_{1g}\rangle = |d_{x^2-y^2}\rangle \quad \hat{1}_z|^2B_{1g}\rangle = 2i|^2B_{2g}\rangle \quad \hat{1}_x|^2B_{1g}\rangle = -i|^2E_g\rangle$$

$$|^2A_{1g}\rangle = |d_{z^2}\rangle \quad \hat{1}_z|^2A_{1g}\rangle = 0 \quad \hat{1}_x|^2A_{1g}\rangle = -i\sqrt{3}|^2E_g\rangle$$

$$|^2B_{2g}\rangle = |d_{xy}\rangle \quad \hat{1}_z|^2B_{2g}\rangle = -2i|^2B_{1g}\rangle \quad \hat{1}_x|^2B_{2g}\rangle = i|^2E_g\rangle$$

$$|^2E_g\rangle = |d_{yz}\rangle \quad \hat{1}_z|^2E_g\rangle = -i|^2E_g\rangle \quad \hat{1}_x|^2E_g\rangle = i\sqrt{3}|^2A_{1g}\rangle + i|^2B_{1g}\rangle$$

$$|^2E_g\rangle = |d_{xz}\rangle \quad \hat{1}_z|^2E_g\rangle = i|^2E_g\rangle \quad \hat{1}_x|^2E_g\rangle = -i|^2B_{2g}\rangle$$

Therefore the parallel A_{zz} -tensor component is

$$\begin{aligned}
 -A_{zz} &= \frac{\langle {}^2B_{1g} | \hat{1}_z | {}^2A_{1g} \rangle \langle {}^2A_{1g} | \hat{1}_z | {}^2B_{1g} \rangle}{\Delta E({}^2B_{1g} \rightarrow {}^2A_{1g})} + \frac{\langle {}^2B_{1g} | \hat{1}_z | {}^2B_{2g} \rangle \langle {}^2B_{2g} | \hat{1}_z | {}^2B_{1g} \rangle}{\Delta E({}^2B_{1g} \rightarrow {}^2B_{2g})} \\
 &\quad + \frac{\langle {}^2B_{1g} | \hat{1}_z | {}^2E_g \rangle \langle {}^2E_g | \hat{1}_z | {}^2B_{1g} \rangle}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)} + \frac{\langle {}^2B_{1g} | \hat{1}_z | {}^2E_g \rangle \langle {}^2E_g | \hat{1}_z | {}^2B_{1g} \rangle}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)} \\
 &= \frac{0 \cdot [2i \langle {}^2A_{1g} | {}^2B_{2g} \rangle]}{\Delta E({}^2B_{1g} \rightarrow {}^2A_{1g})} + \frac{[-2i \langle {}^2B_{1g} | {}^2B_{1g} \rangle][2i \langle {}^2B_{2g} | {}^2B_{2g} \rangle]}{\Delta E({}^2B_{1g} \rightarrow {}^2B_{2g})} \\
 &\quad + \frac{[-i \langle {}^2B_{1g} | {}^2E_g \rangle][2i \langle {}^2E_g | {}^2B_{2g} \rangle]}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)} + \frac{[i \langle {}^2B_{1g} | {}^2E_g \rangle][2i \langle {}^2E_g | {}^2B_{2g} \rangle]}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)}
 \end{aligned}$$

which reduces to

$$A_{zz} = -\frac{4}{\Delta E({}^2B_{1g} \rightarrow {}^2B_{2g})}$$

Analogously, the perpendicular A_{xx} -tensor component is

$$\begin{aligned}
 -A_{xx} &= \frac{\langle {}^2B_{1g} | \hat{1}_x | {}^2A_{1g} \rangle \langle {}^2A_{1g} | \hat{1}_x | {}^2B_{1g} \rangle}{\Delta E({}^2B_{1g} \rightarrow {}^2A_{1g})} + \frac{\langle {}^2B_{1g} | \hat{1}_x | {}^2B_{2g} \rangle \langle {}^2B_{2g} | \hat{1}_x | {}^2B_{1g} \rangle}{\Delta E({}^2B_{1g} \rightarrow {}^2B_{2g})} \\
 &\quad + \frac{\langle {}^2B_{1g} | \hat{1}_x | {}^2E_g \rangle \langle {}^2E_g | \hat{1}_x | {}^2B_{1g} \rangle}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)} + \frac{\langle {}^2B_{1g} | \hat{1}_x | {}^2E_g \rangle \langle {}^2E_g | \hat{1}_x | {}^2B_{1g} \rangle}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)} \\
 &= \frac{[-i\sqrt{3} \langle {}^2B_{1g} | {}^2E_g \rangle][i \langle {}^2A_{1g} | {}^2E_g \rangle]}{\Delta E({}^2B_{1g} \rightarrow {}^2A_{1g})} + \frac{[i \langle {}^2B_{1g} | {}^2E_g \rangle][i \langle {}^2B_{2g} | {}^2E_g \rangle]}{\Delta E({}^2B_{1g} \rightarrow {}^2B_{2g})} \\
 &\quad + \frac{[i\sqrt{3} \langle {}^2B_{1g} | {}^2A_{1g} \rangle + i \langle {}^2B_{1g} | {}^2B_{1g} \rangle][i \langle {}^2E_g | {}^2E_g \rangle]}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)} \\
 &\quad + \frac{[-i \langle {}^2B_{1g} | {}^2B_{2g} \rangle][i \langle {}^2E_g | {}^2E_g \rangle]}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)}
 \end{aligned}$$

which gives

$$A_{xx} = A_{yy} = -\frac{1}{\Delta E({}^2B_{1g} \rightarrow {}^2E_g)}$$

The expressions for the A -tensor components are combined to yield the TIP

$$\begin{aligned}\chi_{\text{TIP}} &= -\frac{2}{3}N_A\mu_0\mu_B^2(2A_{xx} + A_{zz}) \\ &= \frac{2}{3}N_A\mu_0\mu_B^2\left(2\frac{1}{\Delta E(^2B_{1g} \rightarrow ^2E_g)} + \frac{4}{\Delta E(^2B_{1g} \rightarrow ^2B_{2g})}\right)\end{aligned}$$

For a typical Cu(II) complex $[\text{Cu}(\text{NH}_3)_6]^{2+}$ the excitation energies span the values of $\Delta E(^2B_{1g} \rightarrow ^2B_{2g})/hc \approx \Delta E(^2B_{1g} \rightarrow ^2E_g)/hc = 16\,400\text{ cm}^{-1}$ and then we get

$$\begin{aligned}\chi_{\text{TIP}} &= \frac{2}{3}[6.022 \times 10^{23}\text{ mol}^{-1}][4\pi \times 10^{-7}\text{ NA}^{-2}][9.274 \times 10^{-24}\text{ JT}^{-1}]^2 \\ &\quad \times \frac{6}{[16400\text{ cm}^{-1} \times (1.986 \times 10^{-23}\text{ J cm}^{-1})]}\end{aligned}$$

which results in the value of $\chi_{\text{TIP}} = +0.80 \times 10^{-9}\text{ m}^3\text{ mol}^{-1}$. This is very close to the generally accepted experimental estimate of $\chi_{\text{TIP}} = +0.75 \times 10^{-9}\text{ m}^3\text{ mol}^{-1}$.

For an octahedral $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex the first excitation energy $^1A_1 \rightarrow ^1T_1$ is $\Delta E/hc = 21\,000\text{ cm}^{-1}$ and the matrix element is

$$\left\langle ^1A_1 \left| \sum_i \hat{1}_{G_{ia}} \right| ^1T_1 \right\rangle = -2\sqrt{2}$$

These numbers yield $\chi_{\text{TIP}} = +2.50 \times 10^{-9}\text{ m}^3\text{ mol}^{-1}$. On the other hand, the diamagnetic contribution is calculated according to Table 5.8. The final value of $\chi_{\text{dia}} = -1.21 \times 10^{-9}\text{ m}^3\text{ mol}^{-1}$ is only half of the temperature-independent paramagnetism.

Normally the TIP contribution (the van Vleck term) is only a minor correction to the underlying diamagnetism (the Langevin term). In complex systems like metalloproteins the diamagnetic contribution may also dominate the temperature-dependent paramagnetism.

TABLE 5.8
Diamagnetic susceptibility of $[\text{Co}(\text{NH}_3)_6]^{3+}$

Constituent	$\chi_A (10^{-12}\text{ m}^3\text{ mol}^{-1})$
Co^{3+}	-126.0×1
N	-70.0×6
H	-36.8×18
sum	-1208.4

5.3 THE g -TENSOR

The g -tensor (magnetogyric ratio tensor) appears as the crossing contribution to the energy

$$E_{101} = \vec{\mu}_e \cdot \overline{\overline{\Delta g}} \cdot \vec{B} = \vec{B} \cdot \overline{\overline{\Delta g}} \cdot \vec{\mu}_e$$

with the electronic magnetic moment proportional to the spin

$$\vec{\mu}_e = -\frac{\mu_B g_e}{\hbar} \vec{S} = -\mu_B g_e \vec{\tilde{S}}$$

where $\vec{\tilde{S}}$ is dimensionless. The differential g -tensor $\overline{\overline{\Delta g}}$, and the g -tensor are interrelated as follows

$$\overline{\overline{g}} = g_e \overline{\overline{1}} + \overline{\overline{\Delta g}}$$

where the theoretical value of g_e for a free electron

$$g_e = 2(1 + g_1) = 2.002319315$$

is in fair agreement with the experimental data.

The electronic g -tensor is a fundamental quantity in *electron spin resonance* (ESR) spectroscopy. Its experimental reading is based on the assumption that the following equation is fulfilled

$$\Delta E = E_+ - E_- = \mu_B \vec{B} \cdot \overline{\overline{g}} \cdot \vec{\tilde{S}}$$

where $\vec{\tilde{S}}$ is an effective spin operator not coincident with the true spin. This operator is defined with respect to the two Kramers doublets, which are split by the applied magnetic field, and it is related to the Pauli spin matrices through

$$\vec{\tilde{S}}_a = \frac{m}{2} \hat{\sigma}_a$$

($a = x, y, z$) where m is an integer chosen so that the true and effective spin are approximately equal. Such an assumption leads to some arbitrariness in the definition of the effective spin and consequently in the g -tensor. It has been shown that only the symmetric tensor

$$\mathbf{G} \equiv \mathbf{g}^T \mathbf{g}$$

can be directly measured (for oriented crystals) [35–37], or its mean value estimated

$$G_{av} = \frac{1}{3} \text{Tr}(\mathbf{g}^T \mathbf{g})$$

(for liquids and gases).

The g -tensor and the G -tensor can be obtained as the second derivatives of the energy splitting and its square, respectively [38]

$$g_{ab} = \frac{1}{\mu_B} \frac{\partial^2(\Delta E)}{\partial B_a \partial B_b}$$

$$G_{ab} = \frac{1}{2m^2 \mu_B} \frac{\partial^2(\Delta E)^2}{\partial B_a \partial B_b}$$

Methods of evaluating the molecular g -tensor at the *ab initio* level represent a contemporary problem and are still developing [38–45]. Three variants of the molecular orbital calculations are used: the restricted Hartree–Fock, the unrestricted Hartree–Fock and the generalised Hartree–Fock methods.

The differential g -tensor is given as the sum of two contributions: the diamagnetic and paramagnetic terms. Since the diamagnetic term is much lower than the paramagnetic one, it is often neglected.

5.3.1 First-order term

First-order perturbation theory gives the following contribution to the energy of the system

$$\begin{aligned} E_{101} &= \left\langle \Psi^{(0,0,0)} \left| \hat{H}_{101} \right| \Psi^{(0,0,0)} \right\rangle \\ &= \left\langle \Psi^{(0,0,0)} \left| \sum_i \vec{\mu}_{ei} \cdot \overline{\overline{H}}_i^{(1,0,1)} \cdot \vec{B} \right| \Psi^{(0,0,0)} \right\rangle \\ &= \sum_a \sum_b \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{\mu}_{eia} \hat{H}_{iab}^{(1,0,1)} B_b \right| \Psi^{(0,0,0)} \right\rangle \end{aligned}$$

where only the ground-state function occurs. A comparison with

$$E_{101} = \sum_a \sum_b \mu_{ea} \Delta g'_{ab} B_b$$

yields the expression

$$\mu_{ea}\Delta g'_{ab} = \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{\mu}_{eia} \hat{H}_{iab}^{(1,0,1)} \right| \Psi^{(0,0,0)} \right\rangle$$

and when the electron spins are used instead the electronic magnetic moments one has

$$\Delta g'_{ab} = S_a^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{S}_{ia} \hat{H}_{iab}^{(1,0,1)} \right| \Psi^{(0,0,0)} \right\rangle$$

An analogous procedure based on the comparison

$$\begin{aligned} E_{101} &= \sum_a \sum_b \left\langle \Psi^{(0,0,0)} \left| \sum_i B_a \hat{H}_{iab}^{(1,0,1)} \hat{\mu}_{eib} \right| \Psi^{(0,0,0)} \right\rangle \\ &= \sum_a \sum_b B_a \Delta g'_{ab} \mu_{eb} \end{aligned}$$

yields

$$\Delta g'_{ab} = S_b^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{H}_{iab}^{(1,0,1)} \hat{S}_{ib} \right| \Psi^{(0,0,0)} \right\rangle$$

At the same time it holds true that

$$\begin{aligned} \Delta g'_{ab} &= \left(\frac{\partial^2 \langle \Psi^{(0,0,0)} | \hat{H}_{101} | \Psi^{(0,0,0)} \rangle}{\partial B_a \partial \mu_{eb}} \right)_0 \\ &= -\frac{1}{\mu_B g_e} \left(\frac{\partial^2 \langle \Psi^{(0,0,0)} | \hat{H}_{101} | \Psi^{(0,0,0)} \rangle}{\partial B_a \partial S_b} \right)_0 \end{aligned}$$

The terms contributing to $\hat{H}_{101} = f(\vec{S}_i, \vec{B})$ are compiled in Table 4.6(g). The leading contribution is the (electron spin) Zeeman term

$$\hat{H}_{101}(32) = \frac{e\hbar}{2m_e} g_e \sum_i \vec{S}_i \cdot \vec{B} = \mu_B g_e \vec{S} \cdot \vec{B}$$

which is free of orbital variables; it enters the pure spin Hamiltonian. The remaining four terms fill $\Delta \bar{g}$ (the numbering of the term follows Table 4.6):

(a) the *spin-orbit Zeeman gauge correction*

$$\hat{H}_{101}(34) = \left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_e}\right) \frac{e^2}{4m_e} g' \sum_i \sum_N Z_N \hat{k}_0^2(r_{Ni}) \frac{1}{r_{Ni}^3} [(\vec{r}_{Ni} \cdot \vec{r}_{Gi})(\vec{S}_i \cdot \vec{B}) - (\vec{S}_i \cdot \vec{r}_{Gi})(\vec{r}_{Ni} \cdot \vec{B})]$$

where $g' = 2(1 + 2g_1)$ is the magnetogyric spin-orbit factor for electrons; this expression implies that

$$\hat{H}_{iab}^{(1,0,1)}(34) = -\left(\frac{\mu_0}{4\pi}\right) \frac{e^2}{4m_e} \frac{g'}{g_e} \sum_N Z_N \frac{1}{r_{Ni}^3} [(\vec{r}_{Ni} \cdot \vec{r}_{Gi})\delta_{ab} - r_{Gia}r_{Nib}]$$

(b) the *Zeeman-kinetic energy correction*

$$\hat{H}_{101}(33) = \left(\frac{e\hbar}{2m_e}\right) \left(\frac{\hbar}{m_e c}\right)^2 \frac{g_e}{2} \sum_i (\vec{S}_i \cdot \vec{B}) \nabla_i^2$$

(c) the *spin-other orbit Zeeman gauge correction*

$$\hat{H}_{101}(35) = \left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_e}\right) \frac{e^2}{m_e} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}^3} [(\vec{r}_{ji} \cdot \vec{r}_{Gj})(\vec{S}_i \cdot \vec{B}) - (\vec{S}_i \cdot \vec{r}_{Gj})(\vec{r}_{ji} \cdot \vec{B})]$$

(d) the *electron-electron spin-orbit Zeeman gauge correction*

$$\hat{H}_{101}(36) = -\left(\frac{\mu_0}{4\pi}\right) \left(\frac{e\hbar}{2m_e}\right) \frac{e^2}{4m_e} g' \sum_i \sum_{j \neq i} \frac{1}{r_{ij}^3} [(\vec{r}_{ji} \cdot \vec{r}_{Gi})(\vec{S}_i \cdot \vec{B}) - (\vec{S}_i \cdot \vec{r}_{Gi})(\vec{r}_{ji} \cdot \vec{B})]$$

Collecting the one-electron terms

$$\hat{H}_{101}(1e) = \hat{H}_{101}(34) + \hat{H}_{101}(33)$$

we define a one-electron operator of the spatial variables as

$$\begin{aligned} \hat{h}_{1ab} \equiv \hat{H}_{iab}^{(1,0,1)}(1e) = & -\left(\frac{\mu_0}{4\pi}\right) \frac{e^2}{4m_e} \sum_N Z_N \frac{1}{r_{Ni}^3} [(\vec{r}_{Ni} \cdot \vec{r}_{Gi})\delta_{ab} - r_{Gia}r_{Nib}] \\ & - \frac{1}{2} \left(\frac{\hbar}{m_e c}\right)^2 \nabla_i^2 \delta_{ab} \end{aligned}$$

Then the expectation value, when the ground-state determinantal function $|\Psi_0\rangle$ is constructed from the set of occupied molecular spinorbitals $|\varphi_i\rangle$, is

$$\begin{aligned}
 S_a \Delta g'_{ab}(1e) &= \left\langle \Psi_0 \left| \sum_i \hat{S}_{ia} \hat{H}_{iab}^{(1,0,1)}(1e) \right| \Psi_0 \right\rangle \\
 &= \sum_o^{\text{occ}} \langle \varphi_o | \hat{h}_{1ab} \hat{S}_{1a} | \varphi_o \rangle \\
 &= \sum_{o_\alpha}^{\text{occ}_\alpha} \langle \varphi_o^\alpha | \hat{h}_{1ab} \hat{S}_{1a} | \varphi_o^\alpha \rangle + \sum_{o_\beta}^{\text{occ}_\beta} \langle \varphi_o^\beta | \hat{h}_{1ab} \hat{S}_{1a} | \varphi_o^\beta \rangle \\
 &= \sum_{o_\alpha}^{\text{occ}_\alpha} \langle \varphi_o^\alpha | \hat{h}_{1ab} | \varphi_o^\alpha \rangle \langle \alpha | \hat{S}_{1a} | \alpha \rangle + \sum_{o_\beta}^{\text{occ}_\beta} \langle \varphi_o^\beta | \hat{h}_{1ab} | \varphi_o^\beta \rangle \langle \beta | \hat{S}_{1a} | \beta \rangle
 \end{aligned}$$

Since the expectation values of the spin operator for $|\alpha\rangle$ and $|\beta\rangle$ spin functions have opposite signs

$$\langle \alpha | \hat{S}_{1a} | \alpha \rangle = \frac{1}{2}$$

$$\langle \beta | \hat{S}_{1a} | \beta \rangle = -\frac{1}{2}$$

then

$$S_a \Delta g'_{ab}(1e) = \frac{1}{2} \sum_{o_\alpha}^{\text{occ}_\alpha} \langle \varphi_o^\alpha | \hat{h}_{1ab} | \varphi_o^\alpha \rangle - \frac{1}{2} \sum_{o_\beta}^{\text{occ}_\beta} \langle \varphi_o^\beta | \hat{h}_{1ab} | \varphi_o^\beta \rangle$$

After introduction of the LCAO approximation, the above expression becomes

$$\begin{aligned}
 S_a \Delta g'_{ab}(1e) &= \frac{1}{2} \sum_\mu^{\text{AO}} \sum_\nu^{\text{AO}} P_{\mu\nu}^\alpha \langle \chi_\mu | \hat{h}_{1ab} | \chi_\nu \rangle - \frac{1}{2} \sum_\mu^{\text{AO}} \sum_\nu^{\text{AO}} P_{\mu\nu}^\beta \langle \chi_\mu | \hat{h}_{1ab} | \chi_\nu \rangle \\
 &= \frac{1}{2} \sum_\mu^{\text{AO}} \sum_\nu^{\text{AO}} Q_{\mu\nu} \langle \chi_\mu | \hat{h}_{1ab} | \chi_\nu \rangle
 \end{aligned}$$

with

$$Q_{\mu\nu} = P_{\mu\nu}^\alpha - P_{\mu\nu}^\beta$$

forming the *spin density matrix*.

Within the RHF approach the doubly occupied molecular orbitals do not contribute, since the spin parts cancel, so that we are left with

$$S_a \Delta g'_{ab}(1e) = \langle \alpha | \hat{S}_{1a} | \alpha \rangle \sum_j^{\text{SOMO}} \langle \phi_j | \hat{h}_{1ab} | \phi_j \rangle, \quad [\text{for RHF}]$$

The two-electron terms can be combined to yield

$$\begin{aligned} \hat{H}_{101}(2e) = \hat{H}_{101}(35) + \hat{H}_{101}(36) = & \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right) \frac{e^2}{4m_e} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}^3} \\ & \left\{ [4(\vec{r}_{ji} \cdot \vec{r}_{Gj}) - g'(\vec{r}_{ji} \cdot \vec{r}_{Gi})](\vec{S}_i \cdot \vec{B}) \right. \\ & \left. - [4(\vec{S}_i \cdot \vec{r}_{Gj}) - g'(\vec{S}_i \cdot \vec{r}_{Gi})](\vec{r}_{ji} \cdot \vec{B}) \right\} \end{aligned}$$

and then

$$S_a \Delta g'_{ab}(2e) = \left\langle \Psi_0 \left| \sum_i \hat{S}_{ia} \hat{H}_{iab}^{(1,0,1)}(2e) \right| \Psi_0 \right\rangle$$

with the two-electron operator of the spatial variables

$$\begin{aligned} \hat{h}_{12ab} \equiv \hat{H}_{iab}^{(1,0,1)}(2e) = & - \left(\frac{\mu_0}{4\pi} \right) \frac{e^2}{4m_e g_e} \frac{1}{\sum_{j \neq i} r_{ij}^3} \\ & \{ \vec{r}_{ji} \cdot (4\vec{r}_{Gj} - g'\vec{r}_{Gi})\delta_{ab} - (4r_{Gja} - g'r_{Gia})r_{jib} \} \end{aligned}$$

The expectation value of a two-electron operator

$$\hat{H}_{12} = \sum_i \sum_{j < i} \hat{h}_{ij}$$

is

$$\begin{aligned} \left\langle \Psi_0 \left| \sum_i \sum_{j < i} \hat{h}_{ij} \right| \Psi_0 \right\rangle &= \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\langle \varphi_o \varphi_p | \hat{h}_{12} | \varphi_o \varphi_p \rangle - \langle \varphi_o \varphi_p | \hat{h}_{12} | \varphi_p \varphi_o \rangle \right] \\ &= \frac{1}{2} \sum_o^{\text{occ}} \sum_p^{\text{occ}} \left[\langle \varphi_o \varphi_p | \hat{h}_{12} | \varphi_o \varphi_p \rangle - \langle \varphi_o \varphi_p | \hat{h}_{12} | \varphi_p \varphi_o \rangle \right] \end{aligned}$$

Then we have

$$\begin{aligned}
 S_a \Delta g'_{ab}(2e) &= \frac{1}{2} \sum_{o_\alpha}^{\text{occ}_\alpha} \sum_{p_\alpha}^{\text{occ}_\alpha} \left[\langle \varphi_o^\alpha \varphi_p^\alpha | \hat{h}_{12ab} \hat{S}_{1a} | \varphi_o^\alpha \varphi_p^\alpha \rangle - \langle \varphi_o^\alpha \varphi_p^\alpha | \hat{h}_{12ab} \hat{S}_{1a} | \varphi_p^\alpha \varphi_o^\alpha \rangle \right] \\
 &\quad + \frac{1}{2} \sum_{o_\alpha}^{\text{occ}_\alpha} \sum_{p_\beta}^{\text{occ}_\beta} \left[\langle \varphi_o^\alpha \varphi_p^\beta | \hat{h}_{12ab} \hat{S}_{1a} | \varphi_o^\alpha \varphi_p^\beta \rangle \right] \\
 &\quad + \frac{1}{2} \sum_{o_\beta}^{\text{occ}_\beta} \sum_{p_\alpha}^{\text{occ}_\alpha} \left[\langle \varphi_o^\beta \varphi_p^\alpha | \hat{h}_{12ab} \hat{S}_{1a} | \varphi_o^\beta \varphi_p^\alpha \rangle \right] \\
 &\quad + \frac{1}{2} \sum_{o_\beta}^{\text{occ}_\beta} \sum_{p_\beta}^{\text{occ}_\beta} \left[\langle \varphi_o^\beta \varphi_p^\beta | \hat{h}_{12ab} \hat{S}_{1a} | \varphi_o^\beta \varphi_p^\beta \rangle - \langle \varphi_o^\beta \varphi_p^\beta | \hat{h}_{12ab} \hat{S}_{1a} | \varphi_p^\beta \varphi_o^\beta \rangle \right] \\
 &= \frac{1}{4} \sum_{o_\alpha}^{\text{occ}_\alpha} \sum_{p_\alpha}^{\text{occ}_\alpha} \left[\langle \phi_o^\alpha \phi_p^\alpha | \hat{h}_{12ab} | \phi_o^\alpha \phi_p^\alpha \rangle - \langle \phi_o^\alpha \phi_p^\alpha | \hat{h}_{12ab} | \phi_p^\alpha \phi_o^\alpha \rangle \right] \\
 &\quad + \frac{1}{4} \sum_{o_\alpha}^{\text{occ}_\alpha} \sum_{p_\beta}^{\text{occ}_\beta} \left[\langle \phi_o^\alpha \phi_p^\beta | \hat{h}_{12ab} | \phi_o^\alpha \phi_p^\beta \rangle \right] \\
 &\quad - \frac{1}{4} \sum_{o_\beta}^{\text{occ}_\beta} \sum_{p_\alpha}^{\text{occ}_\alpha} \left[\langle \phi_o^\beta \phi_p^\alpha | \hat{h}_{12ab} | \phi_o^\beta \phi_p^\alpha \rangle \right] \\
 &\quad - \frac{1}{4} \sum_{o_\beta}^{\text{occ}_\beta} \sum_{p_\beta}^{\text{occ}_\beta} \left[\langle \phi_o^\beta \phi_p^\beta | \hat{h}_{12ab} | \phi_o^\beta \phi_p^\beta \rangle - \langle \phi_o^\beta \phi_p^\beta | \hat{h}_{12ab} | \phi_p^\beta \phi_o^\beta \rangle \right]
 \end{aligned}$$

Now the introduction of the LCAO approximation yields

$$\begin{aligned}
 S_a \Delta g'_{ab}(2e) &= \frac{1}{4} \sum_{\mu}^{\text{AO}} \sum_{\nu}^{\text{AO}} \sum_{\lambda}^{\text{AO}} \sum_{\sigma}^{\text{AO}} \langle \chi_\mu \chi_\lambda | \hat{h}_{12ab} | \chi_\nu \chi_\sigma \rangle \\
 &\quad \times \left[(P_{\mu\nu}^\alpha - P_{\mu\nu}^\beta)(P_{\lambda\sigma}^\alpha + P_{\lambda\sigma}^\beta) - P_{\mu\sigma}^\alpha P_{\lambda\nu}^\alpha + P_{\mu\sigma}^\beta P_{\lambda\nu}^\beta \right]
 \end{aligned}$$

5.3.2 Second-order term

The second contribution to the molecular g -tensor is given by the second-order perturbation theory. According to Table 4.6 the relevant Hamiltonian terms are:

(a) the orbital Zeeman interaction

$$\hat{H}_{100}(15) = -i \sum_i \left(\frac{e\hbar}{2m_e} \right) \vec{B} \cdot (\vec{r}_{Gi} \times \vec{\nabla}_i)$$

(b) spin-(own)orbit interaction

$$\hat{H}_{001}(22) = -i \sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 g' Z_N \hat{k}_0^2(\vec{r}_{Ni}) \frac{1}{r_{Ni}^3} \vec{S}_i \cdot (\vec{r}_{Ni} \times \vec{\nabla}_i)$$

(c) spin-other orbit interaction

$$\hat{H}_{001}(23) = i \sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 4 \frac{1}{r_{ij}^3} \vec{S}_i \cdot (\vec{r}_{ij} \times \vec{\nabla}_j)$$

(d) electron-electron spin-orbit interaction

$$\hat{H}_{001}(24) = i \sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 g' \frac{1}{r_{ij}^3} \vec{S}_i \cdot (\vec{r}_{ji} \times \vec{\nabla}_i)$$

The pair of two-electron contributions can be combined into a single term

$$\hat{H}_{001}(2e) = \hat{H}_{001}(23) + \hat{H}_{001}(24) = i \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 \sum_i \sum_{j \neq i} \frac{1}{r_{ij}^3} \vec{S}_i \cdot (4\vec{l}_{ij} + g' \vec{l}_{ji})$$

with the vector operator

$$\vec{l}_{ij} \equiv \vec{r}_{ij} \times \vec{\nabla}_j = (\vec{r}_j - \vec{r}_i) \times \vec{\nabla}_j$$

The second-order contribution to the differential g -tensor is

$$\begin{aligned} \Delta g_{ab}'' &= S_a^{-1} \left\langle \Psi^{(0,0,0)} \left| \sum_i \hat{H}_{ia}^{(0,0,1)} \hat{s}_{ia} \right| \Psi_b^{(1,0,0)} \right\rangle \\ &\quad + S_b^{-1} \left\langle \Psi^{(0,0,0)} \left| \hat{H}_a^{(1,0,0)} \left| \sum_i \Psi_{ib}^{(0,0,1)} \hat{s}_{ib} \right| \right\rangle \end{aligned}$$

and the application of the (sum-over-states) perturbation theory for the perturbed kets yields the expressions

$$\begin{aligned}\tilde{\Psi}^{(1,0,0)} &= - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left\langle \Psi_K \left| \tilde{H}^{(1,0,0)} \right| \Psi_0 \right\rangle \Psi_K \\ \tilde{\Psi}^{(0,0,1)} &= - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left\langle \Psi_K \left| \tilde{H}^{(0,0,1)} \right| \Psi_0 \right\rangle \Psi_K \\ \tilde{\Psi}^{(0,0,1)} \cdot \tilde{S} &= - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \left\langle \Psi_K \left| \sum_i \tilde{H}_i^{(0,0,1)} \cdot \tilde{s}_i \right| \Psi_0 \right\rangle \Psi_K\end{aligned}$$

so that we are left with

$$\begin{aligned}\Delta g''_{ab} &= - \sum_{K=1}^{\infty} (E_K - E_0)^{-1} \\ &\quad \left[S_a^{-1} \left\langle \Psi_0 \left| \sum_i \hat{H}_{ia}^{(0,0,1)} \hat{s}_{ia} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \hat{H}_b^{(1,0,0)} \right| \Psi_0 \right\rangle \right. \\ &\quad \left. + S_b^{-1} \left\langle \Psi_0 \left| \hat{H}_a^{(1,0,0)} \right| \Psi_K \right\rangle \left\langle \Psi_K \left| \sum_i \hat{H}_{ib}^{(0,0,1)} \hat{s}_{ib} \right| \Psi_0 \right\rangle \right]\end{aligned}$$

This formula contains two types of integral. The first one is

$$\left\langle \Psi_0 \left| \hat{H}_a^{(1,0,0)} \right| \Psi_K \right\rangle = -i\mu_B \left\langle \Psi_0 \left| \sum_i \hat{l}_{Gia} \right| \Psi_K \right\rangle$$

with the one-electron spinless operator

$$\hat{l}_{Gia} \equiv (\vec{r}_{Gi} \times \vec{\nabla}_i)_a = [(\vec{r}_i - \vec{r}_G) \times \vec{\nabla}_i]_a$$

It can be expressed (with the help of the Slater rules) in terms of spin-orbitals as follows

$$\left\langle \Psi_0 \left| \sum_i \hat{l}_{Gia} \right| \Psi_K \right\rangle = \left\langle \Psi_0 \left| \sum_i \hat{l}_{Gia} \right| \Psi_o^u \right\rangle = \langle \varphi_o | \hat{l}_{G1a} | \varphi_u \rangle$$

when the proper (symmetry- and spin-adapted) wave function for an excited state, $|\Psi_o^u\rangle$, is single-determinantal. Remember, in this connection, the result already obtained for the two-determinantal singlet state function

$$\left\langle \Psi_0 \left| \sum_i \hat{h}_i \right| \Psi_o^u \right\rangle = \frac{1}{\sqrt{2}} \left(\langle \phi_o | \hat{h}_1 | \phi_u \rangle + \langle \phi_u | \hat{h}_1 | \phi_o \rangle \right) = \sqrt{2} \langle \phi_o | \hat{h}_1 | \phi_u \rangle$$

An analogous expression to the above holds true for $\langle \Psi_K | \hat{H}_b^{(1,0,0)} | \Psi_0 \rangle$.

The content of the second integral is

$$\begin{aligned} \left\langle \Psi_0 \left| \sum_i \hat{H}_{ia}^{(0,0,1)} \hat{s}_{ia} \right| \Psi_K \right\rangle &= -i \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 g' \left\langle \Psi_0 \left| \sum_i \left(\sum_N Z_N \frac{1}{r_{Ni}^3} \hat{l}_{Nia} \right) \hat{s}_{ia} \right| \Psi_K \right\rangle \\ &+ i \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 \left\langle \Psi_0 \left| \sum_i \left(\sum_{j \neq i} \frac{1}{r_{ij}^3} (4\vec{l}_{ij} + g' \vec{l}_{ji})_a \right) \hat{s}_{ia} \right| \Psi_K \right\rangle \end{aligned}$$

where

$$\hat{l}_{Nia} \equiv (\vec{r}_{Ni} \times \vec{\nabla}_i)_a = [(\vec{r}_i - \vec{r}_N) \times \vec{\nabla}_i]_a$$

The Slater rules predict that the one-electron term survives only for mono-excited configurations whereas the two-electron term survives also for bi-excited configurations. However, the perturbation formula for $\Delta g''_{ab}$ involves the product of the first-type (one electron only) and the second-type integrals so that the biexcited configurations cannot contribute. This allows to consider the whole second term as if it were constructed of an effective one-electron operator

$$\left\langle \Psi_0 \left| \sum_i \hat{H}_{ia}^{(0,0,1)} \hat{s}_{ia} \right| \Psi_K \right\rangle = i \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 \left\langle \Psi_0 \left| \sum_i \hat{F}_{ia} \hat{s}_{ia} \right| \Psi_K \right\rangle$$

with

$$\hat{F}_{ia} \equiv \hat{h}_i + \sum_{j \neq i} \hat{h}_{ij} = -g' \sum_N Z_N \frac{1}{r_{Ni}^3} \hat{l}_{Nia} + \sum_{j \neq i} \frac{1}{r_{ij}^3} (4\hat{l}_{ija} + g' \hat{l}_{jia})$$

The perturbation formula is then rewritten in the form where the integrals over the molecular spin-orbitals $|\varphi\rangle$ occur

$$\begin{aligned} \Delta g''_{ab} &= -\frac{2}{S} \sum_o^{\text{occ}} \sum_u^{\text{un}} \frac{1}{\Delta E_o^u} \left\langle \Psi_0 \left| \sum_i \hat{H}_{ia}^{(0,0,1)} \hat{s}_{ia} \right| \Psi_o^u \right\rangle \left\langle \Psi_o^u | \hat{H}_b^{(1,0,0)} | \Psi_0 \right\rangle \\ &= -\frac{2}{S} (-i\mu_B) \left(i\mu_B^2 \frac{\mu_0}{4\pi} \right) \sum_o^{\text{occ}} \sum_u^{\text{un}} \frac{1}{\Delta E_o^u} \left\langle \varphi_o | \hat{F}_{1a} \hat{s}_{ia} | \varphi_u \right\rangle \left\langle \varphi_u | \hat{l}_{G1b} | \varphi_o \right\rangle \end{aligned}$$

When the spin part is integrated off, then the integrals over the (spatial) molecular orbitals $|\phi\rangle$ survive and the whole second-order contribution is split into a pure one-electron and a two-electron term

$$\begin{aligned}\Delta g''_{ab}(1e) &= -\frac{2}{S} \left(\mu_B^3 \frac{\mu_0}{4\pi} \right) \left[\sum_{o_\alpha}^{\text{occ}_\alpha} \sum_{u_\alpha}^{\text{un}_\alpha} \frac{1}{\Delta E_{o_\alpha}^{u_\alpha}} \langle \phi_o^\alpha | \hat{h}_{1a} | \phi_u^\alpha \rangle \langle \phi_u^\alpha | \hat{l}_{G1b} | \phi_o^\alpha \rangle \right. \\ &\quad \left. + \sum_{o_\beta}^{\text{occ}_\beta} \sum_{u_\beta}^{\text{un}_\beta} \frac{1}{\Delta E_{o_\beta}^{u_\beta}} \langle \phi_o^\beta | \hat{h}_{1a} | \phi_u^\beta \rangle \langle \phi_u^\beta | \hat{l}_{G1b} | \phi_o^\beta \rangle \right] \\ \Delta g''_{ab}(2e) &= -\frac{2}{S} \left(\mu_B^3 \frac{\mu_0}{4\pi} \right) \left[\sum_{o_\alpha}^{\text{occ}_\alpha} \sum_{u_\alpha}^{\text{un}_\alpha} \frac{1}{\Delta E_{o_\alpha}^{u_\alpha}} \langle \phi_u^\alpha | \hat{l}_{G1b} | \phi_o^\alpha \rangle \right. \\ &\quad \sum_{\sigma=\alpha,\beta} \sum_{k_o} \langle \phi_o^\sigma \phi_k^\sigma | \hat{h}_{12a} | \phi_u^\alpha \phi_k^\sigma \rangle \\ &\quad \left. + \sum_{o_\beta}^{\text{occ}_\beta} \sum_{u_\beta}^{\text{un}_\beta} \frac{1}{\Delta E_{o_\beta}^{u_\beta}} \langle \phi_u^\beta | \hat{l}_{G1b} | \phi_o^\beta \rangle \sum_{\sigma=\alpha,\beta} \sum_{k_o} \langle \phi_o^\sigma \phi_k^\sigma | \hat{h}_{12a} | \phi_u^\beta \phi_k^\sigma \rangle \right]\end{aligned}$$

The evaluation of the excitation energies represents a central problem; these energies are often approximated with the help of the orbital energies as

$$\Delta E_{o_\sigma}^{u_\sigma} = \varepsilon_u^\sigma - \varepsilon_o^\sigma$$

Another problem arises from the fact that some terms are gauge-dependent. These, however, can be collected into groups whose contribution should decrease in size for larger basis sets [42].

5.3.3 Hand calculations

According to the procedure outlined in Section 5.2.5 the contributions to the molecular *A*-tensor, taken with the following sign convention

$$A_{ab} = - \sum_{K \neq 0} \frac{\langle 0 | \hat{L}_a | K \rangle \langle K | \hat{L}_b | 0 \rangle}{E_K - E_0} [\hbar^{-2}]$$

have been found for a copper(II) ion as follows

$$\begin{aligned}A_{xx} = A_{yy} &= - \frac{1}{\Delta E(^2B_{1g} \rightarrow ^2E_g)} \\ A_{zz} &= - \frac{4}{\Delta E(^2B_{1g} \rightarrow ^2B_{2g})}\end{aligned}$$

Then the g -tensor components, ignoring the orbital reduction factor, become

$$g_{xx} = g_e + 2\lambda A_{xx} = g_e - 2\lambda \frac{1}{\Delta E(^2B_{1g} \rightarrow ^2E_g)}$$

$$g_{zz} = g_e + 2\lambda A_{zz} = g_e - 2\lambda \frac{4}{\Delta E(^2B_{1g} \rightarrow ^2B_{2g})}$$

For the $[\text{Cu}(\text{NH}_3)_6]^{2+}$ complex, as an example, the excitation energies are approximately $\Delta E(^2B_{1g} \rightarrow ^2B_{2g})/hc \approx \Delta E(^2B_{1g} \rightarrow ^2E_g) = 16400 \text{ cm}^{-1}$. The spin-orbit coupling constant for Cu^{2+} is $\xi_d/hc = 800 \text{ cm}^{-1}$ and the spin-orbit splitting parameter $\lambda = -\xi_d/2S$ only alters the sign. Then, for the $^2B_{1g}$ ground state, the g -tensor components are

$$g_{xx} = 2.0023 + 2 \frac{800}{16400} \approx 2.1$$

$$g_{zz} = 2.0023 + 2 \frac{800 \times 4}{16400} \approx 2.4$$

If the ground state of the $\text{Cu}(\text{II})$ complex is $^2A_{1g}$ (a square-planar geometry) then the A -tensor components become

$$\begin{aligned} -A_{xx} &= \frac{\langle ^2A_{1g} | \hat{1}_x | ^2B_{1g} \rangle \langle ^2B_{1g} | \hat{1}_x | ^2A_{1g} \rangle}{\Delta E(^2A_{1g} \rightarrow ^2B_{1g})} + \frac{\langle ^2A_{1g} | \hat{1}_x | ^2B_{2g} \rangle \langle ^2B_{2g} | \hat{1}_x | ^2A_{1g} \rangle}{\Delta E(^2A_{1g} \rightarrow ^2B_{2g})} \\ &\quad + \frac{\langle ^2A_{1g} | \hat{1}_x | ^2E_g \rangle \langle ^2E_g | \hat{1}_x | ^2A_{1g} \rangle}{\Delta E(^2A_{1g} \rightarrow ^2E_g)} + \frac{\langle ^2A_{1g} | \hat{1}_x | ^2E_g \rangle \langle ^2E_g | \hat{1}_x | ^2A_{1g} \rangle}{\Delta E(^2A_{1g} \rightarrow ^2E_g)} \\ &= \frac{[-i\langle ^2A_{1g} | ^2E_g \rangle][-\sqrt{3}\langle ^2B_{1g} | ^2E_g \rangle]}{\Delta E(^2A_{1g} \rightarrow ^2B_{1g})} + \frac{[i\langle ^2A_{1g} | ^2E_g \rangle][-\sqrt{3}\langle ^2B_{2g} | ^2E_g \rangle]}{\Delta E(^2A_{1g} \rightarrow ^2B_{2g})} \\ &\quad + \frac{[i\sqrt{3}\langle ^2A_{1g} | ^2A_{1g} \rangle + i\langle ^2A_{1g} | ^2B_{1g} \rangle][-\sqrt{3}\langle ^2E_g | ^2E_g \rangle]}{\Delta E(^2A_{1g} \rightarrow ^2E_g)} \\ &\quad + \frac{[-i\langle ^2A_{1g} | ^2B_{2g} \rangle][-\sqrt{3}\langle ^2E_g | ^2E_g \rangle]}{\Delta E(^2A_{1g} \rightarrow ^2E_g)} \end{aligned}$$

so that

$$A_{xx} = A_{yy} = -\frac{3}{\Delta E(^2A_{1g} \rightarrow ^2E_g)}$$

and

$$A_{zz} = 0$$

Finally, the *g*-tensor components adopt the values of

$$g_{xx} = 2.0023 + 2 \frac{800 \times 3}{16400} \approx 2.3$$

and

$$g_{zz} \approx 2.0$$

5.4 THE *D*-TENSOR

Little attention has been paid to direct ab initio calculations of the molecular *D*-tensor so far, although some limited sources of information exist [35]. In fact, the procedure is similar to the *g*-tensor calculations and the contributing Hamiltonian terms, as they follow from Table 4.5, are:

(a) spin–spin dipolar interaction

$$\hat{H}_{002}(25) = \sum_i \sum_{j < i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 4 \left[\frac{1}{r_{ij}^3} (\vec{s}_i \cdot \vec{s}_j) - \frac{3}{r_{ij}^5} (\vec{s}_i \cdot \vec{r}_{ji})(\vec{s}_j \cdot \vec{r}_{ji}) \right]$$

(b) spin–spin contact interaction

$$\hat{H}_{002}(26) = - \sum_i \sum_{j < i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 \frac{32\pi}{3} \delta(\vec{r}_{ji}) \vec{s}_i \cdot \vec{s}_j$$

(c) spin–(own)orbit interaction

$$\hat{H}_{001}(22) = -i \sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 g' Z_N \tilde{k}_0^2(\vec{r}_{Ni}) \frac{1}{r_{Ni}^3} \vec{s}_i \cdot (\vec{r}_{Ni} \times \vec{\nabla}_i)$$

(d) spin–other orbit interaction

$$\hat{H}_{001}(23) = i \sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 4 \frac{1}{r_{ij}^3} \vec{s}_i \cdot (\vec{r}_{ij} \times \vec{\nabla}_j)$$

(e) electron–electron spin–orbit interaction

$$\hat{H}_{001}(24) = i \sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \left(\frac{e\hbar}{2m_e} \right)^2 g' \frac{1}{r_{ij}^3} \vec{s}_i \cdot (\vec{r}_{ji} \times \vec{\nabla}_i)$$

While the first two terms contribute to first-order perturbation theory, the last three terms contribute to second-order theory and are exactly the same as already known from the second-order g -tensor calculations.

For hand calculations one can use the estimate valid for $S \geq 1$

$$-\frac{1}{2}D_{ab} = \lambda^2 A_{ab}$$

SUMMARY

1. Several quantum-chemical methods have been developed for the direct evaluation of magnetic parameters. These are based either on the Rayleigh–Schrödinger, sum-over-the-states, perturbation theory or, alternatively, on the finite perturbation theory. Two main problems arise: the gauge variance in the limited basis set for $\bar{\kappa}$, $\bar{\Delta}g$ and $\bar{\sigma}_N$ tensors, and the problem of calculation of excitation energies. The first problem is more or less successfully solved by the GIAO, IGLO, LONG, IGIAM, DOGON and CTOCD methods; the second one via the RPA approach. The magnetic parameters are partitioned into the diamagnetic (first-order) and paramagnetic (second-order) contributions.
2. Direct ab initio calculations of magnetic parameters are usually restricted to the magnetic susceptibility and the nuclear shielding tensors. Only recently have calculations of the g -tensor appeared.
3. The evaluation of the magnetic parameters can also be done with the help of the electronic current density. This observable can be visualised by oriented contour lines.
4. The diamagnetic part of the magnetic susceptibility obeys additivity over the atomic or functional groups. Most frequently the set of empirical Pascal constants is exploited in order to give an estimate of the underlying diamagnetism. The temperature-independent paramagnetic term is estimated less accurately.
5. Hand calculations (estimates) of the electronic magnetic parameters $\bar{\kappa}$, $\bar{\Delta}g$ and $\bar{D}$ are enabled through the concept of the molecular A -tensor. It needs the evaluation of the matrix elements of the angular momentum and the (empirical) values of the spin–orbit coupling constant ξ_d and/or splitting parameter λ along with the experimental excitation energies.

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Temperature Dependence of Magnetic Susceptibility

6.1 SUSCEPTIBILITY FORMULAE

6.1.1 Magnetisation formula

Statistical thermodynamics brings the result that the thermal average of the (molar) magnetisation can be evaluated through the formula

$$M = N_A \frac{\sum_i \mu_i \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} = N_A \frac{\sum_i \left(-\frac{\partial \varepsilon_i}{\partial B} \right) \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)}$$

where the energy levels ε_i depend in some way upon the magnetic field. The molar differential magnetic susceptibility is obtained as the first derivative of the magnetisation

$$\tilde{\chi} = \mu_0 \frac{\partial M}{\partial B}$$

If the above functions $\varepsilon_i = f(B)$ and $M = f(B)$ were simple analytic functions, the treatment would be trivial.

Having determined the partition function of the system

$$Z = \sum_i^m \exp(-\varepsilon_i/kT)$$

the magnetisation becomes expressed as

$$\begin{aligned} M &= -\frac{\partial F}{\partial B} = N_A kT \frac{\partial \ln Z}{\partial B} \\ &= N_A \frac{1}{Z} \sum_i \left(-\frac{\partial \varepsilon_i}{\partial B} \right) \exp(-\varepsilon_i/kT) \end{aligned}$$

Then the differential magnetic susceptibility is

$$\tilde{\chi} = \mu_0 \frac{\partial M}{\partial B} = \frac{N_A \mu_0}{kT} \frac{1}{Z^2} \left\{ \left[\sum_i \left(\frac{\partial \varepsilon_i}{\partial B} \right)^2 \exp(-\varepsilon_i/kT) - (kT) \sum_i \left(\frac{\partial^2 \varepsilon_i}{\partial B^2} \right) \exp(-\varepsilon_i/kT) \right] Z - \left[\sum_i \left(\frac{\partial \varepsilon_i}{\partial B} \right) \exp(-\varepsilon_i/kT) \right]^2 \right\}$$

This formula for the magnetic susceptibility is useful when the magnetic energy levels $E_i = f(B)$ are simple analytic functions of the magnetic induction from which the first and second derivatives are easily derived. Normally the situation is more complex and one should follow the following steps.

1. For the system under study an appropriate Hamiltonian must be postulated. This is not necessarily an isotropic Hamiltonian; $\hat{H}_{\parallel}$ (parallel) and $\hat{H}_{\perp}$ (perpendicular) components can be distinguished in the case of axial symmetry, or $\hat{H}_x$, $\hat{H}_y$ and $\hat{H}_z$ components when the symmetry is even lower.
2. Some magnetic parameters enter the matrix elements of the Hamiltonian concerned: these are magnetogyric factors (g -factors, components of the g -tensors) and the coupling constants (components of the spin–spin coupling tensors D , in the case of an isotropic exchange abbreviated as J).
3. The energy levels are received as eigenvalues of the Hamiltonian matrix spanning the space of wave functions. The wave functions concerned are represented by the set of spin functions, or a set of wavefunctions for coupled angular momenta (spin–orbit at one centre, spin–spin among more centres, etc.). Thus the basis set size can vary from two spin functions for a single $s = \frac{1}{2}$ centre to several millions, e.g. $N = 6^8$ for a cluster of eight Fe(III) centres.
4. From the field dependence of the energy levels $\varepsilon_i = f(B)$ the first derivatives should be obtained. In the case of a vanishing field the derivatives should be taken in the limit from the right side ($B \rightarrow 0^+$) because the applied field is non-negative.

As a result of this procedure, the magnetisation and consequently the magnetic susceptibility are complicated (mostly implicit) functions of T , B , and a set of magnetic parameters. For linear magnetics (such as molecular paramagnets) the magnetisation rises linearly with the field and the susceptibility is a field-independent quantity

$$\bar{\chi} = \mu_0 \frac{M}{B} = \frac{M}{H}$$

6.1.2 High-temperature approximation

Frequently we are interested in a region of temperature in which the energy levels are small compared with the thermal energy

$$\varepsilon_i \ll kT$$

The partition function expanded in powers of T , then becomes [1]

$$\begin{aligned} \frac{Z}{N} &= \frac{1}{N} \left[\sum_{i=1}^N \left(1 - \frac{\varepsilon_i}{kT} + \frac{\varepsilon_i^2}{2(kT)^2} - \dots \right) \right] \\ &= 1 - \frac{\bar{\varepsilon}}{kT} + \frac{\overline{\varepsilon^2}}{2(kT)^2} - \dots \\ &= 1 + \sum_{p=1}^{\infty} b_p T^{-p} \end{aligned}$$

Here N is the total number of energy levels ε_i and the expanding coefficients are

$$b_p = (-1)^p \frac{1}{p!k^p} \frac{1}{N} \sum_{i=1}^N (\varepsilon_i)^p = (-1)^p \frac{\overline{(\varepsilon/k)^p}}{p!}$$

Then the series expansion for $\ln Z$ is

$$\ln Z = \ln N - \sum_{n=1}^{\infty} a_n T^{-n}$$

with new coefficients

$$a_n = b_n - \frac{1}{2} \sum_{p=1}^{n-1} b_{n-p} b_p + \frac{1}{3} \sum_{p=1}^{n-2} \sum_{q=1}^{n-2} b_{n-p-q} b_p b_q + \dots$$

Now the molar magnetisation becomes expressed as follows

$$M = N_A \mu_0 k \sum_{n=1}^{\infty} \left(\frac{\partial a_n}{\partial B} \right)_T T^{-(n-1)}$$

This formula is further simplified if the origin of the energy is chosen in such a way that

$$\bar{\varepsilon} = \frac{1}{N} \sum_{i=1}^N \varepsilon_i = 0$$

holds true. In this case the leading terms of the magnetisation are

$$M = N_A \mu_0 \left[\frac{1}{2kT} \left(\frac{\partial \bar{\varepsilon}^2}{\partial B} \right)_T - \frac{1}{6(kT)^2} \left(\frac{\partial \bar{\varepsilon}^3}{\partial B} \right)_T + \dots \right]$$

The advantage of this high-temperature expansion is that we need not determine the individual energy levels but can use the theorem of the invariance of the trace of a matrix. For example, to find the value of $\bar{\varepsilon}^2$ we square the Hamiltonian and pick out only the diagonal terms. On summing these terms over all possible values, many of the sums cancel. For example, the zero-field splitting Hamiltonian of the form

$$\hat{H}^S = \mu_B B (g_x l_x \hat{S}_x + g_y l_y \hat{S}_y + g_z l_z \hat{S}_z) [\hbar^{-1}] + (D_x \hat{S}_x^2 + D_y \hat{S}_y^2 + D_z \hat{S}_z^2) [\hbar^{-2}]$$

yields the mean value of

$$\begin{aligned} \bar{\varepsilon}^2 &= (\mu_B B)^2 (g_x^2 l_x^2 + g_y^2 l_y^2 + g_z^2 l_z^2) \frac{S(S+1)}{3} \\ &\quad + (D_x^2 + D_y^2 + D_z^2) \frac{S(S+1)(2S-1)(2S+3)}{30} \end{aligned}$$

and

$$\bar{\varepsilon}^3 = (\mu_B B)^2 (g_x^2 l_x^2 D_x + g_y^2 l_y^2 D_y + g_z^2 l_z^2 D_z) \frac{S(S+1)(2S-1)(2S+3)}{30}$$

6.1.3 Van Vleck formula

The field dependence of the energy levels of magneto-active particles (atoms, molecules, clusters) can be expressed through a Taylor expansion. This leads to the appearance of several terms: linear in B —the first-order Zeeman term, quadratic in B —the second-order Zeeman term, etc. [2]

$$\varepsilon_i = \varepsilon_i^{(0)} + \varepsilon_i^{(1)} B + \varepsilon_i^{(2)} B^2 + \dots$$

The Boltzmann factors can then be replaced as follows

$$\begin{aligned}
 \exp(-\varepsilon_i/kT) &= \exp[-(\varepsilon_i^{(0)} + \varepsilon_i^{(1)}B + \varepsilon_i^{(2)}B^2 + \dots)/kT] \\
 &\approx \exp(-\varepsilon_i^{(0)}/kT) \exp(-\varepsilon_i^{(1)}B/kT) \\
 &\approx \exp(-\varepsilon_i^{(0)}/kT)[1 - \varepsilon_i^{(1)}B/kT]
 \end{aligned}$$

where only dominating contributions survive. The magnetic moment is truncated at the second term

$$\mu_i = -\frac{\partial \varepsilon_i}{\partial B} = -\frac{\partial}{\partial B} [\varepsilon_i^{(0)} + \varepsilon_i^{(1)}B + \varepsilon_i^{(2)}B^2 + \dots] = -\varepsilon_i^{(1)} - 2\varepsilon_i^{(2)}B + \dots$$

To this approximation the thermal average magnetisation becomes expressed as follows

$$\begin{aligned}
 M &= N_A \frac{\sum_i \mu_i \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} \\
 &= N_A \frac{\sum_i [-\varepsilon_i^{(1)} - 2\varepsilon_i^{(2)}B] \exp(-\varepsilon_i^{(0)}/kT)[1 - \varepsilon_i^{(1)}B/kT]}{\sum_i \exp(-\varepsilon_i^{(0)}/kT)[1 - \varepsilon_i^{(1)}B/kT]} \\
 &= N_A \frac{\sum_i [-\varepsilon_i^{(1)} - 2\varepsilon_i^{(2)}B + (\varepsilon_i^{(1)})^2 B/kT + 2B^2 \varepsilon_i^{(1)} \varepsilon_i^{(2)}/kT] \exp(-\varepsilon_i^{(0)}/kT)}{\sum_i \exp(-\varepsilon_i^{(0)}/kT)[1 - \varepsilon_i^{(1)}B/kT]}
 \end{aligned}$$

In the limit of the vanishing field we have

$$M(B \rightarrow 0) = N_A \frac{\sum_i [-\varepsilon_i^{(1)}] \exp(-\varepsilon_i^{(0)}/kT)}{\sum_i \exp(-\varepsilon_i^{(0)}/kT)} = 0$$

and for paramagnetic substances with zero permanent magnetic polarisation this should vanish. Retaining only terms linear in B , we arrive at an approximate expression for the magnetisation

$$M = N_A B \frac{\sum_i \left[\frac{(-\varepsilon_i^{(1)})^2}{kT} - 2\varepsilon_i^{(2)} \right] \exp(-\varepsilon_i^{(0)}/kT)}{\sum_i \exp(-\varepsilon_i^{(0)}/kT)}$$

This derivation, evidently, is well valid for substances obeying a linear dependence of the magnetisation upon the applied magnetic field (paramagnets), and this cannot be overemphasised. Now the expression for the mean magnetic susceptibility is straightforward

$$\begin{aligned}\bar{\chi} &= \mu_0 \frac{M}{B} \\ &= \mu_0 N_A \frac{\sum_i \left[\frac{(-\varepsilon_i^{(1)})^2}{kT} - 2\varepsilon_i^{(2)} \right] \exp(-\varepsilon_i^{(0)}/kT)}{\sum_i \exp(-\varepsilon_i^{(0)}/kT)}\end{aligned}$$

This is the famous *van Vleck formula* [2].

The van Vleck formula can be improved by maintaining some more terms in the numerator as well as in the denominator in the expression for the magnetisation. The Zeeman coefficients, however, should be accessible and the derivative of the magnetisation provided numerically. Then the magnetic susceptibility becomes a function of the magnetic field.

6.1.4 Generalised van Vleck formula

The van Vleck formula presupposes knowledge of the orientation of the principal molecular susceptibilities. For molecules lacking the symmetry a generalised expression has been derived [3].

The magnetisation in the given direction is expressed as follows

$$M_a = N_A \frac{\sum_i (\mu_a)_i \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} = N_A \frac{\sum_i \left(-\frac{\partial \varepsilon_i}{\partial B_a} \right) \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)}$$

In terms of perturbation theory the energy of a magnetic level, to the second order, is

$$\varepsilon_i = \varepsilon_i^0 + \sum_a \langle i | \hat{\mu}_a | i \rangle B_a + \sum_a \sum_b \sum_{j \neq i} \frac{\langle i | \hat{\mu}_a | j \rangle \langle j | \hat{\mu}_b | i \rangle}{\varepsilon_i^0 - \varepsilon_j^0} B_a B_b$$

The basis set has been chosen in such a way that all groups of the levels degenerate before the perturbation are diagonal with respect to μB . Then the first derivative becomes

$$\frac{\partial \varepsilon_i}{\partial B_a} = \langle i | \hat{\mu}_a | i \rangle + \sum_b \sum_{j \neq i} \frac{\langle i | \hat{\mu}_a | j \rangle \langle j | \hat{\mu}_b | i \rangle + \langle i | \hat{\mu}_b | j \rangle \langle j | \hat{\mu}_a | i \rangle}{\varepsilon_i^0 - \varepsilon_j^0} B_b$$

Following the treatment of van Vleck, much simplification is obtained for a small magnetic field when the following expression is fulfilled

$$\exp(-\varepsilon_i/kT) \approx \exp(-\varepsilon_i^0/kT) \left[1 - \sum_a \langle i | \hat{\mu}_a | i \rangle B_a/kT \right]$$

On substitution into the magnetisation formula, and maintaining only terms linear in the field, we get

$$M_a = N_A \frac{\sum_b B_b \sum_i \left[\langle i | \hat{\mu}_a | i \rangle \langle i | \hat{\mu}_b | i \rangle /kT + \sum_{j \neq i} \frac{\langle i | \hat{\mu}_a | j \rangle \langle j | \hat{\mu}_b | i \rangle + \langle i | \hat{\mu}_b | j \rangle \langle j | \hat{\mu}_a | i \rangle}{\varepsilon_i^0 - \varepsilon_j^0} \right] \exp(-\varepsilon_i^0/kT)}{\sum_i \exp(-\varepsilon_i^0/kT)}$$

It has been claimed that the residual magnetisation disappears in the zero field and coefficients of higher powers of the field are negligible. The *generalised van Vleck formula* for the magnetic susceptibility is [3]

$$\bar{\chi}_{ab} = N_A \mu_0 \frac{\sum_i \left[\langle i | \hat{\mu}_a | i \rangle \langle i | \hat{\mu}_b | i \rangle /kT + \sum_{j \neq i} \frac{\langle i | \hat{\mu}_a | j \rangle \langle j | \hat{\mu}_b | i \rangle + \langle i | \hat{\mu}_b | j \rangle \langle j | \hat{\mu}_a | i \rangle}{\varepsilon_i^0 - \varepsilon_j^0} \right] \exp(-\varepsilon_i^0/kT)}{\sum_i \exp(-\varepsilon_i^0/kT)}$$

This reduces to the common van Vleck formula when applied to a diagonal element of the susceptibility tensor

$$\bar{\chi}_{aa} = N_A \mu_0 \frac{\sum_i \left[\langle i | \hat{\mu}_a | i \rangle^2 /kT + 2 \sum_{j \neq i} \frac{\langle i | \hat{\mu}_a | j \rangle \langle j | \hat{\mu}_a | i \rangle}{\varepsilon_i^0 - \varepsilon_j^0} \right] \exp(-\varepsilon_i^0/kT)}{\sum_i \exp(-\varepsilon_i^0/kT)}$$

The choice of the basis set affects the first term of the magnetic susceptibility. Let us consider two matrices, **A** and **B**, with elements in a completely general basis set

$$A_{kl} = \langle k | \hat{\mu}_a | l \rangle$$

and

$$B_{kl} = \langle k | \hat{\mu}_b | l \rangle$$

There exists a unitary transformation relating the general matrix $\mathbf{B}$ to the diagonal form $\mathbf{D}_b$

$$\mathbf{D}_b = \mathbf{B}' = \mathbf{U}^{-1} \mathbf{B} \mathbf{U}$$

The same transformation when applied to $\mathbf{A}$ may not yield a diagonal matrix

$$\mathbf{A}' = \mathbf{U}^{-1} \mathbf{A} \mathbf{U}$$

The product of the matrices is

$$\mathbf{A}' \mathbf{B}' = (\mathbf{U}^{-1} \mathbf{A} \mathbf{U})(\mathbf{U}^{-1} \mathbf{B} \mathbf{U}) = \mathbf{U}^{-1} (\mathbf{A} \mathbf{B}) \mathbf{U}$$

Since the trace of a matrix ($\mathbf{C} = \mathbf{A} \mathbf{B}$) is invariant under a unitary transformation we can write

$$\sum_k \sum_l A'_{kl} B'_{lk} = \sum_k \sum_l A_{kl} B_{lk}$$

and, because the matrix $\mathbf{B}'$ was diagonal, we get

$$\sum_i A'_{ii} B'_{ii} = \sum_k \sum_l A_{kl} B_{lk}$$

We have proven that the following relationship holds true

$$\sum_i \langle i | \hat{\mu}_a | i \rangle \langle i | \hat{\mu}_b | i \rangle = \sum_k \sum_l \langle k | \hat{\mu}_a | l \rangle \langle l | \hat{\mu}_b | k \rangle$$

where the indices k and l run over all elements of a general basis set including situations when the energy levels are degenerate, $\varepsilon_l^0 = \varepsilon_k^0$.

6.1.5 Partition function formula

The molecular Hamiltonian can be split into the field-independent part and the part linear in the magnetic field [4]

$$\hat{H} = \hat{H}_0 + \hat{H}' = \hat{H}_0 + \sum_a \hat{Z}_a B_a$$

The zero-field Hamiltonian $\hat{H}_0$ includes the spin-orbit and spin-spin interactions and eventually the crystal field operators; the first-order Zeeman term $\hat{H}'$ comprises the orbital and spin contributions. The matrix elements of the full Hamiltonian in the chosen basis set are

$$H_{v\lambda} = \langle v | \hat{H} | \lambda \rangle$$

By the diagonalisation of such a matrix

$$\varepsilon = \mathbf{C}^+ \mathbf{H} \mathbf{C}$$

the set of eigenvalues ε_i and the corresponding eigenvectors

$$|i\rangle = \sum_v C_{iv} |v\rangle$$

are obtained. Using the eigenvectors, the matrix elements of the magnetic moment operator are expressed as

$$(\mu_a)_i = -\frac{\partial \varepsilon_i}{\partial B_a} = -\frac{\partial \langle i | \hat{H} | i \rangle}{\partial B_a} = -\langle i | \hat{Z}_a | i \rangle = -\sum_v \sum_\lambda C_{iv}^+(Z_a)_{v\lambda} C_{\lambda i}$$

Now the application of the magnetisation formula yields

$$\begin{aligned} M_a &= N_A \frac{\sum_i (\mu_a)_i \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} \\ &= -N_A \frac{\sum_i \langle i | \hat{Z}_a | i \rangle \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} \\ &= -N_A \frac{\sum_i \left(\sum_v \sum_\lambda C_{iv}^+(Z_a)_{v\lambda} C_{\lambda i} \right) \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} \end{aligned}$$

The diagonal component of the susceptibility tensor at a temperature T is

$$\begin{aligned}\bar{\chi}_{aa} &= -\frac{N_A \mu_0}{B_a} \frac{\sum_i \langle i | \hat{Z}_a | i \rangle \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} \\ &= -\frac{N_A \mu_0}{B_a} \frac{\sum_i \left(\sum_v \sum_\lambda C_{iv}^+(Z_a)_{v\lambda} C_{\lambda i} \right) \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)}\end{aligned}$$

Powder averaging is achieved using the magnetic fields [4]

$$B_x = B_y = B_z = B/\sqrt{3}$$

and

$$\begin{aligned}\bar{\chi}_{av} &= \frac{1}{3} (\bar{\chi}_{xx} + \bar{\chi}_{yy} + \bar{\chi}_{zz}) \\ &= -\frac{N_A \mu_0}{\sqrt{3} B_a} \frac{\sum_{a=x,y,z} \sum_i \langle i | \hat{Z}_a | i \rangle \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} \\ &= -\frac{N_A \mu_0}{\sqrt{3} B_a} \frac{\sum_{a=x,y,z} \sum_i \left(\sum_v \sum_\lambda C_{iv}^+(Z_a)_{v\lambda} C_{\lambda i} \right) \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)}\end{aligned}$$

6.1.6 Polynomial fit formula

The above treatment requires the determination of the eigenvalues as well as the eigenvectors of the Hamiltonian. However, the evaluation of eigenvalues represents only a fraction of the time required for the determination of all eigenvectors. It may be of great advantage to develop a method where only the eigenvalues need to be calculated [5].

For a given set of trial magnetic parameters the eigenvalues ε_{ai} in the given direction ($a = x, y, z$) are monotonic functions of the magnetic induction B and therefore a Taylor expansion is possible

$$\varepsilon_{ai} = \varepsilon_{ai}^{(0)} + \varepsilon_{ai}^{(1)} \Delta B + \varepsilon_{ai}^{(2)} \Delta B^2 + \varepsilon_{ai}^{(3)} \Delta B^3 + \varepsilon_{ai}^{(4)} \Delta B^4 + \dots$$

with

$$\varepsilon_{ai}^{(n)} = \frac{1}{n!} \left(\frac{\partial^n \varepsilon_{ai}}{\partial B^n} \right) = c_{ai}^{(n)}$$

being the coefficients (derivatives) to be determined.

It is easy to generate $\varepsilon_{ai,m}$ values for $m = 3$ to 5 (or more) discrete points of B_m around a certain reference B_0 , i.e.

$$B_m = B_0 \pm N\delta$$

with $N = 0, 1, 2, \dots$. Thus it holds that

$$\varepsilon_{ai,m} = c_{ai}^{(0)} + c_{ai}^{(1)}(\Delta B_m) + \dots + c_{ai}^{(n)}(\Delta B_m)^n$$

for

$$\Delta B_m = B_m - B_0$$

and $n = m - 1$. In matrix form, the row matrices are interrelated through

$$\begin{pmatrix} \varepsilon_{ai,1} & \varepsilon_{ai,2} & \dots & \varepsilon_{ai,m} \end{pmatrix} = \begin{pmatrix} c_{ai}^{(0)} & c_{ai}^{(1)} & \dots & c_{ai}^{(n)} \end{pmatrix} \begin{pmatrix} 1 & 1 & \dots & 1 \\ \Delta B_1 & \Delta B_2 & \dots & \Delta B_m \\ \dots & \dots & \dots & \dots \\ \Delta B_1^n & \Delta B_2^n & \dots & \Delta B_m^n \end{pmatrix}$$

or

$$\mathbf{e} = \mathbf{cB}$$

with the *working field matrix* defined as follows

$$\mathbf{B} = \begin{pmatrix} 1 & 1 & \dots & 1 \\ \Delta B_1 & \Delta B_2 & \dots & \Delta B_m \\ \dots & \dots & \dots & \dots \\ \Delta B_1^n & \Delta B_2^n & \dots & \Delta B_m^n \end{pmatrix}$$

Then the row matrix $\mathbf{c}$ of expansion coefficients $c_{ai}^{(n)}$ is calculated, provided the inverse $\mathbf{B}^{-1}$ exists

$$\mathbf{c} = \mathbf{eB}^{-1}$$

Assembling the rows into matrices, we have

$$\begin{pmatrix} \varepsilon_{a1,1} & \varepsilon_{a1,2} & \cdots & \varepsilon_{a1,m} \\ \varepsilon_{a2,1} & \varepsilon_{a2,2} & \cdots & \varepsilon_{a2,m} \\ \cdots & \cdots & \cdots & \cdots \\ \varepsilon_{am,1} & \varepsilon_{am,2} & \cdots & \varepsilon_{am,m} \end{pmatrix} = \begin{pmatrix} c_{a1}^{(0)} & c_{a1}^{(1)} & \cdots & c_{a1}^{(n)} \\ c_{a2}^{(0)} & c_{a2}^{(1)} & \cdots & c_{a2}^{(n)} \\ \cdots & \cdots & \cdots & \cdots \\ c_{am}^{(0)} & c_{am}^{(1)} & \cdots & c_{am}^{(n)} \end{pmatrix} \begin{pmatrix} 1 & 1 & \cdots & 1 \\ \Delta B_1 & \Delta B_2 & \cdots & \Delta B_m \\ \cdots & \cdots & \cdots & \cdots \\ \Delta B_1^n & \Delta B_2^n & \cdots & \Delta B_m^n \end{pmatrix}$$

or

$$\mathbf{E} = \mathbf{CB}$$

and thus, in one step, all coefficients in the given direction ($a = x, y, z$) are determined

$$\mathbf{C} = \mathbf{EB}^{-1}$$

Only the $c^{(0)}$, $c^{(1)}$ and $c^{(2)}$ coefficients enter the van Vleck formula for the components of the molar paramagnetic susceptibility which relaxes to the “*polynomial fit formula*” of the form [5]

$$\bar{\chi}_{aa} = N_A \mu_0 \frac{\sum_i \left[\frac{(c_{ai}^{(1)})^2}{kT} - 2c_{ai}^{(2)} \right] \exp(-c_{ai}^{(0)}/kT)}{\sum_i \exp(-c_{ai}^{(0)}/kT)}$$

In order to secure good numerical stability, B_0 and δ should not be too low; instead, the matrix $\mathbf{B}$ tends to be singular. For instance, $H_0 = 800 \text{ A m}^{-1}$ ($B_0 = \mu_0 H_0$) and $\delta = (B_0/10)$ represent a good choice. The stability of the van Vleck coefficients $c^{(0)}$, $c^{(1)}$ and $c^{(2)}$ can be examined by increasing the number m of the terms in the Taylor expansion from 3 to 4 or 5.

From the computational point of view, evaluation of three to five sets of eigenvalues is much faster than one diagonalisation with a full set of eigenvectors. This is more effective especially when large-dimensional matrices are concerned.

For a more precise average of the powder molar susceptibility a numerical integration over the polar angles is possible

$$\chi_{\text{av}} = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} \chi(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi = -\frac{1}{4\pi} \int_{-1}^{+1} \left[\int_0^{2\pi} \chi(\vartheta, \varphi) \, d\varphi \right] d(\cos \vartheta)$$

The (spin) Zeeman term entering the total magnetic Hamiltonian is expressed as

$$\begin{aligned} \hat{H}'(\vartheta_k, \varphi_l) = & \mu_B B_m (g_x \sin \vartheta_k \cos \varphi_l \hat{S}_x + g_y \sin \vartheta_k \sin \varphi_l \hat{S}_y \\ & + g_z \cos \vartheta_k \hat{S}_z) [\hbar^{-1}] \end{aligned}$$

and this generates the angular dependent susceptibility $\chi(\vartheta_k, \varphi_l)$. In practice, a sphere is cut into several discrete grid points, say 25 values for ϑ_k and 25 values for φ_l , at which the susceptibility is evaluated. Then the integral is substituted by the finite sum formula

$$\chi_{\text{av}} = \frac{\sum_k \sum_l \chi(\vartheta_k, \varphi_l) \Delta_k(\cos \vartheta) \Delta_l(\varphi)}{\sum_k \sum_l \Delta_k(\cos \vartheta) \Delta_l(\varphi)}$$

6.1.7 Finite difference formula

The need for numerical determination of the expansion coefficients was emphasised by König and Kremer [6]. They, however, used a *finite difference formula* of the form

$$\mu_{ai}(B_0) = -\left(\frac{\partial \varepsilon_{ai}(B)}{\partial B} \right)_{B_0} \approx -\frac{\Delta \varepsilon_{ai}}{\Delta B} = \frac{[\varepsilon_{ai}(B_0 - \delta)] - [\varepsilon_{ai}(B_0 + \delta)]}{2\delta}$$

where the energy levels are evaluated at three values of the fields: $\varepsilon_i(B_0 - \delta)$, $\varepsilon_i(B_0)$ and $\varepsilon_i(B_0 + \delta)$. Then the magnetisation formula is applied in the form of

$$M_a = N_A \frac{\sum_i \mu_{ai}(B_0) \exp[-\varepsilon_{ai}(B_0)/kT]}{\sum_i \exp[-\varepsilon_{ai}(B_0)/kT]}$$

and the mean magnetic susceptibility results as follows

$$\bar{\chi}_{aa} = \mu_0 \frac{M_a}{B_0}$$

The finite difference formula is applicable when the curvature of the energy levels is almost constant within the interval δ . This can be provided by reducing the value of δ with increasing reference field B_0 .

It will be demonstrated below that the finite difference formula is obtained from the above more general polynomial fit formula under special assumptions. Let us consider the working field matrix in the form of

$$\mathbf{B} = \begin{pmatrix} 1 & 1 & 1 \\ B_0 - \delta & B_0 & B_0 + \delta \\ (B_0 - \delta)^2 & (B_0)^2 & (B_0 + \delta)^2 \end{pmatrix}$$

Its inverse is

$$\mathbf{B}^{-1} = \frac{1}{2\delta^2} \begin{pmatrix} B_0(B_0 + \delta) & -2B_0 - \delta & 1 \\ -(B_0^2 - \delta^2) & 4B_0 & -2 \\ B_0(B_0 - \delta) & -2B_0 + \delta & 1 \end{pmatrix}$$

This immediately yields the first-order expansion coefficient as

$$c_i^{(1)} = \sum_{k=1}^3 \varepsilon_k (B^{-1})_{k,2} = \frac{1}{2\delta^2} \{ [\varepsilon_1(B_0 - \delta)] \cdot (-2B_0 - \delta) \\ + [\varepsilon_2(B_0)] \cdot (4B_0) + [\varepsilon_3(B_0 + \delta)] \cdot (-2B_0 + \delta) \}$$

This can be written as consisting of two terms

$$c_i^{(1)} = \frac{1}{2\delta^2} \{ [\varepsilon_1(B_0 - \delta)] \cdot (-\delta) + [\varepsilon_3(B_0 + \delta)] \cdot (+\delta) \} \\ + \frac{1}{2\delta^2} \{ [\varepsilon_1(B_0 - \delta)] \cdot (-2B_0) + [\varepsilon_2(B_0)] \cdot (4B_0) \\ + [\varepsilon_3(B_0 + \delta)] \cdot (-2B_0) \}$$

or

$$c_i^{(1)} = -\frac{1}{2\delta} \{ [\varepsilon_1(B_0 - \delta)] - [\varepsilon_3(B_0 + \delta)] \} + O(B_0/\delta^2)$$

Omitting the remainder $O(B_0/\delta^2)$, being a correction for the non-constant curvature of the energy level, we get the result

$$\mu_i = -c_i^{(1)} = \frac{1}{2\delta} \{[\varepsilon_1(B_0 - \delta)] - [\varepsilon_3(B_0 + \delta)]\}$$

which is identical with the postulate of König and Kremer [6].

6.1.8 Polynomial magnetisation formula

The polynomial fit formula can be applied to a more exact evaluation of the magnetisation

$$M_a(B_m) = N_A \frac{\sum_i \mu_{ai}(B_m) \exp[-\varepsilon_{ai}(B_m)/kT]}{\sum_i \exp[-\varepsilon_{ai}(B_m)/kT]}$$

Since the expansion coefficients appearing in each energy level are accessible

$$\varepsilon_{ai,m} = c_{ai}^{(0)} + c_{ai}^{(1)}(\Delta B_m) + \dots + c_{ai}^{(n)}(\Delta B_m)^n$$

then the microscopic magnetic moments become expressed as follows

$$\mu_{ai}(B_m) = -\frac{\partial \varepsilon_{ai,m}}{\partial B_m} = -\left[c_{ai}^{(1)}(\Delta B_m) + 2c_{ai}^{(2)}(\Delta B_m) \dots + nc_{ai}^{(n)}(\Delta B_m)^{n-1} \right]$$

This is how the limitations of the van Vleck formula can be overcome. The evaluation of the mean magnetic susceptibility is, as above,

$$\bar{\chi}_{aa} = \mu_0 \frac{M_a}{B_m}$$

The evaluation of the differential susceptibility requires a mapping of the field dependence of the magnetisation; hence

$$\chi_{aa} = \mu_0 \frac{\partial M_a(B)}{\partial B}$$

This no longer represents any conceptual problem: from the field dependence of the microscopic magnetic moments

$$\mu_{ai}(B_m) = -\frac{\partial \varepsilon_{ai,m}}{\partial B_m} = -\left[c_{ai}^{(1)}(\Delta B_m) + 2c_{ai}^{(2)}(\Delta B_m) \dots + nc_{ai}^{(n)}(\Delta B_m)^{n-1} \right]$$

the field dependent magnetisation results

$$M_a(B_m) = N_A \frac{\sum_i \mu_{ai}(B_m) \exp[-\varepsilon_{ai}(B_m)/kT]}{\sum_i \exp[-\varepsilon_{ai}(B_m)/kT]}$$

This can be a subject of the polynomial fit [5]

$$M_a(B_m) = d_a^{(0)} + d_a^{(1)}(\Delta B_m) + d_a^{(2)}(\Delta B_m)^2 + \dots$$

where the expansion coefficients $d_a^{(m)}$ can be determined analogously as outlined above. Let us consider a transformation

$$\begin{pmatrix} M_{a,1} & M_{a,2} & \dots & M_{a,m} \end{pmatrix} = \begin{pmatrix} d_a^{(0)} & d_a^{(1)} & \dots & d_a^{(n)} \end{pmatrix} \begin{pmatrix} 1 & 1 & \dots & 1 \\ \Delta B_1 & \Delta B_2 & \dots & \Delta B_m \\ \dots & \dots & \dots & \dots \\ \Delta B_1^n & \Delta B_2^n & \dots & \Delta B_m^n \end{pmatrix}$$

or

$$\mathbf{M} = \mathbf{d}\mathbf{B}$$

Then the inverse transformation is

$$\mathbf{d} = \mathbf{M}\mathbf{B}^{-1}$$

and the differential magnetic susceptibility is simply given via the first-order expansion coefficient

$$\chi_{aa} = \mu_0 d_a^{(1)}$$

As an example, for the working field matrix

$$\mathbf{B} = \begin{pmatrix} 1 & 1 & 1 \\ B_0 - \delta & B_0 & B_0 + \delta \\ (B_0 - \delta)^2 & (B_0)^2 & (B_0 + \delta)^2 \end{pmatrix}$$

and its inverse

$$\mathbf{B}^{-1} = \frac{1}{2\delta^2} \begin{pmatrix} B_0(B_0 + \delta) & -2B_0 - \delta & 1 \\ -(B_0^2 - \delta^2) & 4B_0 & -2 \\ B_0(B_0 - \delta) & -2B_0 + \delta & 1 \end{pmatrix}$$

we obtain

$$d_a^{(1)} = \sum_{k=1}^3 M_{a,k}(B^{-1})_{k,2} = \frac{1}{2\delta^2} \{ [M_{a,1}(B_0 - \delta)] \cdot (-2B_0 - \delta) \\ + [M_{a,2}(B_0)] \cdot (4B_0) + [M_{a,3}(B_0 + \delta)] \cdot (-2B_0 + \delta) \}$$

and two terms of the differential magnetic susceptibility appear

$$\chi_{aa} = \mu_0 d_a^{(1)} = \mu_0 \frac{1}{2\delta} \{ -[M_{a,1}(B_0 - \delta)] + [M_{a,3}(B_0 + \delta)] \} \\ + \mu_0 \frac{B_0}{\delta^2} \{ -[M_{a,1}(B_0 - \delta)] + 2[M_{a,2}(B_0)] - [M_{a,3}(B_0 + \delta)] \}$$

In the case of linear magnetics there is

$$M_{a,1}(B_0 - \delta) = M_{a,2}(B_0) - \Delta M$$

$$M_{a,3}(B_0 + \delta) = M_{a,2}(B_0) + \Delta M$$

and the above formula correctly collapses to

$$\chi_{aa} = \mu_0 \frac{\Delta M}{\delta} = \bar{\chi}_{aa}$$

6.1.9 Brillouin function

The magnetic energy, expressed as

$$E = -\vec{M} \cdot \vec{B} = -\mu_0 \vec{M} \cdot \vec{H}$$

tends to align the magnetic moments parallel to the applied field. This is in competition with the thermal energy kT which favours the disorder of magnetic moments.

The projection of the magnetic moment along the quantum axis (z) can adopt only discrete values and the corresponding Zeeman Hamiltonian term is

$$\hat{H}^Z = -g_J \mu_B B_z \hat{J}_z [\hbar^{-1}]$$

The energy levels forming a $(2J + 1)$ multiplet are expressed as follows

$$\varepsilon(M_J) = -g_J \mu_B B_z \left\langle J, M_J \left| \hat{J}_z \right| J, M_J \right\rangle [\hbar^{-1}] = -g_J \mu_B B_z M_J$$

This allows one to define the partition function as a sum

$$Z = \sum_{M_J=-J}^{+J} \exp(g_J \mu_B B_z M_J / kT) = \sum_{m=-J}^{+J} \exp(-\eta m)$$

for the parameter

$$\eta = \frac{g_J \mu_B B_z}{kT}$$

This is a finite geometric series which can be summed exactly to yield

$$Z = \frac{\exp(-\eta J) - \exp[\eta(J+1)]}{1 - \exp(\eta)}$$

On multiplying the numerator and denominator by $\exp(-\eta/2)$ we get the expression

$$Z = \frac{\exp[-\eta(J+1)] - \exp[\eta(J+1)]}{\exp(-\eta/2) - \exp(\eta/2)} = \frac{\sinh[\eta(J+1/2)]}{\sinh(\eta/2)}$$

Notice some expressions for the hyperbolic functions

$$\sinh(x) = \frac{\exp(x) - \exp(-x)}{2}$$

$$\cosh(x) = \frac{\exp(x) + \exp(-x)}{2}$$

$$\coth(x) = \frac{\cosh(x)}{\sinh(x)} = \frac{\exp(x) + \exp(-x)}{\exp(x) - \exp(-x)}$$

The magnetisation obeys the relation of statistical thermodynamics according to which

$$\begin{aligned} M &= -\frac{\partial F}{\partial B} = N_A kT \frac{\partial \ln Z}{\partial B} = (N_A kT) \frac{\partial \ln Z(\eta)}{\partial \eta} \frac{\partial \eta}{\partial B} \\ &= (N_A kT) \left(\frac{g_J \mu_B}{kT} \right) \frac{\partial \ln Z(\eta)}{\partial \eta} \end{aligned}$$

The derivative is expressed as follows

$$\begin{aligned}\frac{\partial \ln Z(\eta)}{\partial \eta} &= \frac{\partial}{\partial \eta} \ln \left\{ \frac{\sinh[\eta(J + 1/2)]}{\sinh(\eta/2)} \right\} \\ &= \frac{\partial}{\partial \eta} \ln\{\sinh[\eta(J + 1/2)]\} - \frac{\partial}{\partial \eta} \ln\{\sinh(\eta/2)\} \\ &= \frac{\cosh[\eta(J + 1/2)]}{\sinh[\eta(J + 1/2)]} (J + 1/2) - \frac{\cosh(\eta/2)}{\sinh(\eta/2)} \frac{1}{2}\end{aligned}$$

Then the magnetisation becomes

$$M = (N_A g_J \mu_B J) \left\{ \frac{J + 1/2}{J} \coth[\eta(J + 1/2)] - \frac{1}{2J} \coth(\eta/2) \right\}$$

or

$$M = M_0 \mathcal{B}_J(\eta)$$

where

$$M_0 = N_A g_J \mu_B J$$

is the maximum available magnetisation (at zero temperature). Here the *Brillouin function* has been introduced as

$$\mathcal{B}_J(\eta) = \frac{J + 1/2}{J} \coth[\eta(J + 1/2)] - \frac{1}{2J} \coth(\eta/2)$$

This function is plotted in Fig. 6.1 for some representative values of spins.

The Brillouin function can be met in literature also in the form

$$\mathcal{B}'_J(x) = \mathcal{B}_J(x/J) = \frac{J + 1/2}{J} \coth\left(x \frac{J + 1/2}{J}\right) - \frac{1}{2J} \coth\left(x \frac{1}{2J}\right)$$

which differs from the previous presentation in that the argument is divided by J .

For a small argument (when the field B is small and T is high enough) the expansion can be used

$$\coth(x) \approx \frac{1}{x} + \frac{x}{3}$$

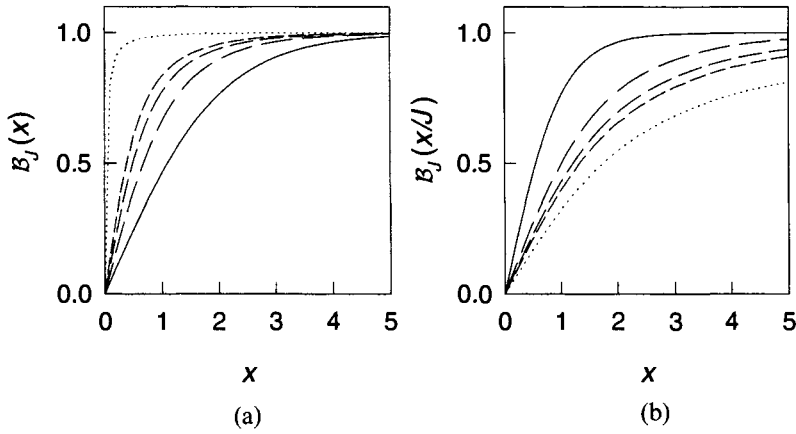


Fig. 6.1. Brillouin function for $J = 1/2$ (solid), $3/2$, $5/2$, $7/2$ and 50 (dotted): (a) for an argument x ; (b) for a reduced argument (x/J) .

which yields an approximate expression for the Brillouin function

$$B_J(\eta) \approx \eta \frac{J+1}{3}$$

Then the magnetisation becomes a linear function of the applied field, hence

$$M = M_0 B_J(\eta) = (N_A g_J \mu_B J) \left(\frac{g_J \mu_B \mu_0 H}{kT} \right) \frac{J+1}{3} = \frac{C}{T} H$$

where the Curie constant is introduced as

$$C = \frac{N_A \mu_0 \mu_B^2 g_J^2 J(J+1)}{3k}$$

This may be rewritten by introducing the *effective magnetic moment*

$$\mu_{\text{eff}} = \mu_B g_J \sqrt{J(J+1)}$$

as follows

$$C = \frac{N_A \mu_0}{3k} \mu_{\text{eff}}^2$$

6.1.10 Langevin function

In the classical model the magnetic entities carry a localised magnetic moment $\vec{m}_0$ having an arbitrary direction. The magnetic energy in an applied field is

$$E = -Bm_0 \cos \theta = -\mu_0 H m_0 \cos \theta$$

where θ is the angle between vectors $\vec{m}_0$ and $\vec{H}$. In the partition function the summation over a continuous change of $\cos \theta$ leads to the integral

$$Z = \int_{-1}^{+1} \exp(\mu_0 m_0 H \cos \theta / kT) d \cos \theta = \int_{-1}^{+1} \exp(xu) du = \frac{2 \sinh(x)}{x}$$

with the parameter

$$x = \frac{\mu_0 m_0 H}{kT}$$

The proportion of magnetic moments whose direction belongs to the solid angle

$$d\Omega = 2\pi \sin \theta d\theta$$

is given by Boltzmann statistics as

$$dN = \frac{\exp(xu) du}{Z}$$

The average value of the magnetic moment $\vec{m}$ along the field is

$$m = \langle m_0 \cos \theta \rangle = kT \frac{\partial \ln Z}{\partial B}$$

This yields the magnetisation expressed as

$$M = M_0 L(x)$$

where the *Langevin function* has been introduced

$$L(x) = \coth(x) - \frac{1}{x}$$

For small values of the argument the Langevin function can be expanded to yield

$$L(x) \approx \frac{x}{3}$$

In such a case the magnetisation varies linearly with the applied field

$$M = M_0 \frac{x}{3} = (N_A m_0) \left(\frac{\mu_0 m_0 H}{3kT} \right) = \frac{C_{cl}}{T} H$$

where the (classical) Curie constant is

$$C_{cl} = \frac{N_A \mu_0 m_0^2}{3k}$$

The Langevin function is obtained in the classical limit to the reduced Brillouin function as

$$L(x) = \lim_{J \rightarrow \infty} B'_J(x)$$

or simply by setting a large number for J in the Brillouin function. The behaviour of the Langevin function is simulated in Fig. 6.1 by setting $J = 50$.

6.2 NUMERICAL ASPECTS

6.2.1 Susceptibility functions

There are two principal situations concerning the temperature dependence of the magnetic susceptibility.

In the first case the molar magnetic susceptibility is an *analytic function* of magnetic parameters $(p_1, \dots, p_n)$, e.g. g, D, J , and the temperature T : $\chi_{mol}^t = f(T, p_1, \dots, p_n)$. This may arise from two sources: a hand solution of the eigenvalue problem when this is tractable; the eigenvalues as roots of the secular equation can be expanded into a Taylor series and then the van Vleck coefficients are identified (this is often met in the zero-field splitting problem). The second treatment utilises such a basis set transformation in which the magnetic Hamiltonian is diagonal (this is often met in isotropic exchange of several, two to four, centres).

In the second case the molar magnetic susceptibility is a non-analytic, *implicit function*, evaluated at the discrete temperature points T_i : $\chi_{mol,i}^t = f(T_i; p_1, \dots, p_n)$. This result follows from the numerical diagonalisa-

tion of the magnetic Hamiltonian in which a trial set of magnetic parameters ($p_1, \dots, p_n$) has been substituted.

As a result of the experiment, the discrete function χ_i^o versus T_i is obtained. The mass susceptibility or magnetisation is converted to the molar susceptibility and subjected to the corrections for the underlying diamagnetism and eventually for the temperature-independent paramagnetism, yielding $\chi_{\text{mol},i}^o = f(T_i)$.

The corrections mentioned, however, are rather approximate and thus one can enlarge the set of magnetic parameters for a temperature-independent term α_{mol} which compensates these uncertainties. Also, some cooperative ordering applicable at a low temperature can be included through the molecular field correction Z so that the theoretical function to be considered becomes

$$\chi_{\text{mol},i}^c = \frac{\chi_{\text{mol}}^t}{1 - Z\chi_{\text{mol}}^t} + \alpha_{\text{mol}}$$

6.2.2 Error functionals

A (non-linear) optimisation is carried out in order to get an optimum set of magnetic parameters which reproduces the magnetic susceptibility as much as possible. In a traditional treatment the error functional of the following form is considered

$$F_1 = \sum_i (\chi_{\text{mol},i}^o - \chi_{\text{mol},i}^c)^2 = \min$$

and subjected to minimisation. However, the susceptibility values can differ one from another by an order of magnitude and thus the minimisation of the above functional will evidently prefer the high-susceptibility data points whereas the low-susceptibility data points can be reproduced less satisfactorily.

Some other error functionals preferring another part of the data points can be postulated, say

$$F_2 = \sum_i (1/\chi_{\text{mol},i}^o - 1/\chi_{\text{mol},i}^c)^2 = \min$$

$$F_3 = \sum_i [(\chi_{\text{mol},i}^o - \chi_{\text{mol},i}^c)T_i]^2 = \min$$

$$F_4 = \frac{\sum_i^n |\chi_{\text{mol},i}^{\text{o}} - \chi_{\text{mol},i}^{\text{c}}|}{(1/n) \sum_i^n \chi_{\text{mol},i}^{\text{o}}} = \min$$

$$F_5 = \sum_i (\mu_i^{\text{o}} - \mu_i^{\text{c}})^2 = \min$$

$$F_6 = \frac{\sum_i^n |\chi_{\text{mol},i}^{\text{o}} - \chi_{\text{mol},i}^{\text{c}}| T_i}{(1/n) \sum_i^n (\chi_{\text{mol},i}^{\text{o}} T_i)} = \min$$

$$F_7 = \frac{\sum_i [(\mu_i^{\text{o}} - \mu_i^{\text{c}}) T_i]^2}{\sum_i [\mu_i^{\text{o}} T_i]^2} = \min$$

In the above expressions the effective magnetic moment is defined as

$$\mu_{\text{eff}}/\mu_{\text{B}} = \left(\frac{3k}{N_{\text{A}}\mu_0} \chi_{\text{av}} T \right)^{1/2}$$

It is difficult to predict which of the functionals is the best one and, in principle, one can deal with several functionals during the data analysis. One can generate one's own error functional with different weights of the data points. Moreover, some magnetic parameters are determined accurately at different temperature windows. For example, the determination of α_{mol} requires an accurate fit at high temperature. On the other hand, the determination of the zero-field splitting parameters (D , E) needs a good quality fit at a very low temperature.

The quality of the fit can be expressed through the residual value of the error functional F , or the conventional discrepancy factor $R(\chi^2)$ defined as

$$R(\chi^2) = \frac{\sum_i (\chi_{\text{mol},i}^{\text{o}} - \chi_{\text{mol},i}^{\text{c}})^2}{\sum_i (\chi_{\text{mol},i}^{\text{o}})^2}$$

6.3 OPTIMISATION ALGORITHMS

6.3.1 Optimisations in multidimension

Most optimisation algorithms are capable of finding a *local minimum* which lies downhill from the starting guess. However, we are interested in finding the *global minimum*, i.e. corresponding to the lowest value of our error functional. Such a process is far from being trivial.

There are two strategies for finding the global minimum of a functional:

- (a) using widely varying starting values of the independent variables, a series of local extremes is localised; the lowest extreme serves as the global minimum;
- (b) using a finite amplitude step away from the local minimum, a lower extreme can be reached.

The local optimisation methods in multidimensions can be classified as follows:

- 1. methods of function evaluation (no gradient information available) are
 - (a) simplex method (Nelder–Mead algorithm),
 - (b) direction set methods for which the Powell algorithm is a prototype;
- 2. gradient methods
 - (a) conjugate gradient methods given by
 - Fletcher–Reeves algorithm
 - Polak–Ribiere algorithm
 - (b) variable metric (quasi-Newton) methods in which the old points $\mathbf{P}^{(i)}$ are updated using the gradient vector $\mathbf{g}^{(i)}$, the metric matrix $\mathbf{A}^{(i)}$ and a scalar $\alpha^{(i)}$ representing a length of the step

$$\mathbf{P}^{(i+1)} = \mathbf{P}^{(i)} - \alpha^{(i)} \mathbf{A}^{(i)} \mathbf{g}^{(i)}$$

These are given by:

- steepest-descent algorithm
- Newton–Raphson algorithm
- Murtagh–Sargent algorithm
- Davidon–Fletcher–Powell algorithm
- Broyden–Fletcher–Goldfarb–Shanno algorithm.

In this section we shall focus on non-gradient methods only. The reader is recommended to consult specialised literature [7].

6.3.2 Simplex method

The simplex method belongs to a group of optimisation methods finding the minimum of a predefined multiparameter function (error functional). The downhill simplex method of Nelder and Mead [8] requires only function

evaluations, not derivatives. This is why it is so popular. The simplex method looks for a path which is capable of localising the (local) function minimum.

A simplex is a geometrical figure defined through a set of $(n + 1)$ vertices corresponding to the n variables. For example, two variables define a plane and the simplex represents a triangle in this plane: $S_i = (\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ with $\mathbf{x}_i = (p_{1i}, p_{2i})$.

The method is started by selecting an initial simplex. For instance, a trial set of parameters defines the first point $\mathbf{x}_1 = (p_1, \dots, p_n)$, the remaining vertices are defined by re-scaling each parameter by λ : $\mathbf{x}_{i+1} = (p_1, \dots, \lambda p_i, \dots, p_n)$; $\lambda = 1.1$ corresponds to an enlargement of each initial parameter by 10%. At each of the simplex vertices $\mathbf{x}_{n+1}$ the function values F_{n+1} are evaluated. The moving path is generated through the following principle. The point $\mathbf{x}_{\max}$ of the highest function value $F_{\max}$ is replaced by another one $\mathbf{x}^*$ which is situated at the opposite face of the surface defined by the remaining n points. This step is called reflection. The position of the new point $\mathbf{x}^*$ is determined from the equation (Fig. 6.2)

$$\mathbf{x}^* - \mathbf{x} = \mathbf{x} - \mathbf{x}_{\max}$$

where $\mathbf{x}$ represents the centre of mass of the remaining n points. At the new point $\mathbf{x}^*$ the function value is evaluated. If this is not the worst point, the procedure continues; instead, another point at the line $(\mathbf{x}_{\max} - \mathbf{x})$ is to be selected for the new search of $\mathbf{x}^*$.

The actual routine utilises a series of steps [7]:

- (a) a reflection away from the highest function value (to conserve the volume of the simplex);
- (b) a reflection and expansion away from the high point;
- (c) a contraction along one dimension from the high point;
- (d) a contraction along all dimensions towards the low point.

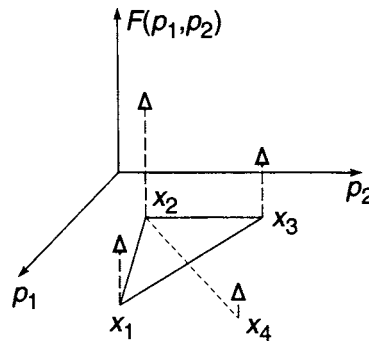


Fig. 6.2. Reflection of the simplex: $S_i = (\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ yields $\mathbf{x}_{\max} = \mathbf{x}_2$; then the reflection implies that $S_{i+1} = (\mathbf{x}_1, \mathbf{x}_4, \mathbf{x}_3)$.

An appropriate sequence of such steps will always converge to a minimum of the function. The whole process is terminated when some convergence criteria are fulfilled (which is rather risky in the multidimensional optimisation). Thus it is recommended to restart the procedure with reinitialisation of the vertices of the claimed minimum.

6.3.3 Simulated annealing method

The essence of “simulated annealing” is the slow cooling of a liquid, allowing ample time for reconfiguration of the entities and anneal: to adopt a configuration of the lowest energy. An analogy to such a process is utilised in global optimisation methods.

A thermodynamic system in thermal equilibrium at a temperature T has its energy probabilistically distributed among all the different energy states E . At any temperature (thermal energy kT) there is a finite probability $P(E)$ of the system being in a high energy state

$$P(E) \approx \exp(-E/kT)$$

Thus there is a chance for the system to get out of a local energy minimum in favour of finding the lower (global) energy minimum.

These ideas were utilised in the Metropolis algorithm [9]: a thermodynamic system was assumed to change its configuration from energy E_1 to energy E_2 with the probability

$$(a) P = \exp[-(E_2 - E_1)/kT] \text{ for } E_2 > E_1$$

$$(b) P = 1 \text{ for } E_2 < E_1$$

This means that the system is taking a downhill step; sometimes, however, an uphill step.

For a global optimisation problem the simulated annealing method is applicable with the following specifications [10, 11]:

1. *Configuration*. The set of independent variables defines a point $\mathbf{x}_i(p_1, \dots, p_n)$ called the configuration. When the downhill simplex method is used, the configuration is replaced by a simplex $S_i = (\mathbf{x}_1, \dots, \mathbf{x}_{n+1})$ of $(n + 1)$ points.
2. *Objective function*. The objective function subjected to minimisation is represented by our choice of the error functional.
3. *Rearrangements*. In addition to the internal movements of the simplex method (reflections, expansions, contractions)

- (a) a positive variable δ is added to a stored function value associated with every vertex of the simplex;
- (b) a similar variable is subtracted from the function value of every new point that is tried as a replacement point.

The above-mentioned δ is a logarithmically distributed random variable proportional to the “temperature” parameter T . Thus for vanishing T the parameter d escapes and the algorithm reduces exactly to the simple simplex method, converging to a local minimum. For $T > 0$ the method accepts a true downhill step, but sometimes accepts an uphill one: the simplex expands to a scale proportional to the temperature and then executes a set of random reconfigurations (Fig. 6.3).

4. *Annealing schedule.* For a constant T the number of reconfigurations is, say, $100N$ random reconfigurations, or $10N$ successful reconfigurations. Then the temperature parameter is reduced slowly, say by 10 or 20%. There is no universal recipe for the annealing schedule; it requires experimentation.

6.3.4 Powell method

Direction set (Powell’s) methods belong to a class of local optimisation methods in multidimensions. The starting point $\mathbf{x}(p_1, \dots, p_n)$ in n -dimensional space is evolved in some vector direction $\mathbf{v}$ so that the function $F(\mathbf{x})$ is minimised along the line $\mathbf{v}$. The method proceeds as follows:

- (a) give the vectors $\mathbf{x}$ and $\mathbf{v}$ on input;
- (b) find the scalar λ that minimises $F(\mathbf{x} + \lambda\mathbf{v})$;
- (c) replace the old point by the next one $\mathbf{x}^{(i+1)} = \mathbf{x}^{(i)} + \lambda\mathbf{v}$;

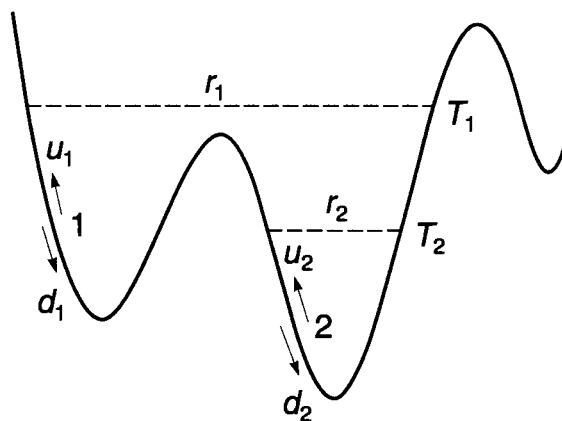


Fig. 6.3. Moves in the simulated annealing method: 1—old configuration; d—downhill step; u—uphill step; r—random reconfigurations; 2—new configuration.

(d) replace the direction by λv .

The method utilises a subroutine for the minimisation of a function of one variable. This can be done either without or with the calculation of the gradient. For one-dimensional minimisation without evaluating a derivative:

(a) bracket the minimum, i.e. find a triplet of points $a < b < c$ so that

$$F(a) > F(b) < F(c);$$

(b) apply a parabolic interpolation (Brent's method [12]).

In the simplest version, the Powell method utilises the unit vectors as a set of directions. Using one-dimensional minimisation, the algorithm moves along the first direction to its minimum, then from there along the second direction to its minimum, etc. The whole process is repeated as many times as necessary until the function stops decreasing. All the direction set methods consist of prescriptions for updating the set of directions as the method proceeds.

Alternative optimisation algorithms are accessible. Among them the MINUIT system of the CERN centre is often utilised [13]. A rather new approach is based on genetic algorithms [14–16].

6.4 FITTING THE MAGNETIC SUSCEPTIBILITY

A reduced FORTRAN code to fit the magnetic susceptibility is available on request from the author [17]. The optimisation algorithms selected there cover the simulated annealing method combined with the simplex method.

SUMMARY

1. The magnetisation and consequently the magnetic susceptibility can be generated by several methods. Among them the van Vleck formula belongs to the most popular treatment. However, it can be violated at a low temperature and at a high magnetic field. It can then be substituted by more complex numerical treatments.
2. For Curie paramagnets analytic functions were derived: the Brillouin function and its classical analogue, the Langevin function.
3. Fitting the magnetic susceptibility to experimental data needs a proper definition of the error functional which is being minimised. There are several optimisation algorithms based either on the gradient or on non-gradient philosophy. Some of them, like the simulated annealing method, are capable of identifying the global minimum of the error functional.

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Types of Magnetic Materials

7.1 DIAMAGNETISM

Diamagnetic materials are often defined as substances which are lifted out of the magnetic field region. More precisely, the diamagnetic materials possess a negative value of magnetic susceptibility. Diamagnetic substances have no uncompensated spin or angular momenta so that their ground state is ^1A (or ^1B). In other words, all the electrons are paired. The observed diamagnetism reflects the fact that the ground state is a singlet and there are no thermally populated states of higher spin multiplicity.

7.1.1 Normal diamagnets

Weak diamagnetic materials have magnetic susceptibility values close to zero; their molar magnetic susceptibility is of the order of $\chi_{\text{mol}} = -10 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$. Diamagnetic susceptibility is a temperature independent quantity (Fig. 7.1). Some diamagnetic materials (water, benzene) are used to calibrate (check) the experimental equipment.

The measurement of diamagnetic susceptibilities for some components (building units, ligands) of more complex substances serves as a better estimate of the underlying diamagnetism than any empirical additive scheme (e.g. the method of Pascal constants). In order to establish the underlying diamagnetism in paramagnetic metal complexes (manganese(II), copper(II)), their diamagnetic analogues (magnesium(II), zinc(II)) can be prepared and measured.

Some substances exhibiting diamagnetic behaviour can switch to the paramagnetic state when the temperature is increased. These spin-crossover (mostly Fe(II)) systems will be discussed in more detail later.

Some oligonuclear systems may show a diamagnetic ground state and thus they behave as diamagnetic materials at a low temperature. With increasing temperature, however, paramagnetic excited states are populated and the substance shows an increased positive magnetic susceptibility. When the excited paramagnetic states lie rather far from the ground singlet, the onset temperature when the admixed paramagnetism is observable can be relatively

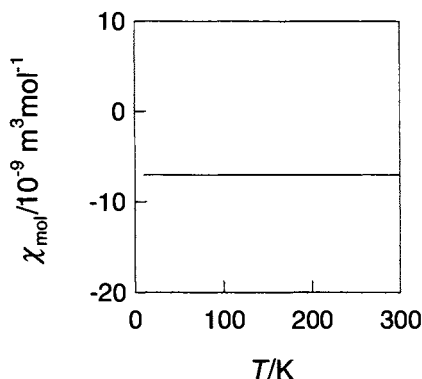


Fig. 7.1. Temperature behaviour of magnetic susceptibility for normal diamagnetics.

high. This is the case with copper acetate $[\text{Cu}_2(\text{ac})_4(\text{H}_2\text{O})_2]$ which apparently shows a near-zero susceptibility until 50 K.

7.1.2 Diamagnetic anisotropy

Since the magnetic susceptibility is a second-rank tensor, its principal components may differ from each other. For example, in the benzene molecule the anisotropy parameter

$$\Delta = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy})$$

is as high as $\Delta = -0.75 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$.

Diamagnetic anisotropy in single crystals may even be enhanced. For example, the diamagnetic mass susceptibility of graphite, with fields either parallel or perpendicular to the hexagonal c axis, is $\chi_{\parallel} = -264$ and $\chi_{\perp} = -3.8$ (in units of $10^{-9} \text{ m}^3 \text{ kg}^{-1}$).

7.1.3 Superconductors

Strong diamagnetic materials exhibit a volume susceptibility close to the limit of $\chi = -1$ (dimensionless). These obey perfect diamagnetic screening due to a superconducting current and in fact they are superconductors. Thus the measurement of magnetic susceptibility serves as a convenient and fast identification of superconductivity, even for powder materials (the Meissner effect). However, due to the considerable susceptibility value, the demagnetisation effect becomes substantial and thus a correct determination of

volume susceptibility needs to account for demagnetisation. This is even more critical when thin films are concerned (see Chapter 2).

The transition from the normal diamagnetic state to superconductive diamagnetism is characterised by one or more transition temperatures T_c identified by the inflection points on the χ versus T curve. A very good identification of the transition temperature is provided by the maximum of the imaginary (out of phase) susceptibility χ'' measured in an alternating magnetic field (Fig. 7.2).

7.2 PARAMAGNETISM

As opposed to diamagnetic substances, paramagnetic ones are those which are attracted into a magnetic field. Their magnetic susceptibility is positive and temperature dependent. Paramagnetism reflects the presence of uncompensated spins or angular momenta. In other words, some electrons remain unpaired. The tendency for angular momenta to be aligned parallel with the field direction is in competition with the thermal disorder. Therefore, the greater the temperature (the greater the thermal disorder), the lower the degree of alignment and the susceptibility drops inversely with temperature (Curie law).

7.2.1 Normal paramagnets

For normal paramagnets organic radicals, transition metal complexes and lanthanide compounds serve as examples. As the p -block elements may have a maximum of 3 unpaired electrons, d -block 5, and f -block 7, these numbers

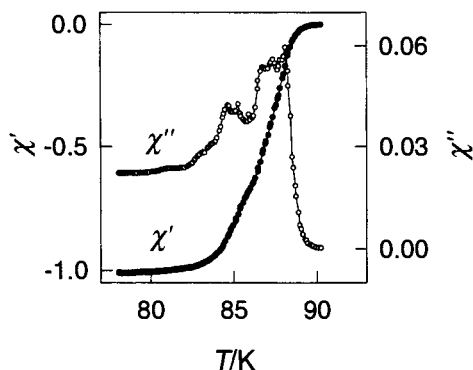


Fig. 7.2. Temperature behaviour of the volume AC susceptibility components for a superconductor (single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_7$).

determine the normally attainable spins. The clear condition for the high spin state is that the unpaired electrons occupy orthogonal orbitals; in the opposite case the pairing applies. For example, in the paramagnetic O_2 molecule both electrons are situated in different π^* orbitals. In a high-spin $Mn(II)$ complex all five d -orbitals (which are orthogonal) are singly occupied.

Some organic radicals can survive their spin even after combination with metal centres. An example is the nitronyl-nitroxide radical. Under certain circumstances the spin state of the central atom, say $Cu(II)$, can be increased by ligand radicals.

The molar magnetic susceptibility of a normal paramagnet (a free radical with spin $s = 1/2$) is of the order of $\chi_{mol} = 16 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ at 293 K. It would be $\chi_{mol} = 61 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ at 77 K and $\chi_{mol} = 1122 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ at 4.2 K.

Ideal paramagnets obey the empirical *Curie law*

$$\chi = \frac{C}{T}$$

where C is the Curie constant (this law will be theoretically derived later with the result $C = N_A \mu_0 \mu_B^2 g^2 S(S+1)/3k$). The Curie law implies that the function $1/\chi = f(T)$ is a straight line intercepting zero; alternatively the function $(\chi \cdot T) = f(T)$ is simply a Curie constant (Fig. 7.3). Several inorganic salts and complexes serve as examples of Curie law paramagnets, as exemplified by Table 7.1.

In fact, deviations from the Curie law are positive (ferromagnetic) or negative (antiferromagnetic), as is seen from Fig. 7.3. These can be phenomenologically ascribed through the empirical *Curie-Weiss law*

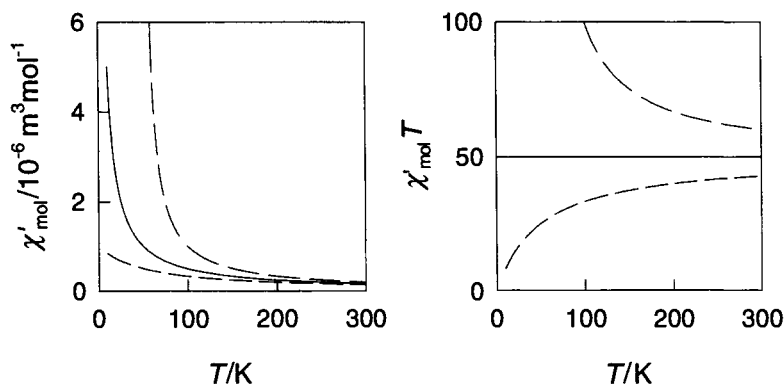


Fig. 7.3. Temperature behaviour of a paramagnet: solid—the perfect Curie law; long dashed—a ferromagnetic interaction ($\theta > 0$); short dashed—an antiferromagnetic interaction ($\theta < 0$).

TABLE 7.1
Some Curie law paramagnets

<i>S</i>	Example	Curie constant, <i>C</i> (10 ⁻⁶ K m ³ mol ⁻¹)	Effective magnetic moment, $\mu_{\text{eff}}/\mu_{\text{B}}$
1/2	CuSO ₄ ·5H ₂ O	4.71	1.73
1	[Ni(en) ₃]SO ₄	12.6	2.83
3/2	HgCo(NCS) ₄	23.6	3.87
2		37.7	4.90
5/2	NH ₄ Fe(SO ₄) ₂ ·12H ₂ O	55.0	5.91
3		75.4	6.93
7/2	Gd ₂ (SO ₄) ₃ ·8H ₂ O	99.0	7.94

$$\chi = \frac{C}{T - \Theta}$$

where the Weiss constant Θ (positive or negative) is introduced. The deviations from the Curie law may originate in: (a) zero-field splitting, (b) the orbital contribution to the total angular momentum, (c) the presence of exchange interactions, (d) the presence of an effective molecular field, and/or (e) long-range ordering. The Curie–Weiss law can be transcribed to an equivalent form

$$\chi = \frac{\chi^*}{1 - Z \cdot \chi^*} = \frac{C}{T - Z \cdot C}$$

where $\chi^* = C/T$ is a perfect Curie function; this form, however, brings indication of the presence of an effective (correcting) field which either increases (when Z or Θ is positive) or decreases (when these are negative) with the applied magnetic field.

The terms ferromagnetic and/or antiferromagnetic interactions reflect a continuous tendency for positive or negative deviations from the Curie law. They should not be confused with ferromagnetic (antiferromagnetic) states or transitions which are long-range phenomena and characterised by discontinuous changes of the magnetic susceptibility at the transition temperature T_c and T_N , respectively.

7.2.2 Temperature-independent paramagnetism

In addition to the temperature-independent diamagnetism, any substance possesses a temperature-independent paramagnetism. Both these components form the magnetic susceptibility tensor and their partitioning, like $\chi = \chi_{\text{dia}} + \chi_{\text{TIP}}$, is somehow artificial; better to speak about the underlying

temperature-independent magnetism. Experimentally, TIP is attainable in the high temperature limit

$$\chi_{\text{TIP}} = \lim_{T \rightarrow \infty} (\chi - \chi_{\text{dia}})$$

when the Curie part of the susceptibility vanishes (Fig. 7.4). However, the data scattering at high temperature is enhanced and, moreover, the sample itself can decompose.

TIP is usually estimated only for some typical cases. For example, it is generally accepted that each Cu(II) centre in a complex (cluster) brings the value of $\chi_{\text{TIP}} = 0.75 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$. Some other estimates are listed in Table 5.8. TIP becomes substantial when the system has close lying excited states, which is a frequent situation in metal complexes. For example, several planar Ni(II) complexes show a slight, temperature-independent paramagnetism. For organic substances the TIP values are ignored.

It is normally assumed that the magnetic susceptibility subjected to analysis (fitting procedure) has already been corrected for the underlying diamagnetism and eventually for the temperature-independent paramagnetism, so that that quantity is the net temperature-dependent paramagnetic susceptibility.

7.2.3 Paramagnetic anisotropy

In crystalline solids the magnetic susceptibility forms a tensor which is not necessarily symmetric. In the presence of axial symmetry two different susceptibility components are experimentally distinguishable: $\chi_{\parallel}$ parallel, and $\chi_{\perp}$ perpendicular to the field direction. If the symmetry is even lower, three components of the susceptibility tensor should be considered.

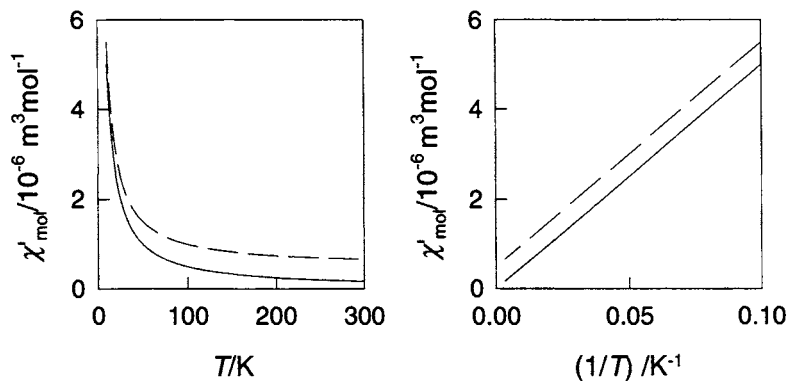


Fig. 7.4. Determination of TIP: solid—no TIP; dashed—a paramagnet with TIP.

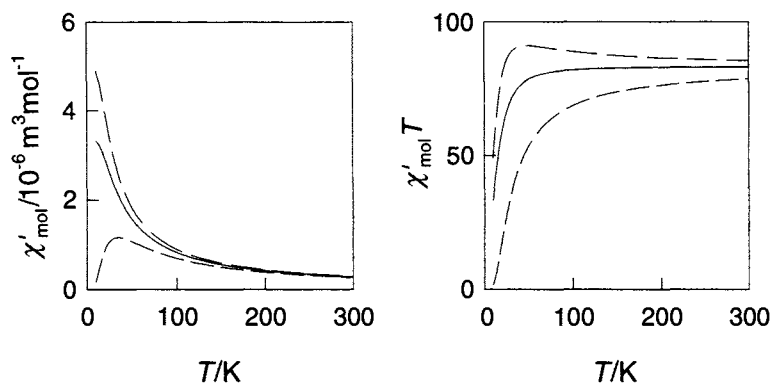


Fig. 7.5. Components of paramagnetic susceptibility: long dashed—perpendicular; short dashed—parallel; solid—average.

Each susceptibility component has its own characteristic temperature dependence and, usually at low temperature, their evolution may be completely different (Fig. 7.5).

For powder materials the microcrystals are oriented randomly and the measured susceptibility refers to the average

$$\chi_{\text{av}} = \frac{1}{3}(\chi_x + \chi_y + \chi_z)$$

However, when the measurements are done at higher fields (e.g. using a Faraday balance with the typical value of $B = 1.5$ T) the microcrystals may tend to orient themselves and the measured susceptibility is no longer a correct average. It is apparently higher than χ_{av} .

7.2.4 Spin crossover systems

As already mentioned, some substances having a high-spin (or intermediate-spin) state close to the ground low-spin state can show a spin transition, often termed the spin crossover. The *cis*-[Fe(phen)₂(NCS)₂] complex, which switches from the diamagnetic $S = 0$ ground state to the paramagnetic $S = 2$ state at temperature $T_c = 176$ K, serves as a prototype of such transitions. The magnetic susceptibility below the transition temperature is close to zero, it increases abruptly within a few K, and then it escapes according to the Curie law for the high-spin paramagnet (Fig. 7.6).

The driving force for the spin crossover is the change in the Gibbs energy: the enthalpy-unfavourable high-spin state becomes entropy-favoured above T_c . An opposite transition from the high-spin to a low-spin state with rising temperature has not been reported so far.

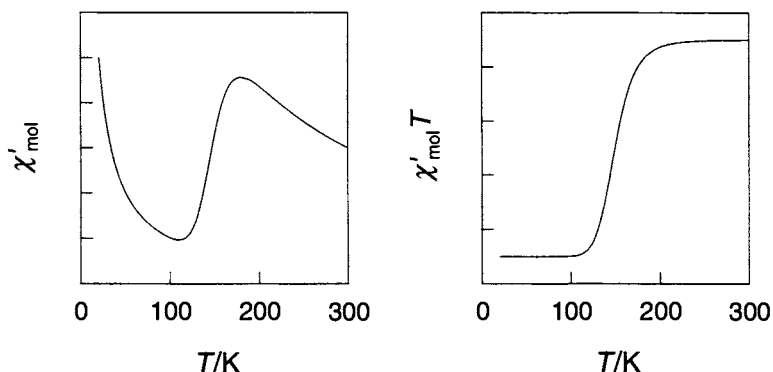


Fig. 7.6. Temperature behaviour of a spin crossover system.

7.2.5 High spin molecules

In polynuclear complexes and clusters the spin angular momenta of individual centres are interacting; their addition results in the energy spectrum covering several states of different multiplicities. For example, four Cu(II) centres, each possessing the spin $s = 1/2$, produce 16 energy levels of which two are singlets, three triplets, and one the quintet state. If the ground state is the quintet, $S = 2$, well separated from other states, then the magnetic susceptibility follows the Curie law for four completely aligned spins; the Curie constant is $C_{\text{mol}} = N_A \mu_0 \mu_B^2 g^2 S(S+1)/3k = 37.7 \times 10^{-6} \text{ m}^3 \text{ K mol}^{-1}$. If the spins do not interact (when the Cu . . . Cu separation is long enough) then each $s = 1/2$ centre follows the Curie law independently and we arrive at $C_{\text{mol}} = 4C_{s=1/2} = 4 \times 4.71 \times 10^{-6} \text{ m}^3 \text{ K mol}^{-1} = 18.8 \times 10^{-6} \text{ m}^3 \text{ K mol}^{-1}$, which is only half of the above value for a complete alignment of four spins. Now it becomes evident that a clear way to enhance paramagnetism is to building high spin molecules.

An assembly of several spin-carrying centres, however, does not guarantee that the ground state is the state of the maximum spin multiplicity. This is only the case when the overall exchange interaction is of a ferromagnetic nature (positive coupling constants J). If the exchange interaction in the above $\{\text{Cu}_4\}$ example were antiferromagnetic (negative coupling constants), the ground state would be the singlet with the zero susceptibility value at low temperature. However, as the rest of the states are thermally accessible, they become populated with increasing temperature and thus the susceptibility rises from zero, passes through a maximum and then escapes according to a Curie-like law (Fig. 7.7).

A more pronounced enhancement of the paramagnetism is obtained when several Fe(III) or Mn(II) centres, each bringing $s = 5/2$, are assembled in a

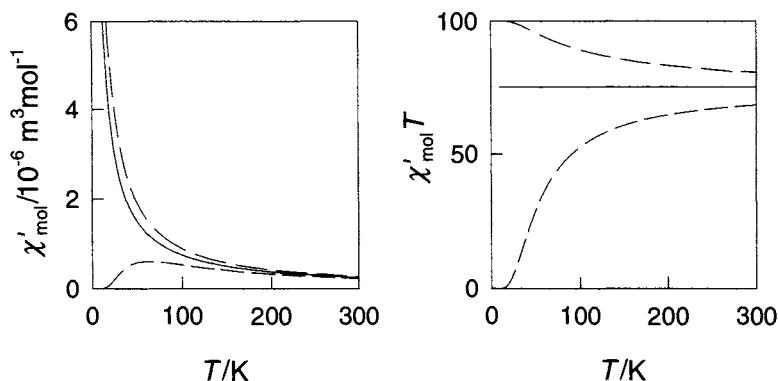


Fig. 7.7. Temperature behaviour of a dimeric spin system: long dashed—ferromagnetic coupling ($J > 0$); short dashed—antiferromagnetic coupling ($J < 0$); solid—no coupling ($J = 0$).

complex. For example, the complex $[\text{Mn}(\text{hfac})_2(\text{NITPh})]_6$ has a ground state as high as $S = 12$.

7.2.6 Pauli paramagnetism

Some metals (like Cu, Ag, Zn, Au, Hg) show diamagnetism; some others, on the contrary a weak paramagnetism (Table 7.2). This kind of temperature-independent (slightly dependent) paramagnetism is termed *Pauli paramagnetism*. It originates in the re-occupancy of energy levels in an applied magnetic field. In the zero field both spin-up (α) and spin-down (β) electrons occupy the same energy levels within a dense conduction band. When the field is on, the energies are shifted slightly by

$$\varepsilon_i \rightarrow \varepsilon_i \pm \mu_B B$$

Such a shift in metals is large enough for the re-occupancy of energy levels (Fig. 7.8). The difference in populations ($n_\beta - n_\alpha$) generates the magnetisation

TABLE 7.2
Magnetic susceptibility of some metals

Paramagnetics	$\chi_{\text{mol}} (10^{-6} \text{ m}^3 \text{ mol}^{-1})$	Diamagnetics	$\chi_{\text{mol}} (10^{-6} \text{ m}^3 \text{ mol}^{-1})$
Li	+46	Cu	-1.08
Na	+8.5	Zn	-2.20
K	+6.7	Ag	-2.39
Mg	+3.1	Cd	-2.14
Ca	+13.8	Hg	-2.14
Al	+7.7	Pb	-1.38

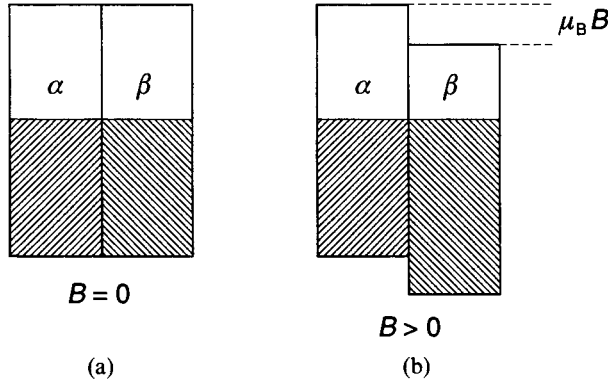


Fig. 7.8. The origin of Pauli paramagnetism: (a) equal occupancy $n_\alpha = n_\beta$ at $B = 0$; (b) re-occupancy $n_\alpha < n_\beta$ at $B > 0$.

$$M = (n_\beta - n_\alpha)\mu_B = \mu_B^2 B D(\varepsilon_F)$$

and consequently the paramagnetic susceptibility

$$\chi = \mu_0 \frac{\partial M}{\partial B} = \mu_0 \mu_B^2 D(\varepsilon_F)$$

where $D(\varepsilon_F)$ stands for the density of states at the Fermi level.

7.3 COOPERATIVE ORDERING

The spin angular momenta on a given lattice tend to be aligned spontaneously. Thus for a low enough temperature a kind of perfect ordering exists and no external field is required to support this. The spin material has a certain, well defined, long-range persistent, periodic structure (Fig. 7.9). The spontaneous ordering of spins results from long-range and short-range interactions and is a cooperative effect of the solid state. The spontaneous ordering of spins persists below the *critical temperature* T_c . Above T_c the thermal energy overcomes the ordering energy: the solid material obeys a magnetic phase transition (similar to the melting of a solid) and normal paramagnetic behaviour appears [1–4].

7.3.1 Ferromagnetics

If the spins on a given lattice are all aligned spontaneously in the same direction, then the ordered phase refers to the ferromagnetic phase. The transition occurs at the *Curie temperature* T_c which is a characteristic of any material. Above the Curie temperature the magnetic susceptibility (refer-

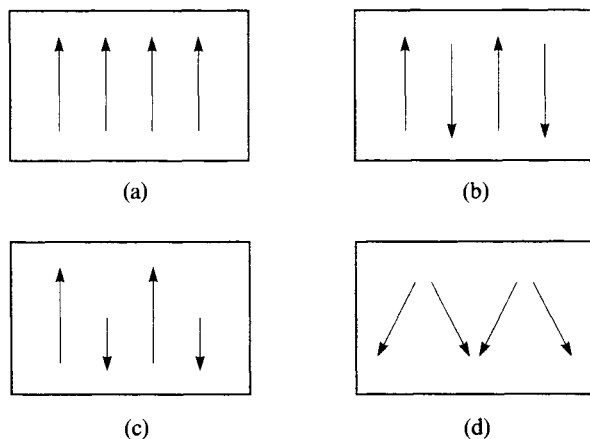


Fig. 7.9. Schematic representation of the orientation of magnetic moments in ordered materials: (a) ferromagnetics; (b) antiferromagnetics; (c) ferrimagnetics; (d) canted spin materials.

ring to the zero field, χ_0) behaves like a paramagnet. The existence of exchange interactions implies that a Curie-like law is obeyed; the Curie constant, however, differs from the spin-only formula. The ordering can be phenomenologically described by the *molecular field* theory.

At the microscopic level the interaction between the pairs of magnetic moments is given by the Hamiltonian term

$$\hat{H}_{ij} = -\mu_0 n_{ij} \vec{\mu}_i \cdot \vec{\mu}_j$$

where n_{ij} stands for an interaction parameter (a local molecular field coefficient, in units of m^{-3}). By introducing a local magnetic field—the molecular field

$$\vec{H}_i = \sum_{j \neq i} n_{ij} \vec{\mu}_j$$

the overall Hamiltonian becomes expressed as

$$\hat{H} = -\frac{1}{2} \mu_0 \sum_i \sum_{j \neq i} n_{ij} \vec{\mu}_i \cdot \vec{\mu}_j = -\frac{1}{2} \mu_0 \sum_i \vec{\mu}_i \cdot \vec{H}_i$$

In fact the molecular field fluctuates in time and depends on the instantaneous magnetic moments $\vec{\mu}_j$. A mean field model abstracts from this fluctuating character and assumes a thermal average in the form

$$\vec{H}_{\text{int}} = \langle \vec{H}_i \rangle_T = \sum_{j \neq i} n_{ij} \langle \vec{\mu}_j \rangle_T$$

so that the interaction energy is

$$E = \langle \hat{H} \rangle_T = -\frac{1}{2} \mu_0 \sum_i \langle \vec{\mu}_i \rangle_T \cdot \vec{H}_{\text{int}}$$

If all the neighbouring magnetic moments are identical

$$\langle \vec{\mu}_j \rangle_T = \langle \vec{\mu} \rangle_T$$

then the internal magnetic field is proportional to the magnetisation

$$\vec{H}_{\text{int}} = \left(\frac{\sum_{j \neq i} n_{ij}}{N/V} \right) \left(\frac{N}{V} \langle \vec{\mu} \rangle_T \right) = W \vec{M}$$

Here

$$\vec{M} = \frac{N}{V} \langle \vec{\mu} \rangle_T$$

is the magnetisation per volume unit which contains N entities and

$$W = \frac{\sum_{j \neq i} n_{ij}}{(N/V)}$$

is the proportionality coefficient (dimensionless in SI units).

The magnetisation is expected to follow the expression

$$M = M_0 \mathcal{B}_J \left(\frac{\mu_0 g_J \mu_B H}{kT} \right)$$

where

$$M_0 = N_A g_J \mu_B J$$

is the magnetisation at zero temperature. For a temperature above T_c (provided the temperature is large and the magnetic field small enough) the Brillouin function can be expanded as follows

$$\mathcal{B}_J(x) \approx \frac{J+1}{3}x$$

and the magnetisation in the paramagnetic state becomes simplified to

$$M_p \approx (N_A g_J \mu_B J) \left(\frac{J+1}{3} \right) \left(\frac{\mu_0 g_J \mu_B H}{kT} \right) = \frac{C}{T} H$$

with the Curie constant

$$C = \frac{N_A \mu_0 \mu_B^2 g_J^2 J(J+1)}{3k} = C_0 \frac{g_J^2 J(J+1)}{3}$$

and

$$C_0 = \frac{N_A \mu_0 \mu_B^2}{k}$$

Let us introduce the Weiss (long-range) field constant $W_f > 0$ which generates an internal field $\vec{H}_{\text{int}}$ proportional to the magnetisation

$$\vec{H} = \vec{H}_{\text{ext}} + \vec{H}_{\text{int}} = \vec{H}_{\text{ext}} + W_f \vec{M}$$

Within the mean field approach the magnetisation in the paramagnetic state is

$$\vec{M}_p = \chi_{\text{int}} \vec{H} = \frac{C}{T} (\vec{H}_{\text{ext}} + W_f \vec{M}_p)$$

with internal susceptibility

$$\chi_{\text{int}} = \frac{\vec{M}_p}{\vec{H}} = \frac{\vec{M}_p}{\vec{H}_{\text{ext}} + W_f \vec{M}_p} = \frac{C}{T}$$

Then the measured external magnetic susceptibility becomes

$$\chi_{\text{ext}} = \frac{\vec{M}_p}{\vec{H}_{\text{ext}}} = \frac{C}{T - W_f C}, \quad [T > T_c]$$

which is the form of the *Curie–Weiss law* (Fig. 7.10). In zero applied field the magnetisation does not vanish at T_c , because of the internal field $\vec{H}_{\text{int}}$. Then the condition

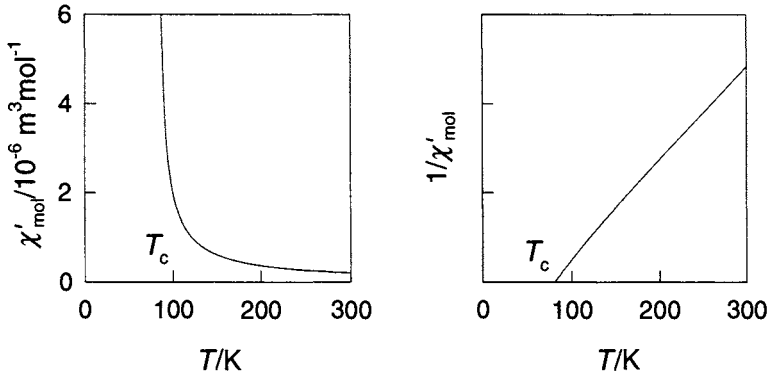


Fig. 7.10. Temperature behaviour of a ferromagnet.

$$\chi_{\text{int}} = \frac{\vec{M}_p}{W_f \vec{M}_p} = \frac{C}{T_c}$$

implies a simple relationship (valid within the approximations used)

$$T_c = W_f C = \Theta_p$$

The magnetisation below the critical temperature T_c is given through the Brillouin function as

$$\frac{M}{M_0} = \mathcal{B}_J\left(\frac{\mu_0 g_J \mu_B H}{kT}\right) = \mathcal{B}_J(\eta)$$

with

$$H = H_{\text{ext}} + W_f M$$

The spontaneous magnetisation, when $\vec{H}_{\text{ext}} = 0$, is

$$H = W_f M_s$$

and since the spontaneous magnetisation at $T = 0$ is

$$M_{s,0} = N_A g_J \mu_B J$$

one can write

$$\frac{M_s}{M_{s,0}} = \frac{H}{N_A g_J \mu_B J W_f} = \frac{\eta k T}{N_A \mu_0 \mu_B^2 g_J^2 J W_f} = \frac{\eta T}{C_0 g_J^2 J W_f}$$

For the spontaneous magnetisation the two conditions must be fulfilled simultaneously; hence

$$\frac{M_s}{M_{s,0}} = \frac{\eta T}{C_0 g_J^2 J W_f} = \mathcal{B}_J(\eta)$$

In addition to a trivial solution ($M_s/M_{s,0} = 0$ for $\eta = 0$) the non-trivial solution is obtained either graphically or by an iterative procedure. It exists, however, only below the critical temperature T_c . Above T_c the spontaneous magnetisation vanishes (the equation has only a trivial solution).

Just at T_c we have obtained the relationship

$$T_c = W_f C = W_f C_0 \frac{g_J^2 J(J+1)}{3}$$

and since

$$\eta = \frac{M_s}{M_{s,0}} \frac{C_0 g_J^2 J W_f}{T} = \frac{M_s}{M_{s,0}} \frac{T_c}{T} \frac{3}{J+1}$$

we arrive at the implicit equation

$$\frac{M_s}{M_{s,0}} = \mathcal{B}_J \left(\frac{M_s}{M_{s,0}} \frac{T_c}{T} \frac{3}{J+1} \right), \quad [H_{\text{ext}} = 0]$$

This equation can be solved by an iterative procedure for each (T_c/T) value. The spontaneous magnetisation decreases with temperature according to Fig. 7.11; it escapes at $T \geq T_c$. For spins $s = 1/2$ a simpler transcendent equation is obeyed

$$\frac{M_s}{M_{s,0}} = \tanh \left(\frac{M_s}{M_{s,0}} \frac{T_c}{T} \right), \quad [s = 1/2]$$

For ferromagnetics the *magnetic hysteresis* is characteristic: the magnetisation (M) or magnetisation per spin (σ) versus H_{ext} shows a behaviour depicted in Fig. 7.12. At zero field the spontaneous magnetisation exists within *domains* of certain nuclearity and shape; the domains, however are oriented randomly, which brings a compensation effect. With increasing field the magnetisation rises from its spontaneous, zero-field value to a *saturation limit* M_s where all the available spins are aligned with the field direction. On lowering the field the magnetisation curve drops slightly and crosses the zero field at the value of the *remanent magnetisation* M_r . When a field of the opposite direction is applied, again the saturation value of magnetisation—

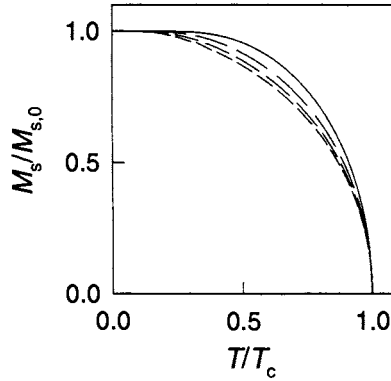


Fig. 7.11. Temperature behaviour of spontaneous magnetisation for a ferromagnet: individual curves correspond to spins 1/2 (solid), 3/2 (long dashed), 5/2 (medium dashed) and 7/2 (short dashed).

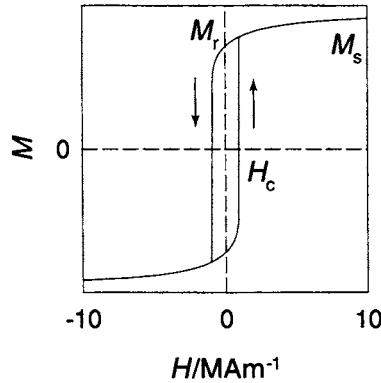


Fig. 7.12. A hysteresis curve for ferromagnetics.

this time of the opposite sign—is reached. The field reversal results in a hysteresis curve; zero magnetisation appears at a positive field strength called the *coercive field* or coercivity H_c .

The magnetisation of a ferromagnet is expressed through the implicit equation

$$\begin{aligned}
 M &= M_0 \mathcal{B}_J \left[\frac{\mu_0 g_J \mu_B}{kT} (H_{\text{ext}} + W_f M) \right] \\
 &= (N_A g_J \mu_B J) \mathcal{B}_J \left[\frac{\mu_0 g_J \mu_B}{kT} \left(H_{\text{ext}} + \frac{3kT_c}{N_A \mu_0 \mu_B^2 J(J+1)} M \right) \right]
 \end{aligned}$$

which, for the given set of parameters (g_J , J , T_c , T), can be solved through an iterative procedure for a fixed value of H_{ext} . The iteration procedure for the

field H_{i+1} starts from the self-consistent value of the magnetisation M_i corresponding to the previous field value H_i . The shape of the hysteresis curve depends upon the T/T_c ratio.

The heat capacity for a ferromagnetic material exhibits a discontinuity at T_c , with the characteristically λ -shaped C versus T curve indicating a phase transition.

7.3.2 Antiferromagnetics

Most of the magnetically ordered materials prefer an antiparallel arrangement of neighbouring spins. When the spins are completely compensated, then the ordered phase refers to an antiferromagnet. Such an ordering survives below the transition temperature—the *Néel temperature* T_N . Above it a usual paramagnetic behaviour exists (Fig. 7.13), with a negative deviation from the Curie law giving rise to the negative Weiss constant Θ .

The usual antiferromagnet can be viewed as a system consisting of two interpenetrating sublattices. Each sublattice is uniformly magnetised with spins aligned parallel, but the magnetisations of the sublattices are cancelled exactly. The molecular field theory assumes that the field acting on sublattice A is

$$\vec{H}_A = \vec{H}_{\text{ext}} + \vec{H}_{\text{int}}(B) = \vec{H}_{\text{ext}} + W_{AB}\vec{M}_B + W_{AA}\vec{M}_A$$

and, analogously, the field acting on sublattice B is

$$\vec{H}_B = \vec{H}_{\text{ext}} + \vec{H}_{\text{int}}(A) = \vec{H}_{\text{ext}} + W_{BA}\vec{M}_A + W_{BB}\vec{M}_B$$

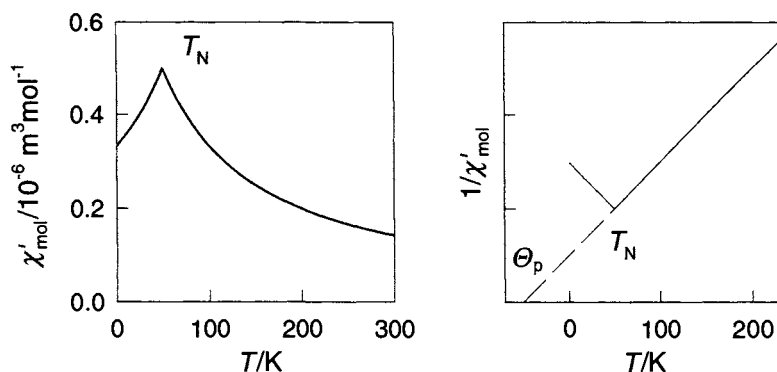


Fig. 7.13. Temperature behaviour of an antiferromagnet.

with the negative field coefficient between the two sublattices (antiferromagnetic contribution)

$$W_{AB} = W_{BA} = -W_a, \quad (W_a > 0)$$

and the positive field coefficient within each sublattice (ferromagnetic contribution)

$$W_{AA} = W_{BB} = W_f, \quad (W_f > 0)$$

When the magnetic field is small and the temperature large enough one can expand the Brillouin function appearing in the magnetisation as follows

$$M_A = M_{A,0} B_J \left(\frac{\mu_0 g_J \mu_B H_A}{kT} \right) \approx (N_A g_J \mu_B J) \left(\frac{\mu_0 g_J \mu_B H_A}{kT} \right) \left(\frac{J+1}{3} \right) = \frac{C}{T} H_A$$

with the Curie constant

$$C = \frac{N_A \mu_0 \mu_B^2 g_J^2 J(J+1)}{3k}$$

and analogously for subsystem B . Then the magnetisation obeys the relationships

$$\vec{M}_A = \frac{C}{T} (\vec{H}_{\text{ext}} - W_a \vec{M}_B + W_f \vec{M}_A)$$

$$\vec{M}_B = \frac{C}{T} (\vec{H}_{\text{ext}} - W_a \vec{M}_A + W_f \vec{M}_B)$$

In zero external field these equations give the non-vanishing magnetisations $\vec{M}_A \neq 0$ and $\vec{M}_B \neq 0$ only at or below the ordering (Néel) temperature which becomes determined by solving the above system of equations. Hence, the first equation gives the expression

$$\vec{M}_A = -\frac{W_a C}{T - W_f C} \vec{M}_B$$

which, after substitution into the second equation, yields

$$\vec{M}_B = \left[\frac{(W_a C)^2}{T(T - W_f C)} + \frac{W_f C}{T} \right] \vec{M}_B$$

or

$$1 = \frac{(W_a C)^2}{T(T - W_f C)} + \frac{W_f C}{T} \Big|_{T=T_N}$$

This condition implies the Néel temperature

$$T_N = C(W_a + W_f)$$

Since the total magnetisation is

$$\begin{aligned} \vec{M}_p &= \vec{M}_A + \vec{M}_B \\ &= \frac{C}{T}(\vec{H}_{\text{ext}} - W_a \vec{M}_B + W_f \vec{M}_A) + \frac{C}{T}(\vec{H}_{\text{ext}} - W_a \vec{M}_A + W_f \vec{M}_B) \\ &= \frac{C}{T}[2\vec{H}_{\text{ext}} + (W_f - W_a)\vec{M}_p] \end{aligned}$$

again a form of the Curie–Weiss law is obtained for a temperature above T_N

$$\chi_{\text{ext}} = \frac{\vec{M}_p}{\vec{H}_{\text{ext}}} = \frac{2C}{T - \Theta_p}, \quad [T > T_N]$$

with the Weiss constant for the paramagnetic state

$$\Theta_p = C(W_f - W_a)$$

Because $W_f \neq 0$, evidently, the following relationship holds valid

$$|\Theta_p| < T_N$$

Also, the proper ordering temperature may differ from the temperature at which a maximum occurs in the susceptibility.

A better indication of the ordering temperature is seen from the discontinuity in the heat capacity C versus T curve, which is sharply λ -shaped. The observation of a λ -shaped C versus T curve is a good proof that a phase transition has occurred. This in itself is incapable of distinguishing between transitions to ferromagnetic or antiferromagnetic phases.

Experiments with oriented single crystals of antiferromagnetics show that there exists some crystallographic direction along which the spins are aligned. This direction is termed the *easy axis* (antiferromagnetic direction D) and can be determined only experimentally; this has no relationship to crystallographic axes.

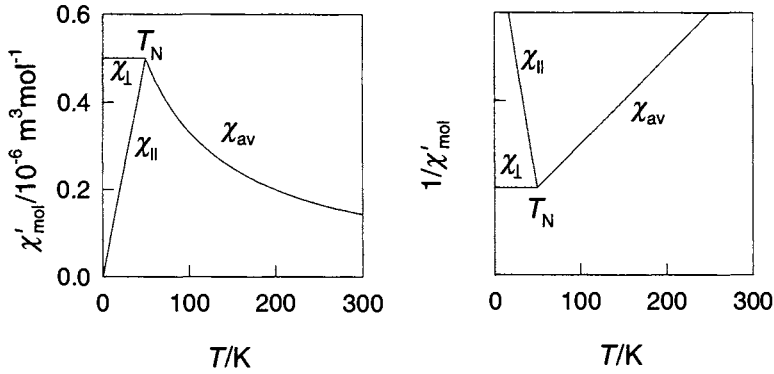


Fig. 7.14. Susceptibility components of an oriented single crystal antiferromagnet.

A field applied parallel to the easy axis will reflect only the cancellation of the spins and thus zero parallel susceptibility will be measured: $\chi_{\parallel(D)} \rightarrow 0$ as $T \rightarrow 0$ (Fig. 7.14). On the other hand, a field applied perpendicular to the easy axis will reflect the constant perpendicular susceptibility below T_c . This implies that the susceptibility of a powder sample antiferromagnet at $T = 0$ is just $2/3$ of its value at T_N

$$\chi_{av}(T=0) = [2\chi_{\perp}(T=0) + \chi_{\parallel}(T=0)]/3 = \frac{2}{3} \chi_{\perp}(T=T_N)$$

7.3.3 Ferrimagnetics

The two (or more) magnetic lattices need not be equivalent, so that the compensation of magnetic moments is only partial. The net result is that some ferromagnetic ordering survives and the material is termed ferrimagnetic. The temperature variation of the magnetisation near the transition temperature becomes very complex. A typical example is represented by spinel ferrites (such as ferrous ferrite, Fe_3O_4 —magnetite).

The molecular field theory assumes that the field acting on sublattice A is

$$\vec{H}_A = \vec{H}_{\text{ext}} + \vec{H}_{\text{int}}(B) = \vec{H}_{\text{ext}} + W_{AB}\vec{M}_B + W_{AA}\vec{M}_A$$

and analogously, the field acting on sublattice B is

$$\vec{H}_B = \vec{H}_{\text{ext}} + \vec{H}_{\text{int}}(A) = \vec{H}_{\text{ext}} + W_{BA}\vec{M}_A + W_{BB}\vec{M}_B$$

while the sublattices are not equivalent. The molecular field coefficients are

$$W_{AB} = W_{BA} = -W, \quad (W > 0)$$

but

$$W_{AA} = \alpha W$$

$$W_{BB} = \beta W$$

yielding the expressions for the total fields

$$\vec{H}_A = \vec{H}_{\text{ext}} - W(\vec{M}_B - \alpha \vec{M}_A)$$

$$\vec{H}_B = \vec{H}_{\text{ext}} - W(\vec{M}_A - \beta \vec{M}_B)$$

By expanding the Brillouin function for system A

$$\begin{aligned} M_A &= M_{A,0} \mathcal{B}_{J_A} \left(\frac{\mu_0 g_A \mu_B H_A}{kT} \right) \\ &\approx (N_A g_A \mu_B J_A) \left(\frac{\mu_0 g_A \mu_B H_A}{kT} \right) \left(\frac{J_A + 1}{3} \right) = \frac{C_A}{T} H_A \end{aligned}$$

with the Curie constant

$$C_A = \frac{N_A \mu_0 \mu_B^2 g_A^2 J_A (J_A + 1)}{3k}$$

and analogously for system B , the magnetisations become expressed as

$$\vec{M}_A = \frac{C_A}{T} (\vec{H}_{\text{ext}} - W \vec{M}_B + \alpha W \vec{M}_A)$$

$$\vec{M}_B = \frac{C_B}{T} (\vec{H}_{\text{ext}} - W \vec{M}_A + \beta W \vec{M}_B)$$

In zero external field the first equation yields

$$\vec{M}_A = - \frac{C_A W}{T - \alpha W C_A} \vec{M}_B$$

which, after substitution into the second equation, gives a condition for the ordering temperature T_c

$$1 = \frac{C_A C_B W^2}{T(T - \alpha W C_A)} + \frac{C_B \beta W}{T} \Big|_{T=T_c}$$

The corresponding quadratic equation has roots

$$T_c = \frac{W}{2} \left[(\alpha C_A + \beta C_B) \pm \sqrt{(\alpha C_A - \beta C_B)^2 + 4C_A C_B} \right]$$

To a first approximation, when $\alpha = \beta = 0$ is assumed, the ordering temperature is expressed as

$$T_c = W\sqrt{C_A C_B}$$

The temperature behaviour of a typical ferrimagnet is shown in Fig. 7.15. Notice a considerable non-linearity of the $1/\chi$ versus T curve near the critical temperature. Above the ordering temperature the susceptibility obeys a relationship (*Neél hyperbola*)

$$\frac{1}{\chi} = \frac{T + \Theta_p}{C} - \frac{\gamma}{T - \Theta}$$

where the new parameters ($C, \gamma, \Theta, \Theta_p$) can be expressed in terms of the microscopic constants ($W, \alpha, \beta, C_A, C_B$). The thermal variation of the reciprocal susceptibility has two asymptotes: one for the infinite T crossing of the temperature axis at $T = -\Theta_p$ (the asymptotic Curie point), and the second for $T = \Theta$.

The magnetic behaviour of a ferrimagnetic compound is not very different from that of a ferromagnetic one, especially when the magnetisation of one site dominates. The main differences may be seen in the thermal dependence of spontaneous magnetisation.

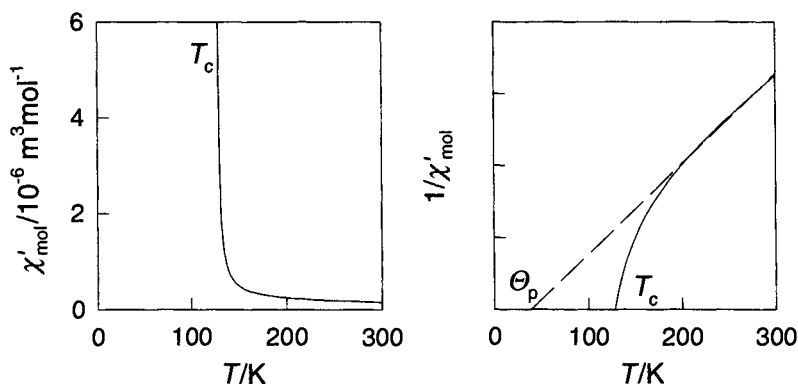


Fig. 7.15. Temperature behaviour of a ferrimagnet.

7.3.4 Metamagnetism

A metamagnetic transition for antiferromagnetic compounds occurs as soon as the applied field is large enough to overcome the antiferromagnetic coupling. As the field is increased beyond a critical value H_c , the magnetic moment antiparallel to the field flips over into parallelism. This field-induced transition below T_N is reflected in a jump in the magnetisation curve M versus H (Fig. 7.16). The resulting metastable state is either a ferromagnetic or a ferrimagnetic phase.

7.3.5 Non-collinear ordered materials

The orientation of the magnetic moments of the two sublattices in a ferrimagnet need not be strictly antiparallel. In such a case the alternate magnetic moments are nearly antiparallel but a small canting occurs to give a spontaneous magnetisation in a direction perpendicular to the approximate spin axis. These *canted spin materials* are also termed *sperimagnets* (canted ferrimagnets).

For a uniaxial crystal (hexagonal, tetragonal, with the principal axis A), in which the magnetic entities are in identically parallel layers, the magnetic moments can be aligned within the layers ($\vec{\mu}_{\perp(A)}$). They need not, however, be collinear but arranged in such a way that the magnetic moment in the next layer is shifted by a constant angle (keeping the same amplitude). This arrangement results in a *helimagnetic structure* (Fig. 7.17). The bulk magnetic properties of a helimagnet are analogous to those of a collinear antiferromagnet: a small susceptibility, the existence of the Néel temperature and the metamagnetic transition above H_c .

When, in a helimagnetic structure, a strong uniaxial anisotropy favouring the axis perpendicular to the layers exists, the magnetic moments become

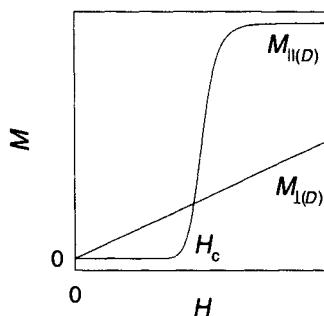


Fig. 7.16. Metamagnetic transition for an antiferromagnet.

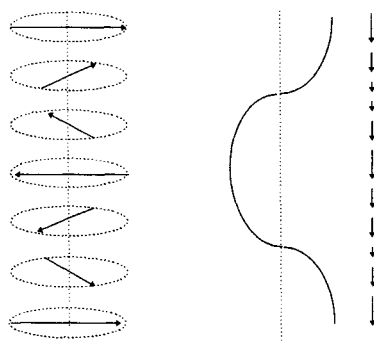


Fig. 7.17. Arrangement of magnetic moments in more complex ordered materials: (a) a helimagnetic structure; (b) a sine wave modulated structure.

oriented along this axis ($\vec{\mu}_{||(\mathcal{A})}$). Their amplitude, however, varies sinusoidally with the distance, having a certain periodicity. We call this the *sine wave modulated structure*.

7.3.6 More complex ordering

The ordering of magnetic moments in a solid material can be even more complex. This leads to new classes of magnetic behaviour: superparamagnetism, incipient ferromagnetism, speromagnetism, asperomagnetism, micro-magnetism and ideal spin glasses [5,6] (see Table 7.3 for overview).

It should be mentioned that, in addition to the localised model (when the magnetic entities are well localised in their spatial positions), there exists an itinerant (or band) model which considers that each magnetic carrier is itinerant through the solid. Whereas the localised model is applicable predominantly to insulators and rare-earth metals, the band model is more relevant to $3d$ metals as an effect of the great diffuseness of the $3d$ orbitals.

SUMMARY

There are three principal classes of magnetic materials: diamagnetics, paramagnetics and ordered materials.

1. The diamagnetics (including superconductors) possess a negative magnetic susceptibility which is temperature independent. In general, diamagnetism is a property of all substances and originates in the presence of spin-paired electrons.

TABLE 7.3
Types of magnetic behaviour

Magnetism	Nature/Origin	Temperature variation
Diamagnetism	closed shell system	
—normal diamagnet	compensated spins	temperature invariance
—superconductor		→ to diamagnet above T_c
Paramagnetism	isolated spin system	
—normal paramagnet	temperature disorder of isolated spins	Curie (Weiss) law
—temperature-independent paramagnetism	low-lying excited states	temperature invariance
—spin crossover system	spin transition	→ to high spin above T_c
—dimers and clusters	exchange coupled spins	continuous variation
—Pauli paramagnetism	field induced band shift	small variation
—superparamagnetism	temperature disorder of small ferromagnetic particles	
Ferromagnetism	spontaneous spin ordering	
—collinear ferromagnet	complete alignment of spins	→ to paramagnet above T_c
—asperomagnetism	random ferromagnet	
—helimagnetism	crystalline asperomagnetism	
—modulated structures	sine modulation	
—itinerant ferromagnetism	electron delocalisation	
—metamagnetism	field-induced spin flop	
—incipient ferromagnetism		
Antiferromagnetism	spontaneous spin compensation	
—collinear antiferromagnet	complete compensation	→ to paramagnet above T_N , → to ferromagnet above H_c
—speromagnetism	random antiferromagnet, concentrated spin glass	
Ferrimagnetism	incomplete spin compensation	
—collinear ferrimagnet	partial spin compensation	→ to paramagnet above T_c
—sperimagnetism	canted ferrimagnetism, random ferrimagnet	
Spin glasses	random, frozen-in structural disorder	
Mictomagnetism	cluster glass	

2. The paramagnetics have a positive magnetic susceptibility which, at higher temperatures, follows the Curie law. The paramagnetism is generated by unpaired electrons behaving uncorrelated to each other. There is, however, a small contribution of temperature-independent paramagnetism originating in the presence of low-lying excited states.
3. The magnetically ordered materials include the numerous class of the ferromagnetics (spin magnetic moments of unpaired electrons aligned parallel below T_c) and the antiferromagnetics (an antiparallel alignment of

spin magnetic moments below T_N). An incomplete compensation of the magnetic moments occurs in ferrimagnetics. The temperature behaviour of magnetisation in these materials is, in general, complex.

4. There are several other classes of magnetically ordered materials where the spatial distribution of the microscopic magnetic moments is more complex.

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Single Magnetic Centres

8.1 FREE ATOM

8.1.1 Hydrogen atom

The Schrödinger equation for a hydrogen atom can be solved exactly. Since this procedure is well described in elementary textbooks of quantum mechanics, e.g. [1–3], only a brief overview is given below.

The Schrödinger equation takes the form

$$\left\{ -\frac{\hbar^2}{2m_p} \nabla_p^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\epsilon_0 r_{pe}} - E \right\} \Psi(\vec{r}_p, \vec{r}_e) = 0$$

which accounts for the kinetic energy of the nucleus (proton), the kinetic energy of the electron as well as the potential energy of the electron–nuclear attraction ($Z = 1$). Its solution is based on the following steps:

- (1) introduction of the centre of mass and the reduced mass μ of the system;
- (2) separation of the translation motion of an atom as a whole and the internal motion of an electron in the central Coulomb field, giving the internal energy E_{int} ;
- (3) introduction of polar coordinates (r, ϑ, φ) which are suitable for the problems in the central field where the factor $1/r$ occurs;
- (4) transformation of the electronic Laplace operator into the polar coordinates, viz. $\nabla^2(r, \vartheta, \varphi)$;
- (5) introduction of the dimensionless variables—the radius in units of bohr, $\rho = r/a_0$, and the energy in units of hartree, $\varepsilon = E_{\text{int}}/E_h$, yielding

$$\left\{ -\frac{1}{2} \nabla^2(\rho) - \frac{1}{2\rho^2} \nabla^2(\vartheta, \varphi) - \frac{Z}{\rho} - \varepsilon \right\} \Psi(\rho, \vartheta, \varphi) = 0$$

- (6) separation of the angular and radial parts of the electronic Schrödinger equation, i.e.

$$\nabla^2(\vartheta, \varphi) Y(\vartheta, \varphi) = \lambda Y(\vartheta, \varphi)$$

$$\left\{ -\frac{1}{2} \nabla^2(\rho) - \frac{1}{2\rho^2} \lambda - \frac{Z}{\rho} \right\} R(\rho) = \varepsilon R(\rho)$$

The angular Schrödinger equation describes the quantisation of the angular momentum and its projection; its solutions are represented by the set of spherical harmonic functions $Y_{l,m}(\vartheta, \varphi)$, the eigenvalues being $\lambda = l(l+1)\hbar^2$. This is a universal result which is used also in other atoms.

The radial equation has solutions in the form of Laguerre polynomials

$$R_{n,l}(\rho) = N_{n,l} \exp(-p/2) p^l L_{n-l}(p)$$

for the argument $p = 2\rho/n$. This is a specific result which needs to be recreated for other atoms in another form.

The solutions of the Schrödinger equation are labelled by the set of quantum numbers obeying the relationships (Table 8.1)

$$n = 1, 2, 3, \dots$$

$$l = 0, 1, \dots, n-1$$

$$m_l = -l, -(l-1), \dots, l-1, l$$

8.1.2 Many-electron atoms

The set of quantum numbers in many-electron atoms has to be completed by the spin quantum number

$$m_s = \pm 1/2$$

TABLE 8.1
Quantum numbers in the hydrogen atom

Principal n	Azimuthal l	Magnetic m_l	Orbital	ε_n/E_h $= -1/2n^2$	$\langle L \rangle/\hbar$ $= \sqrt{l(l+1)}$	$\langle L_z \rangle/\hbar = m_l$
1	0	0	1s	-1/2	0	0
2	0	0	2s	-1/8	0	0
	1	0	2p _z	-1/8	$\sqrt{2}$	0
3	1	± 1	2p _x , 2p _y	-1/8	$\sqrt{2}$	± 1
		0	3s	-1/18	0	0
	1	0	3p _z	-1/18	$\sqrt{2}$	0
	2	± 1	3p _x , 3p _y	-1/18	$\sqrt{2}$	± 1
		0	3d _{z²}	-1/18	$\sqrt{6}$	0
		± 1	3d _{xz} , 3d _{yz}	-1/18	$\sqrt{6}$	± 1
		± 2	3d _{xy} , 3d _{x²-y²}	-1/18	$\sqrt{6}$	± 2

Then the one-electron wave function characterised by the four quantum numbers is termed the *atomic spin-orbital*

$$\psi_i(n, l, m_l, m_s) = R_{n,l}(r_i) Y_{l,m_l}(\vartheta_i, \varphi_i) \eta_{m_s}(\xi_i)$$

Because of the vector nature of the angular momenta, addition of angular momenta in atoms is feasible. The total orbital angular momentum and its projection are expressed through the sums

$$\vec{L} = \sum_i \vec{l}_i$$

$$L_z = \sum_i l_{zi}$$

and they are quantised through the quantum numbers L and M_L , respectively

$$\langle \vec{L} \rangle = \sqrt{L(L+1)} \hbar$$

$$\langle L_z \rangle = M_L \hbar$$

where

$$L = \sum_i l_i$$

and

$$M_L = -L, -(L-1), \dots, -1, 0, +1, \dots, L-1, L$$

The same algebra holds true for the total spin angular momentum $\vec{S}$, its projection S_z and the corresponding quantum numbers S and M_S .

On the set of atomic spin-orbitals various configuration functions

$$|\Phi_u(M_L, M_S)\rangle \equiv |M_L, M_S\rangle$$

can be generated; these are immediately eigenfunctions of the operators of the projection of the total orbital angular momentum $\hat{L}_z$ and the projection of the total spin angular momentum $\hat{S}_z$

$$\hat{L}_z |\Phi_u(M_L, M_S)\rangle = M_L \hbar |\Phi_u(M_L, M_S)\rangle$$

$$\hat{S}_z |\Phi_u(M_L, M_S)\rangle = M_S \hbar |\Phi_u(M_L, M_S)\rangle$$

For an electron configuration of the type $s^\alpha p^\beta d^\gamma$ the number of different configuration (determinantal) functions is equal to

$$n = \binom{2}{\alpha} \binom{6}{\beta} \binom{10}{\gamma}$$

(There are, for example, 45 configuration functions in the case of the d^2 configuration.) A proper linear combination of these functions

$$|L, M_L, S, M_S\rangle = \sum_u C_u |\Phi_u(M_L, M_S)\rangle$$

yields the proper eigenfunctions of the operators $\hat{L}^2$ and $\hat{S}^2$ as required for eigenfunctions of many-electron atoms

$$\hat{L}^2 |L, M_L, S, M_S\rangle = L(L+1)\hbar^2 |L, M_L, S, M_S\rangle$$

$$\hat{S}^2 |L, M_L, S, M_S\rangle = S(S+1)\hbar^2 |L, M_L, S, M_S\rangle$$

The combination coefficients can be determined as follows. By substituting the expansion we have

$$\hat{L}^2 \sum_u C_u |\Phi_u\rangle = L(L+1)\hbar^2 \sum_u C_u |\Phi_u\rangle$$

and by multiplying from the left side by the bra vector $\langle\Phi_v|$ a homogeneous system of linear equations is obtained

$$\sum_u C_u \left[\langle\Phi_v|\hat{L}^2|\Phi_u\rangle - L(L+1)\hbar^2 \delta_{vu} \right] = 0$$

and analogously

$$\sum_u C_u \left[\langle\Phi_v|\hat{S}^2|\Phi_u\rangle - S(S+1)\hbar^2 \delta_{vu} \right] = 0$$

The solution of these equations is straightforward. The linear combination of the configuration functions means, in fact, a configuration interaction. This is one way of overcoming the one-electron approximation.

The set of state vectors $|L, M_L, S, M_S\rangle$ for a many-electron atom is called the *electron term*. The terms are denoted according to the scheme

Orbital angular momentum quantum number L	0	1	2	3	4	5	6	...
Term symbol	S	P	D	F	G	H	I	...

The *spin multiplicity* is a number

$$m = 2S + 1$$

which means a degree of the spin degeneracy of the system (the number of spin states with the same energy). It is placed as an upper-right index of the term symbol, say ^2S .

The terms arising from the simple electron configurations (of equivalent electrons) are listed in Table 8.2.

According to the *Hund rules*:

- (1) of the terms of a configuration, those with maximum multiplicity tend to lie lowest;
- (2) of the terms with maximum multiplicity, that with the largest value of L lies lowest.

8.1.3 Energies of atomic terms

The electronic Hamiltonian of an atom is written in the form of a sum of the one-electron and two-electron parts

$$\hat{H} = \sum_i^n \hat{h}_i + \sum_i^n \sum_{j<i}^n \hat{g}_{ij}$$

Therefore the electronic energy with a configurational function $|\Phi_u(M_L, M_S)\rangle$ constructed of orthogonal spin-orbitals is

$$\bar{E}_u = \langle \Phi_u | \hat{H} | \Phi_u \rangle = \sum_i^n H_{ii} + \sum_i^n \sum_{j<i}^n (J_{ij} - K_{ij})$$

TABLE 8.2
A list of atomic terms

Configuration	Terms
p^0, p^6	^1S
p^1, p^5	^2P
p^2, p^4	$^1S, ^3P, ^1D$
p^3	$^4S, ^2P, ^2D$
d^0, d^{10}	^1S
d^1, d^9	^2D
d^2, d^8	$^1S, ^3P, ^1D, ^3F, ^1G$
d^3, d^7	$^2P, ^4P, ^2D(2\times), ^2F, ^4F, ^2G, ^2H$
d^4, d^6	$^1S(2\times), ^3P(2\times), ^1D(2\times), ^3D, ^5D, ^1F, ^3F(2\times), ^1G(2\times), ^3G, ^3H, ^1I$
d^5	$^2S, ^6S, ^2P, ^4P, ^2D(3\times), ^4D, ^2F(2\times), ^4F, ^2G(2\times), ^4G, ^2H, ^2I$

where the one-electron integrals are

$$H_{ii} = \langle i | \hat{h} | i \rangle = \left\langle i \left| -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{4\pi\epsilon_0} \frac{Z_A}{r_{A1}} \right| i \right\rangle$$

and the two-electron integrals belong to the class of Coulomb integrals

$$J_{ij} = \langle ij | \hat{g} | ij \rangle = \frac{e^2}{4\pi\epsilon_0} \langle ij | r_{12}^{-1} | ij \rangle$$

and exchange integrals

$$K_{ij} = \langle ij | \hat{g} | ji \rangle = \frac{e^2}{4\pi\epsilon_0} \langle ij | r_{12}^{-1} | ji \rangle$$

The above three types of integrals in atoms can be expressed through a limited number of more fundamental quantities.

In evaluating the one-electron integral the radial $R(r)$ and the angular $Y(\vartheta, \varphi)$ parts of the wave function are specified. As the angular functions are orthonormal, viz.

$$\langle Y | Y' \rangle = \int_0^\pi \int_0^{2\pi} Y_{lm}^*(\vartheta, \varphi) Y_{l'm'}(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi = \delta_{l,l'} \delta_{m,m'}$$

then

$$H_{ii} = \langle i | \hat{h} | i \rangle = \langle R | \hat{h} | R \rangle = \int_0^\infty R_{nl}^*(r) \hat{h} R_{nl}(r) r^2 \, dr \equiv U_{nl}$$

Such an integral does not depend on the magnetic quantum number m , which means that there are five integrals with the same value for the $3d$ orbitals, for instance.

Evaluation of the two-electron integrals needs an appropriate expression for the reciprocal interelectron separation r_{12}^{-1} in terms of the distances r_1 and r_2 . For this purpose one can apply a cosine lemma according to which

$$r_{12} = |\vec{r}_1 - \vec{r}_2| = [r_1^2 + r_2^2 - 2r_1 r_2 \cos \gamma_{12}]^{1/2}$$

Using the polar coordinates $1 \equiv (r_1, \vartheta_1, \varphi_1)$ and $2 \equiv (r_2, \vartheta_2, \varphi_2)$ the angle between the two positional vectors $\gamma_{12} \equiv \angle \vec{r}_1 \vec{r}_2$ is given as

$$\cos \gamma_{12} = \cos \vartheta_1 \cos \vartheta_2 + \sin \vartheta_1 \sin \vartheta_2 \cos(\varphi_1 - \varphi_2)$$

Of the two spheres one is lower

$$r \equiv r_{<} \equiv \min\{r_1, r_2\}$$

whereas the other one is greater

$$R \equiv r_{>} \equiv \max\{r_1, r_2\}$$

Therefore it is possible to write

$$r_{12} = R \left[1 + \left(\frac{r}{R} \right)^2 - 2 \left(\frac{r}{R} \right) \cos \gamma_{12} \right]^{1/2}$$

Using the substitutions

$$t = r/R$$

and

$$x = \cos \gamma_{12}$$

an equivalent form is obtained

$$\frac{1}{r_{12}} = \frac{1}{R} (1 - 2tx + t^2)^{-1/2}$$

Just the last expression can be expanded in terms of the *Legendre polynomials*

$$(1 - 2tx + t^2)^{-1/2} = \sum_{k=0}^{\infty} t^k P_k(x) = P_0(x) + tP_1(x) + t^2P_2(x) + \dots$$

for $|x| \leq 1$ and $|t| < 1$. The Legendre polynomials are generated as

$$P_k(x) = \frac{1}{2^k k!} \frac{d^k}{dx^k} (x^2 - 1)^k$$

By combining these equations, the expression for the reciprocal interelectron distance contains only the separated radial variables

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \gamma_{12})$$

On the other hand, an expansion of the Legendre polynomials over spherical harmonic functions is known in the following form

$$P_k(\cos \gamma_{12}) = \frac{4\pi}{2k+1} \sum_{m=-k}^{+k} Y_{km}^*(\vartheta_1, \varphi_1) Y_{km}(\vartheta_2, \varphi_2)$$

so that the inverse interelectron separation becomes

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} \sum_{m=-k}^{+k} Y_{km}^*(\vartheta_1, \varphi_1) Y_{km}(\vartheta_2, \varphi_2)$$

All these expressions can be utilised in a factorisation of a two-electron integral into radial and angular parts

$$\langle ij | r_{12}^{-1} | i'j' \rangle = \sum_{k=0}^{\infty} R_{ij i' j'}^k A_{ii'}^k A_{jj'}^k \delta_{m_{si}, m_{s'j'}} \delta_{m_{sj}, m_{s'j'}} \delta_{(m_{li} + m_{lj}), (m_{li'} + m_{lj'})}$$

The radial integrals contain

$$\begin{aligned} R_{ij i' j'}^k &= \left\langle R_i R_j \left| \frac{r_{<}^k}{r_{>}^{k+1}} \right| R_{i'} R_{j'} \right\rangle \\ &= \int_0^{\infty} \int_0^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} R_{n_i l_i}^*(r_1) R_{n_j l_j}^*(r_1) R_{n_{i'} l_{i'}}(r_2) R_{n_{j'} l_{j'}}(r_2) r_1^2 r_2^2 dr_1 dr_2 \end{aligned}$$

and they do not depend upon the magnetic quantum number m . The radial integrals in atoms are of the type

$$R_{ijij}^k \equiv F_{l_i l_j}^k$$

and

$$R_{ijji}^k \equiv G_{l_i l_j}^k$$

and these are termed the *Slater–Condon parameters*.

TABLE 8.3

Angular coefficients for d^n configurations [1]

l_i	l_j	m_i	m_j	$c_{l_i m_i l_j m_j}^0$	$c_{l_i m_i l_j m_j}^2$	$c_{l_i m_i l_j m_j}^4$
2	2	± 2	± 2	1	$-\sqrt{4/49}$	$\sqrt{1/441}$
2	2	± 2	± 1	0	$\sqrt{6/49}$	$-\sqrt{5/441}$
2	2	± 2	0	0	$-\sqrt{4/49}$	$\sqrt{15/441}$
2	2	± 1	± 1	1	$\sqrt{1/49}$	$-\sqrt{16/441}$
2	2	± 1	0	0	$\sqrt{1/49}$	$\sqrt{30/441}$
2	2	0	0	1	$\sqrt{4/49}$	$\sqrt{36/441}$
2	2	± 2	± 2	0	0	$\sqrt{70/441}$
2	2	± 2	± 1	0	0	$-\sqrt{35/441}$
2	2	± 1	± 1	0	$-\sqrt{6/49}$	$-\sqrt{40/441}$

The angular part can be integrated simply, yielding the numerical coefficients (Table 8.3)

$$\begin{aligned}
 A_{ii'}^k &= \left(\frac{4\pi}{2k+1} \right)^{1/2} \left\langle A_i \left| \sum_{m=-k}^{+k} Y_{km} \right| A_{i'} \right\rangle \\
 &= \left(\frac{4\pi}{2k+1} \right)^{1/2} \int_0^\pi \int_0^{2\pi} Y_{lm}^*(\vartheta_1, \varphi_1) Y_{k,m-m'}(\vartheta_1, \varphi_1) Y_{l'm'}(\vartheta_1, \varphi_1) \sin \vartheta_1 d\vartheta_1 d\varphi_1 \\
 &\equiv c_{lm'l'm'}^k
 \end{aligned}$$

Now the two-electron integrals are expressed through the series

$$J_{ij} = \sum_{k=0}^{\infty} F_{l_i l_j}^k c_{l_i m_i l_i m_i}^k c_{l_j m_j l_j m_j}^k$$

$$K_{ij} = \sum_{k=0}^{\infty} G_{l_i l_j}^k (c_{l_i m_i l_j m_j}^k)^2$$

In fact, the series contain only a few non-zero terms so that the repulsion integrals can be expressed through a limited number of fundamental parameters. For instance,

$$J_{ss} = \langle ss | r_{12}^{-1} | ss \rangle = F_{ss}^0$$

$$J_{pp} = \langle pp | r_{12}^{-1} | pp \rangle = F_{pp}^0 + (4/25)F_{pp}^2$$

$$K_{pp} = \langle pp' | r_{12}^{-1} | p'p \rangle = (3/25)F_{pp}^2$$

$$J_{pp'} = \langle pp' | r_{12}^{-1} | pp' \rangle = F_{pp}^0 - (2/25)F_{pp}^2$$

$$J_{dd} = \langle dd' | r_{12}^{-1} | dd' \rangle = F_{dd}^0 - (4/441)F_{dd}^2 - (4/441)F_{dd}^4$$

$$K_{dd} = \langle dd' | r_{12}^{-1} | d'd \rangle = (5/98)F_{dd}^2 + (5/98)F_{dd}^4$$

$$J_{sp} = \langle sp | r_{12}^{-1} | sp \rangle = F_{sp}^0$$

$$K_{sp} = \langle sp | r_{12}^{-1} | ps \rangle = (1/3)G_{sp}^1$$

$$J_{sd} = \langle sd | r_{12}^{-1} | sd \rangle = F_{sd}^0$$

$$K_{sd} = \langle sd | r_{12}^{-1} | ds \rangle = (1/5)G_{sd}^2$$

$$J_{pd} = \langle pd | r_{12}^{-1} | pd \rangle = F_{pd}^0$$

$$K_{pd} = \langle pd | r_{12}^{-1} | dp \rangle = (2/15)G_{pd}^1 + (3/35)G_{pd}^3$$

The empirical values of the Slater–Condon parameters have been compiled by several authors for the p -block and d -block elements (see e.g. [4] for a review).

The energy of an electron term ${}^mT$ is expressed with the help of the CI coefficients as follows

$$E({}^mT) = \sum_u \sum_v C_u^* C_v \langle \Phi_u(M_L, M_S) | \hat{H} | \Phi_v(M_L, M_S) \rangle$$

and consequently this is a linear function of the $U_{l_i l_j}$, $F_{l_i l_j}^k$ and $G_{l_i l_j}^k$ integrals. These are listed in Table 8.4 for the electron configurations d^n . The only Slater–Condon parameters appearing in terms of the d^n configurations are

$$F_0 = F_{dd}^0$$

$$F_2 = F_{dd}^2/49$$

$$F_4 = F_{dd}^4/441$$

TABLE 8.4
Energies of atomic terms^a

d^n	Term	via Slater–Condon parameters	via Racah parameters
d^1, d^9	${}^2D$	nU_{dd}	
d^2, d^8	${}^3F$	$nU_{dd} + F_0 - 8F_2 - 9F_4$	$U + A - 8B$
	${}^3P$	$nU_{dd} + F_0 + 7F_2 - 84F_4$	$U + A + 7B$
	${}^1G$	$nU_{dd} + F_0 + 4F_2 + F_4$	$U + A + 4B + 2C$
	${}^1D$	$nU_{dd} + F_0 - 3F_2 + 36F_4$	$U + A - 3B + 2C$
	${}^1S$	$nU_{dd} + F_0 + 14F_2 + 126F_4$	$U + A + 14B + 7C$
d^3, d^7	${}^4F$	$nU_{dd} + 3F_0 - 15F_2 - 72F_4$	$U + 3A - 15B$
	${}^4P$	$nU_{dd} + 3F_0 - 147F_4$	$U + 3A$
	${}^2H$	$nU_{dd} + 3F_0 - 6F_2 - 12F_4$	$U + 3A - 6B + 3C$
	${}^2G$	$nU_{dd} + 3F_0 - 11F_2 + 13F_4$	$U + 3A - 11B + 3C$
	${}^2F$	$nU_{dd} + 3F_0 + 9F_2 - 87F_4$	$U + 3A + 9B + 3C$
	${}^2D_{a,b}$	$nU_{dd} + 3F_0 + 5F_2 + 3F_4$	$U + 3A + 5B + 5C$
		$\pm \sqrt{193F_2^2 - 1650F_2F_4 + 8325F_4^2}$	$\pm \sqrt{193B^2 + 8BC + 4C^2}$
d^4, d^6	${}^2P$	$nU_{dd} + 3F_0 - 6F_2 - 12F_4$	$U + 3A - 11B + 3C$
	${}^5D$	$nU_{dd} + 6F_0 - 21F_2 - 189F_4$	$U + 6A - 21B$
	${}^3H$	$nU_{dd} + 6F_0 - 17F_2 - 69F_4$	$U + 6A - 17B + 4C$
	${}^3G$	$nU_{dd} + 6F_0 - 12F_2 - 94F_4$	$U + 6A - 12B + 4C$
	${}^3F_{a,b}$	$nU_{dd} + 6F_0 - 5F_2 - (153/2)F_4$	$U + 6A - 5B + (1/2)C$
		$\pm (1/2)\sqrt{612F_2^2 - 4860F_2F_4 + 20025F_4^2}$	$\pm (3/2)\sqrt{68B^2 + 4BC + C^2}$
	${}^3D$	$nU_{dd} + 6F_0 - 5F_2 - 129F_4$	$U + 6A - 5B + 4C$
	${}^3P_{a,b}$	$nU_{dd} + 6F_0 - 5F_2 - (153/2)F_4$	$U + 6A - 5B + (1/2)C$
		$\pm (1/2)\sqrt{912F_2^2 - 9960F_2F_4 + 38025F_4^2}$	$\pm (1/2)\sqrt{912B^2 - 24BC + 9C^2}$
	${}^1I$	$nU_{dd} + 6F_0 - 15F_2 - 9F_4$	$U + 6A - 15B + 6C$
	${}^1G_{a,b}$	$nU_{dd} + 6F_0 - 5F_2 - (13/2)F_4$	$U + 6A - 5B + (15/2)C$
		$\pm (1/2)\sqrt{708F_2^2 - 7500F_2F_4 + 30825F_4^2}$	$\pm (1/2)\sqrt{708B^2 - 12BC + 9C^2}$
	${}^1F$	$nU_{dd} + 6F_0 - 48F_4$	$U + 6A + 6C$
	${}^1D_{a,b}$	$nU_{dd} + 6F_0 + 9F_2 - (153/2)F_4$	$U + 6A + 9B + (15/2)C$
		$\pm (1/2)\sqrt{1296F_2^2 - 10440F_2F_4 + 30825F_4^2}$	$\pm (3/2)\sqrt{144B^2 + 8BC + C^2}$
	${}^1S_{a,b}$	$nU_{dd} + 6F_0 + 10F_2 + 6F_4$	$U + 6A + 10B + 10C$
		$\pm (1/2)\sqrt{3088F_2^2 - 26400F_2F_4 + 133200F_4^2}$	$\pm (1/2)\sqrt{193B^2 + 8BC + 4C^2}$
d^5	${}^6S$	$nU_{dd} + 10F_0 - 35F_2 - 315F_4$	$U + 10A - 35B$
	${}^4G$	$nU_{dd} + 10F_0 - 25F_2 - 190F_4$	$U + 10A - 25B + 5C$
	${}^4F$	$nU_{dd} + 10F_0 - 13F_2 - 180F_4$	$U + 10A - 13B + 7C$
	${}^4D$	$nU_{dd} + 10F_0 - 18F_2 - 225F_4$	$U + 10A - 18B + 5C$
	${}^4P$	$nU_{dd} + 10F_0 - 28F_2 - 105F_4$	$U + 10A - 28B + 7C$

(contd.)

TABLE 8.4

Energies of atomic terms^a (*contd.*)

d^n	Term	via Slater-Condon parameters	via Racah parameters
d^5	^2I	$nU_{dd} + 10F_0 - 24F_2 - 90F_4$	$U + 10A - 24B + 8C$
	^2H	$nU_{dd} + 10F_0 - 22F_2 - 30F_4$	$U + 10A - 22B + 10C$
	^2G_a	$nU_{dd} + 10F_0 - 13F_2 - 145F_4$	$U + 10A - 13B + 8C$
	^2G_b	$nU_{dd} + 10F_0 - 3F_2 - 155F_4$	$U + 10A - 3B + 10C$
	^2F_a	$nU_{dd} + 10F_0 - 9F_2 - 165F_4$	$U + 10A - 9B + 8C$
	^2F_b	$nU_{dd} + 10F_0 - 25F_2 - 15F_4$	$U + 10A - 25B + 10C$
	^2D_a	$nU_{dd} + 10F_0 - 4F_2 - 120F_4$	$U + 10A - 4B + 10C$
	$^2D_{b,c}$	$nU_{dd} + 10F_0 - 3F_2 - 90F_4$	$U + 10A - 3B + 11C$
		$\pm (1/2)\sqrt{513F_2^2 - 4500F_2F_4 + 20700F_4^2}$	$\pm 3\sqrt{57B^2 + 2BC + C^2}$
	^2P	$nU_{dd} + 10F_0 + 20F_2 - 240F_4$	$U + 10A + 20B + 10C$
	^2S	$nU_{dd} + 10F_0 - 3F_2 - 195F_4$	$U + 10A - 3B + 8C$

^aSubstitutions: $F_0 = F_{dd}^0$, $F_2 = F_{dd}^2/49$, $F_4 = F_{dd}^4/441$, $U = nU_{dd}$, $A = F_0 - 49F_4 = F_{dd}^0 - (49/441)F_{dd}^4$, $B = F_2 - 5F_4 = F_{dd}^2/49 - (5/441)F_{dd}^4$, $C = 35F_4 = (35/441)F_{dd}^4$.

These are frequently substituted by the set of Racah parameters defined as

$$A = F_0 - 49F_4$$

$$B = F_2 - 5F_4$$

$$C = 35F_4$$

A compilation of empirical values for these parameters exists in special monographs, e.g. in [5, 6].

The mean energy of an electron configuration is given as a weighted average of the electron terms

$$\bar{E}(d^n) = \frac{\sum_i g_i E_i(^m T)}{\sum_i g_i}$$

where $g = (2S + 1)(2L + 1)$ are the total degeneracies of the respective terms.

Another expression for the mean energy of an electron configuration $s^x p^y d^z f^w$ is [1]

$$\begin{aligned}
\overline{E}(s^x p^y d^z f^w) = & xU_s + yU_p + zU_d + wU_f \\
& + \frac{x(x-1)}{2}\overline{G}_{ss} + \frac{y(y-1)}{2}\overline{G}_{pp} + \frac{z(z-1)}{2}\overline{G}_{dd} \\
& + \frac{w(w-1)}{2}\overline{G}_{ff} + xy\overline{G}_{sp} + xz\overline{G}_{sd} + xw\overline{G}_{sf} \\
& + yz\overline{G}_{ps} + yw\overline{G}_{pf} + zw\overline{G}_{df}
\end{aligned}$$

where the averaged interelectron repulsion increments are

$$\overline{G}_{ss} = J_{ss} = F_{ss}^0$$

$$\overline{G}_{pp} = J_{pp} - (2/5)K_{pp} = F_{pp}^0 - (2/25)F_{pp}^2$$

$$\overline{G}_{dd} = J_{dd} - (4/9)K_{dd} = F_{dd}^0 - (2/63)F_{dd}^2 - (2/63)F_{dd}^4$$

$$\overline{G}_{ff} = F_{ff}^0 - (4/195)F_{ff}^2 - (2/143)F_{ff}^4 - (100/5577)F_{ff}^6$$

$$\overline{G}_{sp} = J_{sp} - (1/2)K_{sp} = F_{sp}^0 - (1/6)G_{sp}^1$$

$$\overline{G}_{sd} = J_{sd} - (1/2)K_{sd} = F_{sd}^0 - (1/10)G_{sd}^2$$

$$\overline{G}_{sf} = F_{sf}^0 - (1/14)G_{sf}^3$$

$$\overline{G}_{pd} = J_{pd} - (1/2)K_{pd} = F_{pd}^0 - (1/15)G_{pd}^1 - (3/70)G_{pd}^3$$

$$\overline{G}_{pf} = F_{pf}^0 - (3/70)G_{pf}^2 - (2/63)G_{pf}^4$$

$$\overline{G}_{df} = F_{df}^0 - (3/70)G_{df}^1 - (2/105)G_{df}^3 - (5/231)G_{df}^5$$

8.1.4 Energies of multiplets

The spin-orbit coupling in the atomic system manifests itself in a further splitting of atomic terms into *multiplets* (Table 8.5).

The orbital angular momentum $\vec{l}_i$ adds to the spin angular momentum $\vec{s}_i$ for each electron and yields the total angular momentum of an electron

$$\vec{j}_i = \vec{l}_i + \vec{s}_i$$

and its projection

$$j_{zi} = l_{zi} + s_{zi}$$

TABLE 8.5
Energy levels in a free atom

	Electron configuration	Atomic terms	Multiplets	Magnetic levels
symbol	p^n, d^n, f^n	^mT	^mT_J	
state vectors	$ l, m_l\rangle$	$ L, M_L, S, M_S\rangle$	$ J, M_J\rangle$	$ J, M_J\rangle$
degeneracy		$(2S+1)(2L+1)$	$(2J+1)$	removed
model	independent electrons in an effective field	interelectron repulsion, $\hat{V}^{ee}$	spin-orbit coupling, $\hat{H}^{so}$	magnetic field, $\hat{H}^Z$
method of calculation	variation method (SCF)	variation method (CI)	first-order perturbation theory	perturbation theory

The quantisation of the total angular momentum for a given electron is given as

$$\langle \vec{j}_i \rangle = \sqrt{j_i(j_i + 1)}\hbar$$

and that of the projection of the total angular momentum for a given electron as

$$\langle j_{iz} \rangle = m_{ji}\hbar$$

The quantum numbers are

$$j_i = l_i + s_i = l_i \pm 1/2$$

$$m_{ji} = -j_i, -(j_i + 1), \dots, j_i - 1, j_i$$

The corresponding spin-orbitals are labelled according to Table 8.6.

The angular momenta for individual electrons can be summed up to yield the total angular momentum of an atom

$$\vec{J} = \sum_i \vec{j}_i$$

and the projection of the total angular momentum of an atom

$$J_z = \sum_i j_{zi}$$

TABLE 8.6
Spin-orbitals in a one-electron atom

l	j	Symbol	m_j	g	Energy
0	1/2	$s_{1/2}$	$\pm 1/2$	2	E_{ns}
1	1/2	$p_{1/2}$	$\pm 1/2$	2	$E_{np} - \xi_{np}$
	3/2	$p_{3/2}$	$\pm 1/2, \pm 3/2$	4	$E_{np} + (1/2)\xi_{np}$
2	3/2	$d_{3/2}$	$\pm 1/2, \pm 3/2$	4	$E_{nd} - (3/2)\xi_{nd}$
	5/2	$d_{5/2}$	$\pm 1/2, \pm 3/2, \pm 5/2$	6	$E_{nd} + \xi_{nd}$
3	5/2	$f_{5/2}$	$\pm 1/2, \pm 3/2, \pm 5/2$	6	$E_{nf} - 2\xi_{nf}$
	7/2	$f_{7/2}$	$\pm 1/2, \pm 3/2, \pm 5/2, \pm 7/2$	8	$E_{nf} + (3/2)\xi_{nf}$

The quantisation of the total angular momentum of an atom is given by the formulae

$$\langle \vec{J} \rangle = \sqrt{J(J+1)}\hbar$$

$$\langle J_z \rangle = M_J \hbar$$

with the quantum number of the total angular momentum

$$J = \sum_i j_i$$

and the quantum number of the projection of the total angular momentum

$$M_J = -J, -(J+1), \dots, J-1, J$$

This scheme of adding angular momenta is called the *j-j coupling scheme*; however, despite its fundamental validity it is rarely used in applications. The reason for this lies in the fact that the spin-orbitals $|j, m_j\rangle$ need to be determined by a two-component or four-component Dirac equation, which implies a complex algebra and much more computational effort. Definitely such a procedure is ultimate for heavy element atoms. The *j-j* coupling scheme assumes that the spin-orbit coupling dominates over the interelectron repulsion: $\hat{H}^{\text{so}} > \hat{V}^{\text{ee}}$.

For light element atoms an alternative *L-S coupling scheme* is applied (this is also termed the *Russell-Saunders scheme*) which is based on a reverse assumption: $\hat{H}^{\text{so}} < \hat{V}^{\text{ee}}$. Non-relativistic (or quasi-relativistic) spatial orbitals are used as a basis set $|l, m_l\rangle$ in creating the electron configurations $|\Phi_u(M_L, M_S)\rangle$. These functions are combined via CI to evaluate the electron term state vectors $|L, M_L, S, M_S\rangle$. Now the addition of the angular momenta proceeds, being based on the assumption

$$\vec{J} = \vec{L} + \vec{S}$$

The atomic Hamiltonian is modified by the operator of the spin-orbit coupling

$$\hat{H} \rightarrow \hat{H}^0 + \hat{H}^{\text{so}}$$

which, in the simplest form, contains only the one-electron part

$$\hat{H}^{\text{so}} = \sum_{k=1}^n \xi_k(r) \vec{l}_k \cdot \vec{s}_k [\hbar^{-2}]$$

Such an operator does not commute with the operators $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_z$ and, consequently, it has non-zero (and complex) off-diagonal matrix elements in the basis set of the state vectors $|\Psi_i^{LS}\rangle = |L, M_L, S, M_S\rangle$

$$H_{ij}^{\text{so}} = \langle \Psi_i^{LS} | \hat{H}^{\text{so}} | \Psi_j^{LS} \rangle \neq 0$$

A solution of the secular equation

$$\det\{H_{ij}^{\text{so}} - \Delta E \delta_{ij}\} = 0$$

then yields the energy shifts due to the spin-orbit coupling. In determining the selection rules for these matrix elements one can apply the identity of resolution

$$\begin{aligned} H_{ij}^{\text{so}} &= \left\langle \Psi_i^{LS} \left| \sum_{k=1}^n \xi_k(r) \vec{l}_k \cdot \vec{s}_k \right| \Psi_j^{LS} \right\rangle [\hbar^{-2}] \\ &= \sum_{k=1}^n \sum_m \left\langle \Psi_i^{LS} \left| \xi_k(r) \vec{l}_k \right| \Psi_m^{LS} \right\rangle \cdot \left\langle \Psi_m^{LS} \left| \vec{s}_k \right| \Psi_j^{LS} \right\rangle [\hbar^{-2}] \end{aligned}$$

with

$$|\Psi_i^{LS}\rangle = |L, M_L, S, M_S\rangle$$

$$|\Psi_j^{LS}\rangle = |L', M'_L, S', M'_S\rangle$$

$$|\Psi_m^{LS}\rangle = |L', M'_L, S, M_S\rangle$$

Therefore the non-zero matrix elements are those for which the following relations hold true: $\Delta L = 0, \pm 1$; $\Delta S = 0, \pm 1$; $\Delta J = 0$; $\Delta M_J = 0$.

We can apply the identity of resolution within a term (for the same L and S) as follows

$$\begin{aligned} & \langle L, M_L, S, M_S | \hat{H}^{so} | L, M'_L, S, M'_S \rangle \\ &= \sum_{k=1}^n \sum_m \langle L, M_L, S, M_S | \xi_k(r) \vec{l}_k | L, M'_L, S, M_S \rangle \\ & \cdot \langle L, M'_L, S, M_S | \vec{s}_k | L, M'_L, S, M'_S \rangle [\hbar^{-2}] \end{aligned}$$

and the replacement theorem (Section 1.5.3) according to which a mutual proportionality of the matrix elements having the same angular part exists

$$\begin{aligned} & \langle L, M_L, S, M_S | \xi_k(r) \vec{l}_k | L, M'_L, S, M_S \rangle \\ &= \gamma_L(L, S) \langle L, M_L, S, M_S | \vec{L} | L, M'_L, S, M_S \rangle \\ & \langle L, M'_L, S, M_S | \vec{s}_k | L, M'_L, S, M'_S \rangle \\ &= \gamma_S(L, S) \langle L, M'_L, S, M_S | \vec{S} | L, M'_L, S, M'_S \rangle \end{aligned}$$

Thus we get

$$\begin{aligned} & \langle L, M_L, S, M_S | \hat{H}^{so} | L, M'_L, S, M'_S \rangle \\ &= \sum_{k=1}^n \sum_m \gamma_L(L, S) \gamma_S(L, S) \\ & \times \left(\langle L, M_L, S, M_S | \vec{L} | L, M'_L, S, M_S \rangle \right. \\ & \cdot \left. \langle L, M'_L, S, M_S | \vec{S} | L, M'_L, S, M'_S \rangle \right) [\hbar^{-2}] \end{aligned}$$

which can be rewritten as

$$\begin{aligned} & \langle L, M_L, S, M_S | \hat{H}^{so} | L, M'_L, S, M'_S \rangle \\ &= \langle L, M_L, S, M_S | \vec{L} \cdot \vec{S} | L, M'_L, S, M'_S \rangle \sum_{k=1}^n \sum_m \gamma_L(L, S) \gamma_S(L, S) [\hbar^{-2}] \\ &= \lambda \langle L, M_L, S, M_S | \vec{L} \cdot \vec{S} | L, M'_L, S, M'_S \rangle [\hbar^{-2}] \end{aligned}$$

where a *spin-orbit splitting parameter* λ (constant within a term) has been introduced

$$\lambda = \sum_{k=1}^n \sum_m \gamma_L(L, S) \gamma_S(L, S)$$

This parameter is difficult to relate to the integrals over the $\xi_i(r)$ functions

$$\xi_{nl} = \int_0^{\infty} R_{nl}^*(r) \xi(r) R_{nl}(r) r^2 dr$$

which are usually taken as *spin-orbit coupling constants*.

It is possible, however, to seek a new basis set

$$\begin{aligned} |L, S, J, M_J\rangle &= \sum_i C_i |\Psi_i^{LS}\rangle \\ &= \sum |L, M_L, S, M_S\rangle \langle L, M_L, S, M_S | L, S, J, M_J \rangle \end{aligned}$$

where $\langle L, M_L, S, M_S | L, S, J, M_J \rangle$ are the coupling coefficients (the Clebsch-Gordan coefficients). In this transformed basis the spin-orbit coupling operator adopts a block-diagonal form: the off-diagonal matrix elements between the states of the different J or M_J are zero.

For light element atoms, however, the off-diagonal matrix elements are much lower than the diagonal ones and, to a good approximation, they can be neglected. To this approximation the matrix elements within a term fulfil

$$H_{ij}^{\text{so}} = \left\langle \Psi_i^{LS} \left| \sum_k \xi_k(r) \vec{l}_k \cdot \vec{s}_k \right| \Psi_j^{LS} \right\rangle [\hbar^{-2}] = \lambda \left\langle \Psi_i^{LS} \left| \vec{L} \cdot \vec{S} \right| \Psi_j^{LS} \right\rangle [\hbar^{-2}]$$

Since the following expression holds true

$$2\vec{L} \cdot \vec{S} = \hat{J}^2 - \hat{L}^2 - \hat{S}^2$$

then

$$H_{ij}^{\text{so}} = \lambda \left\langle \Psi_i^{LS} \left| \vec{L} \cdot \vec{S} \right| \Psi_j^{LS} \right\rangle [\hbar^{-2}] = \frac{\lambda}{2} \left\langle \Psi_i^{LS} \left| \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \right| \Psi_j^{LS} \right\rangle [\hbar^{-2}]$$

Finally, first-order perturbation theory yields the following contributions to the energies of the electron terms

$$\Delta E = E(^mT_J) - E(^mT) = \lambda \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)]$$

Now the atomic terms are split into a set of multiplets. The number of multiplets is $(2S + 1)$, each one being labelled according to the quantum number

$$J = |L - S|, \dots, L + S$$

as the right-lower index of the term symbol, i.e. ${}^mT_J$. The energies of adjacent multiplets are given by the formula

$$E_{J+1} = E_J + \lambda(J + 1)$$

which is known as the *Landé interval rule*. Each multiplet has a degeneracy $d_J = 2J + 1$ which can be removed in the presence of a magnetic field.

The splitting of terms into multiplets is associated with the conservation of the centre of gravity of the states

$$\sum_{J=|L-S|}^{L+S} (2J + 1) \Delta E_J = 0$$

Some splittings are displayed in Table 8.7.

The spin-orbit coupling constant ξ_{nl} (which is characteristic for an electron configuration) is related to the spin-orbit splitting parameter λ (which is characteristic for a term) through

$$\lambda = \pm \frac{\xi}{2S}$$

TABLE 8.7
Splitting of ground terms into multiplets

d^n	Term	Normal multiplet	ΔE_J $\lambda > 0$	d_J	d^n	Term	Inverted multiplet	ΔE_J $\lambda < 0$	d_J
d^1	${}^2D$	${}^2D_{3/2}$	$-(3/2)\lambda$	4	d^9	${}^2D$	${}^2D_{5/2}$	λ	6
		${}^2D_{1/2}$	λ	6			${}^2D_{3/2}$	$-(3/2)\lambda$	4
d^2	${}^3F$	${}^3F_2$	-4λ	5	d^8	${}^3F$	${}^3F_4$	3λ	9
		${}^3F_3$	$-\lambda$	7			${}^3F_3$	$-\lambda$	7
		${}^3F_4$	3λ	9			${}^3F_2$	-4λ	5
d^3	${}^4F$	${}^4F_{3/2}$	-6λ	4	d^7	${}^4F$	${}^4F_{9/2}$	$(9/2)\lambda$	10
		${}^4F_{5/2}$	$-(7/2)\lambda$	6			${}^4F_{7/2}$	0	8
		${}^4F_{7/2}$	0	8			${}^4F_{5/2}$	$-(7/2)\lambda$	6
		${}^4F_{9/2}$	$(9/2)\lambda$	10			${}^4F_{3/2}$	-6λ	4
d^4	${}^5D$	${}^5D_0$	-6λ	1	d^6	${}^5D$	${}^5D_4$	4λ	9
		${}^5D_1$	-5λ	3			${}^5D_3$	0	7
		${}^5D_2$	-3λ	5			${}^5D_2$	-3λ	5
		${}^5D_3$	0	7			${}^5D_1$	-5λ	3
		${}^5D_4$	4λ	9			${}^5D_0$	-6λ	1
d^5	${}^6S$	${}^6S_{5/2}$	0	6					

The coupling constants are positive and thus the plus sign is valid for a shell less than half full; positive λ yields *normal multiplets*. However, a shell more than half full of electrons may be regarded as a set of holes in a filled shell. Therefore, for “positively charged” electrons the sign of the λ parameter is altered; the negative λ yields *inverted multiplets*.

8.2 CRYSTAL FIELD THEORY

8.2.1 Basic principles

The crystal field theory is based on the assumption that the chromophore $\{ML_n\}$ of a coordination compound can be described by the model according to which the central atom with its valence d -orbitals is under the influence of point charges generated at the ligand positions. The electrostatic potential acting as a sum of the ligand contributions is termed the *crystal field potential* and it is

$$\hat{V}^{\text{cf}} = \sum_{i=1}^n \sum_{L=1}^N \frac{1}{4\pi\epsilon_0} \frac{-eq_L}{|\vec{r}_i - \vec{R}_L|} = \sum_{i=1}^n \hat{v}_i$$

The individual terms of the one-electron operator $\hat{v}_i$ are

$$\hat{v}_i = \frac{e^2}{4\pi\epsilon_0} \sum_{L=1}^N \frac{q_L^0}{|\vec{r}_i - \vec{R}_L|}$$

where we assume that ligands bear the negative charges $q_L = -eq_L^0$.

The action of the crystal field potential should be considered in relationship to other “perturbations” such as the interelectron repulsion $\hat{V}^{\text{ee}}$ and eventually the spin-orbit coupling operator $\hat{H}^{\text{so}}$. According to these relationships, several types of crystal field are distinguished (Table 8.8). The principal difference between them is which basis set is generated prior to the application of the actual perturbation operator.

8.2.2 Crystal field potential

The matrix elements of the crystal field potential between the atomic orbitals can be written in the form

$$v_{ij} = \langle i | \hat{v}_1 | j \rangle = \frac{e^2}{4\pi\epsilon_0} \sum_{L=1}^N q_L^0 \left\langle R_i Y_i \left| \frac{1}{r_{1L}} \right| R_j Y_j \right\rangle$$

TABLE 8.8

Types of crystal field

Type	Operator relationship	Basis set	Actual operator	Method of calculation
(1) weak field	$\hat{V}^{ee} > \hat{V}^{cf} > \hat{H}^{so}$	electron terms of free atom configurations $ L, M_L, S, M_S\rangle$	$\hat{V}^{cf}$	perturbation theory for degenerate states
(2) strong field	$\hat{V}^{cf} > \hat{V}^{ee} > \hat{H}^{so}$	split electron configurations	$\hat{V}^{ee}$	
(3) intermediate field	$\hat{V}^{ee} \approx \hat{V}^{cf} > \hat{H}^{so}$	either of weak or of strong field		variation configuration interaction
(4) very weak field	$\hat{V}^{ee} > \hat{H}^{so} > \hat{V}^{cf}$	atomic multiplets $ J, M_J\rangle$	$\hat{V}^{cf}$	perturbation theory for degenerate states

We shall restrict ourselves to the d -atomic orbitals only, so that the orbitals differ only in the magnetic quantum numbers m . The inverse of the electron–ligand separation can be expanded into the basis of the Legendre polynomials; such an expansion follows an analogous philosophy to that for r_{12}^{-1} in a free atom. Hence

$$\frac{1}{r_{1L}} = \frac{1}{|\vec{r}_1 - \vec{R}_L|} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \gamma_{1L})$$

with $r_{<} = \min\{r_1, R_L\}$ and $r_{>} = \max\{r_1, R_L\}$. This allows a separation of the crystal field potential into radial and angular parts

$$v_{ij} = \sum_{L=1}^N q_L^0 \sum_{k=0}^{\infty} F_k(R_L) \Theta_{ij}^k(\vartheta_L, \varphi_L)$$

The integral of the radial functions is

$$\begin{aligned} F_k(R_L) &= \int_0^{\infty} R_{n,2}^*(r) \frac{r_{<}^k}{r_{>}^{k+1}} R_{n,2}(r) r^2 dr \\ &= \frac{1}{R_L^{k+1}} \int_0^{R_L} r^k [R_{n,2}(r)]^2 r^2 dr + R_L^k \int_{R_L}^{\infty} \frac{1}{r^{k+1}} [R_{n,2}(r)]^2 r^2 dr \end{aligned}$$

These numbers should not be confused with the multiples of the Slater-Condon parameters F_0 , F_2 and F_4 . The integral of the angular functions is

$$\Theta_{ij}^k(\vartheta_L, \varphi_L) = \int_0^\pi \int_0^{2\pi} Y_{2,i}^*(\vartheta, \varphi) P_k(\cos \gamma_{1L}) Y_{2,j}(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi$$

This can be modified to the following form

$$\begin{aligned} \Theta_{m,m'}^k(\vartheta_L, \varphi_L) &= A_{m,m'} Y_{4,m-m'}(\vartheta_L, \varphi_L) \delta_{k,4} \\ &+ B_{m,m'} Y_{2,m-m'}(\vartheta_L, \varphi_L) \delta_{k,2} \\ &+ C_{m,m'} Y_{0,m-m'}(\vartheta_L, \varphi_L) \delta_{k,0} \end{aligned}$$

The new coefficients are expressed through the Clebsch-Gordan coefficients $\langle l_1 m_1 l_2 m_2 | l_3 m_3 \rangle$ as follows

$$A_{m,m'} = (-1)^{m'} \frac{5\sqrt{4\pi}}{27} \langle 2, -m', 2, m | 4, m-m' \rangle \langle 2, 0, 2, 0 | 4, 0 \rangle$$

$$B_{m,m'} = (-1)^{m'} \frac{\sqrt{4\pi}}{5} \langle 2, -m', 2, m | 2, m-m' \rangle \langle 2, 0, 2, 0 | 2, 0 \rangle$$

$$C_{m,m'} = (-1)^{m'} 5\sqrt{4\pi} \langle 2, -m', 2, m | 0, m-m' \rangle \langle 2, 0, 2, 0 | 0, 0 \rangle = \sqrt{4\pi} \delta_{m,m'}$$

These coefficients are readily evaluable and are collected in Table 8.9.

TABLE 8.9
Angular coefficients for the crystal field potential^a

	$a_{m,m'}$					$b_{m,m'}$				
m'	2	1	0	-1	-2	2	1	0	-1	-2
2	1	$-\sqrt{5}$	$\sqrt{15}$	$-\sqrt{35}$	$\sqrt{70}$	$-\sqrt{20}$	$\sqrt{30}$	$-\sqrt{20}$	0	0
1	$\sqrt{5}$	-4	$\sqrt{30}$	$-\sqrt{40}$	$\sqrt{35}$	$-\sqrt{30}$	$\sqrt{5}$	$\sqrt{5}$	$-\sqrt{30}$	0
0	$\sqrt{15}$	$-\sqrt{30}$	6	$-\sqrt{30}$	$\sqrt{15}$	$-\sqrt{20}$	$-\sqrt{5}$	$\sqrt{20}$	$-\sqrt{5}$	$-\sqrt{20}$
-1	$\sqrt{35}$	$-\sqrt{40}$	$\sqrt{30}$	-4	$\sqrt{5}$	0	$-\sqrt{30}$	$\sqrt{5}$	$\sqrt{5}$	$-\sqrt{30}$
-2	$\sqrt{70}$	$-\sqrt{35}$	$\sqrt{15}$	$-\sqrt{5}$	1	0	0	$-\sqrt{20}$	$\sqrt{30}$	$-\sqrt{20}$

^a $A_{m,m'} = (\sqrt{4\pi}/63)a_{m,m'}$; $B_{m,m'} = (\sqrt{4\pi}/35)b_{m,m'}$.

With the angular coefficients determined, the matrix elements of the crystal field potential become

$$v_{m,m'} = \sum_{L=1}^N q_L^0 [F_4(R_L) A_{m,m'} Y_{4,m-m'}(\vartheta_L, \varphi_L) + F_2(R_L) B_{m,m'} Y_{2,m-m'}(\vartheta_L, \varphi_L) + F_0(R_L) \sqrt{4\pi} Y_{0,m-m'}(\vartheta_L, \varphi_L) \delta_{m,m'}]$$

Using spherical harmonic functions, the final expressions for matrix elements among d -orbitals are obtained (Table 8.10). Since such a matrix is Hermitian, only the upper triangle elements are displayed. A similar procedure applied to f -orbitals yields the results summarised in Table 8.11.

In general, a charge distribution $\rho(\vec{R}) \equiv \rho(R, \Theta, \Phi)$ produces at the reference point $\vec{r}(r, \vartheta, \varphi)$ the electrostatic potential

$$V(\vec{r}) = \int \frac{\rho(\vec{R})}{|\vec{R} - \vec{r}|} dV(R, \Theta, \Phi)$$

After the expansion of the reciprocal separation into the basis of spherical harmonics one obtains

$$V(\vec{r}) = \sum_{k=0}^{\infty} \sum_{m=-k}^{+k} \frac{4\pi}{2k+1} Y_{k,m}(\vartheta, \varphi) \int \rho(\vec{R}) \frac{r_{<}^k}{r_{>}^{k+1}} Y_{k,m}^*(\Theta, \Phi) dV(R, \Theta, \Phi)$$

The action of the crystal field potential is of interest inside the radius R of the ligand sphere so that, in such a special case, always $r_{<} = r$ and $r_{>} = R$. Consequently we get

$$V(\vec{r}) = \sum_{k=0}^{\infty} \sum_{m=-k}^{+k} A_{k,m} r^k Y_{k,m}(\vartheta, \varphi)$$

with the coefficients depending only on the ligand coordinates

$$A_{k,m} = \frac{4\pi}{2k+1} \int \frac{\rho(\vec{R}) Y_{k,m}^*(\Theta, \Phi)}{R^{k+1}} dV(R, \Theta, \Phi)$$

In the point charge model of the crystal field these coefficients become a summation over the ligands

TABLE 8.10

Matrix elements of the crystal field potential for d -orbitals

Element	Formula
$\langle 0 \hat{v}_1 0\rangle$	$\sum_L q_L^0 \{F_0(R_L) + (1/7)(2 \cos^2 \vartheta_L - \sin^2 \vartheta_L)F_2(R_L) \\ + (1/28)(35 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 3)F_4(R_L)\}$
$\langle \pm 1 \hat{v}_1 \pm 1\rangle$	$\sum_L q_L^0 \{F_0(R_L) + (1/14)(2 \cos^2 \vartheta_L - \sin^2 \vartheta_L)F_2(R_L) \\ - (1/42)(35 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 3)F_4(R_L)\}$
$\langle \pm 2 \hat{v}_1 \pm 2\rangle$	$\sum_L q_L^0 \{F_0(R_L) - (1/7)(2 \cos^2 \vartheta_L - \sin^2 \vartheta_L)F_2(R_L) \\ + (1/168)(35 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 3)F_4(R_L)\}$
$\langle 2 \hat{v}_1 1\rangle = \langle -1 \hat{v}_1 -2\rangle$	$\sum_L q_L^0 \{\cos \vartheta_L \sin \vartheta_L \exp(i\varphi_L) \\ \times [-(3/7)F_2(R_L) + (5/4\sqrt{7})(7 \cos^2 \vartheta_L - 3)F_4(R_L)]\}$
$\langle 1 \hat{v}_1 0\rangle = \langle 0 \hat{v}_1 -1\rangle$	$\sum_L q_L^0 \{(\sqrt{6}/14) \cos \vartheta_L \sin \vartheta_L \exp(i\varphi_L) \\ \times [-F_2(R_L) - (1/30)(7 \cos^2 \vartheta_L - 3)F_4(R_L)]\}$
$\langle 2 \hat{v}_1 0\rangle = \langle 0 \hat{v}_1 -2\rangle$	$\sum_L q_L^0 \{(1/7\sqrt{6}) \sin^2 \vartheta_L \exp(2i\varphi_L) \\ \times [-3F_2(R_L) + (5/4)(7 \cos^2 \vartheta_L - 1)F_4(R_L)]\}$
$\langle 1 \hat{v}_1 -1\rangle$	$\sum_L q_L^0 \{(1/14) \sin^2 \vartheta_L \exp(2i\varphi_L) \\ \times [-3F_2(R_L) - (5/3)(7 \cos^2 \vartheta_L - 1)F_4(R_L)]\}$
$\langle 2 \hat{v}_1 -1\rangle = \langle 1 \hat{v}_1 -2\rangle$	$\sum_L q_L^0 \{(5/12) \sin^3 \vartheta_L \cos \vartheta_L \exp(3i\varphi_L)F_4(R_L)\}$
$\langle 2 \hat{v}_1 -2\rangle$	$\sum_L q_L^0 \{(5/24) \sin^4 \vartheta_L \exp(4i\varphi_L)F_4(R_L)\}$

$$A_{k,m} = \frac{4\pi}{2k+1} \sum_{L=1}^N \frac{e^2}{4\pi\epsilon_0} \frac{q_L^0}{R_L^{k+1}} Y_{k,m}^*(\Theta_L, \Phi_L)$$

Although the crystal field potential has an infinite number of terms, only the first few terms will contribute on integration over the atomic d - or f -orbitals. The restrictions are:

TABLE 8.11

Independent matrix elements of the crystal field potential for f -orbitals^a

Element	Formula
$\langle 0 \hat{v}_1 0\rangle$	$\sum_L q_L^0 \{F_0(R_L) + (2/15)(3 \cos^2 \vartheta_L - 1)F_2(R_L)$ $+ (1/44)(35 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 3)F_4(R_L)$ $+ (25/1716)(231 \cos^6 \vartheta_L - 315 \cos^4 \vartheta_L + 105 \cos^2 \vartheta_L - 5)F_6(R_L)\}$
$\langle \pm 1 \hat{v}_1 \pm 1\rangle$	$\sum_L q_L^0 \{F_0(R_L) + (1/10)(3 \cos^2 \vartheta_L - 1)F_2(R_L)$ $+ (1/264)(35 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 3)F_4(R_L)$ $+ (25/2288)(231 \cos^6 \vartheta_L - 315 \cos^4 \vartheta_L + 105 \cos^2 \vartheta_L - 5)F_6(R_L)\}$
$\langle \pm 2 \hat{v}_1 \pm 2\rangle$	$\sum_L q_L^0 \{F_0(R_L) - (7/264)(35 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 3)F_4(R_L)$ $+ (5/1144)(231 \cos^6 \vartheta_L - 315 \cos^4 \vartheta_L + 105 \cos^2 \vartheta_L - 5)F_6(R_L)\}$
$\langle \pm 3 \hat{v}_1 \pm 3\rangle$	$\sum_L q_L^0 \{F_0(R_L) - (1/6)(3 \cos^2 \vartheta_L - 1)F_2(R_L)$ $+ (1/88)(35 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 3)F_4(R_L)$ $- (5/6864)(231 \cos^6 \vartheta_L - 315 \cos^4 \vartheta_L + 105 \cos^2 \vartheta_L - 5)F_6(R_L)\}$
$\langle 3 \hat{v}_1 2\rangle$	$\sum_L q_L^0 (1/\sqrt{6}) \sin \vartheta_L \cos \vartheta_L \exp(-i\varphi_L)$ $\times \{-F_2(R_L) + (5/22)(7 \cos^2 \vartheta_L - 3)F_4(R_L)$ $- (35/1144)(33 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 5)F_6(R_L)\}$
$\langle 3 \hat{v}_1 1\rangle$	$\sum_L q_L^0 (\sqrt{15}/2) \sin^2 \vartheta_L \exp(-2i\varphi_L)$ $\times \{-(1/15)F_2(R_L) + (1/22)(7 \cos^2 \vartheta_L - 1)F_4(R_L)$ $- (35/3432)(33 \cos^4 \vartheta_L - 18 \cos^2 \vartheta_L + 1)F_6(R_L)\}$
$\langle 3 \hat{v}_1 0\rangle$	$\sum_L q_L^0 (7\sqrt{5}/44) \sin^3 \vartheta_L \cos \vartheta_L \exp(-3i\varphi_L)$ $\times \{F_4(R_L) - (5/26)(11 \cos^2 \vartheta_L - 3)F_6(R_L)\}$
$\langle 3 \hat{v}_1 -1\rangle$	$\sum_L q_L^0 (7\sqrt{15}/88) \sin^4 \vartheta_L \exp(-4i\varphi_L)$ $\times \{(1/3)F_4(R_L) - (5/26)(11 \cos^2 \vartheta_L - 1)F_6(R_L)\}$
$\langle 3 \hat{v}_1 -2\rangle$	$\sum_L q_L^0 (-385\sqrt{6}/2288) \sin^5 \vartheta_L \cos \vartheta_L \exp(-5i\varphi_L)F_6(R_L)$
$\langle 3 \hat{v}_1 -3\rangle$	$\sum_L q_L^0 (-385/2288) \sin^6 \vartheta_L \exp(-6i\varphi_L)F_6(R_L)$

(contd.)

TABLE 8.11

Independent matrix elements of the crystal field potential for f -orbitals^a (*contd.*)

Element	Formula
$\langle 2 \hat{v}_1 -2\rangle$	$\sum_L q_L^0 (35/88) \sin^4 \vartheta_L \exp(-4i\varphi_L)$ $\times \{(1/3)F_4(R_L) + (3/13)(11 \cos^2 \vartheta_L - 1)F_6(R_L)\}$
$\langle 1 \hat{v}_1 -1\rangle$	$-\sum_L q_L^0 \sin^2 \vartheta_L \exp(-2i\varphi_L)$ $\times \{(1/5)F_2(R_L) + (5/66)(7 \cos^2 \vartheta_L - 1)F_4(R_L)$ $+ (175/2288)(33 \cos^4 \vartheta_L - 18 \cos^2 \vartheta_L + 1)F_6(R_L)\}$
$\langle 1 \hat{v}_1 0\rangle$	$-\sum_L q_L^0 (\sqrt{3}) \sin \vartheta_L \cos \vartheta_L \exp(-i\varphi_L)$ $\times \{(1/15)F_2(R_L) + (5/132)(7 \cos^2 \vartheta_L - 3)F_4(R_L)$ $+ (175/3432)(33 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 5)F_6(R_L)\}$
$\langle 2 \hat{v}_1 1\rangle$	$\sum_L q_L^0 (\sqrt{10}) \sin \vartheta_L \cos \vartheta_L \exp(-i\varphi_L)$ $\times \{-(1/10)F_2(R_L) - (1/33)(7 \cos^2 \vartheta_L - 3)F_4(R_L)$ $+ (35/2288)(33 \cos^4 \vartheta_L - 30 \cos^2 \vartheta_L + 5)F_6(R_L)\}$
$\langle 2 \hat{v}_1 0\rangle$	$\sum_L q_L^0 (\sqrt{30}/6) \sin^2 \vartheta_L \exp(-i\varphi_L)$ $\times \{-(1/5)F_2(R_L) - (1/44)(7 \cos^2 \vartheta_L - 1)F_4(R_L)$ $+ (35/572)(33 \cos^4 \vartheta_L - 18 \cos^2 \vartheta_L + 1)F_6(R_L)\}$
$\langle 2 \hat{v}_1 -1\rangle$	$\sum_L q_L^0 (7\sqrt{10}/44) \sin^3 \vartheta_L \cos \vartheta_L \exp(-3i\varphi_L)$ $\times \{(1/3)F_4(R_L) + (15/52)(11 \cos^2 \vartheta_L - 3)F_6(R_L)\}$

^aThe matrix elements are symmetric with respect to the secondary diagonal and form a Hermitian matrix.

- (1) there is $k \leq 2l$; this implies that for d -orbitals $k \leq 4$ and for f -orbitals $k \leq 6$;
- (2) k is even; this holds true because in the opposite cases

$$\langle \psi(\text{odd}) | V_k(\text{odd}) | \psi(\text{odd}) \rangle = 0$$

or

$$\langle \psi(\text{even}) | V_k(\text{odd}) | \psi(\text{even}) \rangle = 0$$

These requirements lead to a more restricted form of the crystal field potential

$$V(\vec{r}) = A_{0,0}r^0 Y_{0,0} + \sum_{m=-2}^{+2} A_{2,m}r^2 Y_{2,m} + \sum_{m=-4}^{+4} A_{4,m}r^4 Y_{4,m} \\ + \sum_{m=-6}^{+6} A_{6,m}r^6 Y_{6,m}$$

which is truncated after the third term when dealing with the d -orbitals only. The first term is evaluated as

$$V_0 = A_{0,0}r^0 Y_{0,0} = \frac{e^2}{4\pi\epsilon_0} \frac{q_L^0}{R_L} N$$

and it can be omitted from further consideration since it affects only the zero point of energy.

The above general form of the crystal field potential becomes even more restricted when the actual symmetry of the ligand environment is considered. Each symmetry operation $\hat{R}_i$ of the symmetry point group G must leave the potential invariant, i.e.

$$\hat{R}_i V(\vec{r}) = V(\vec{r})$$

This requirement leads to some relationships among the expansion coefficients $A_{k,m}$ valid for the particular symmetry group. For example, within the O_h group it is [7]

$\hat{R}_i$	Restriction
$\hat{C}_4$	$k = 0, \pm 4, \pm 8, \dots$
$\hat{\sigma}_{xz}$	$A_{4,4} = A_{4,-4}$
$\hat{C}_3$	$A_{2,0} = 0; A_{4,4} = \sqrt{5/14} A_{4,0}$

and the crystal field potential adopts the form of

$$V'(\vec{r}) = V(\vec{r}) - V_0 = A_{4,0}r^4[Y_{4,0} + \sqrt{5/14}Y_{4,-4}], \quad (\text{for } O_h)$$

TABLE 8.12

Crystal field potentials applicable for *d*-electrons [7]^a

Group	Coord. No.	Potential $V'(\vec{r})/(e^2/4\pi\epsilon_0)q_L^0$
D_{4d}	8 (antiprism)	$-(14/3\sqrt{\pi})a_4r^4Y_{4,0}$
O_h	8 (cube)	$-(14/3\sqrt{\pi})a_4r^4[Y_{4,0} + \sqrt{5/14}(Y_{4,4} + Y_{4,-4})]$
O_h	6 (octahedron)	$(21/4\sqrt{\pi})a_4r^4[Y_{4,0} + \sqrt{5/14}(Y_{4,4} + Y_{4,-4})]$
O_h	6 (octahedron)	$-\sqrt{\pi}(14/9)R_L^{-5}r^4[Y_{4,0} + \sqrt{10/7}(Y_{4,3} - Y_{4,-3})]$
D_{4h}	6 (bipyramide)	$2\sqrt{2\pi}\sqrt{49/72}R_L^{-5}r^4[Y_{4,0} + \sqrt{5/14}(Y_{4,4} + Y_{4,-4})]$
	[MA ₄ B ₂]	$-2\sqrt{2\pi}\sqrt{2/5}r^2(R_A^{-3} - R_B^{-3})Y_{2,0} - 2\sqrt{2\pi}\sqrt{2/9}r^4(R_A^{-5} - R_B^{-5})Y_{4,0}$
D_{3d}	6 (antiprism)	$(12/5)\sqrt{2\pi}\sqrt{5/8}R_L^{-3}r^2(3\cos^2\vartheta - 1)Y_{2,0}$ $+ (12/9)\sqrt{2\pi}\sqrt{9/128}R_L^{-5}r^4(35\cos^4\vartheta - 30\cos^2\vartheta + 3)Y_{4,0}$ $+ (35/2)\sqrt{2\pi}R_L^{-5}r^4\sin^3\vartheta\cos\vartheta(Y_{4,3} - Y_{4,-3})$
T_d	4 (tetrahedron)	$-(7/3\sqrt{\pi})a_4r^4[Y_{4,0} + \sqrt{5/14}(Y_{4,4} + Y_{4,-4})]$
D_{4h}	4 (square)	$-(5/\sqrt{\pi})a_2r^2Y_{2,0} + (9/4\sqrt{\pi})a_4r^4[Y_{4,0} + \sqrt{35/18}(Y_{4,4} + Y_{4,-4})]$
D_{2d}	4 (bisphenoid)	$(8/5)\sqrt{2\pi}\sqrt{5/8}R_L^{-3}r^2(3\cos^2\vartheta - 1)Y_{2,0}$ $+ (8/9)\sqrt{2\pi}\sqrt{9/128}R_L^{-5}r^4(35\cos^4\vartheta - 30\cos^2\vartheta + 3)Y_{4,0}$ $+ (8/9)\sqrt{2\pi}\sqrt{315/256}R_L^{-5}r^4\sin^4\vartheta(Y_{4,4} + Y_{4,-4})$

^aThe ligand integrals are equal to: $a_2 = (4\pi/5)R_L^{-3}$ and $a_4 = (4\pi/9)R_L^{-5}$.

When the actual positions of every ligand are taken into account, the coefficients $A_{k,m}$ can be easily evaluated. Some crystal field potentials are presented in Table 8.12.

8.2.3 Symmetry descent

A free atom belongs to the continuous *rotation group* **R**₃. The irreducible representations of group **R**₃ are labelled by the quantum number *l*. The spherical harmonic functions $Y_{l,m}$ form the basis of the irreducible representation of **R**₃ with the dimension $2l + 1$.

The operation of rotation through an angle α about the *z*-axis yields

$$\hat{R}_\alpha Y_{l,m} = \exp(im\alpha) Y_{l,m}$$

Such a rotation has a representation expressed through the $2l + 1$ dimensional matrix

$$D_l(\hat{R}_\alpha) = \begin{pmatrix} \exp[i/l\alpha] & 0 & \dots & 0 \\ 0 & \exp[i(l-1)\alpha] & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \exp[-il\alpha] \end{pmatrix}$$

Therefore the character of this operation (a trace of the transformation matrix) is the sum of the geometric series, i.e.

$$\chi_l(\alpha) = \frac{\sin[(l+1/2)\alpha]}{\sin(\alpha/2)}$$

One can then arrive at the progression

α	$\hat{R}_\alpha$	$\chi_l(\hat{R}_\alpha)$
0	$\hat{E}$	$2l+1$
π	$\hat{C}_2$	$(-1)^l$
$(2/3)\pi$	$\hat{C}_3$	$1, l=3k$ $0, l=3k+1$ $-1, l=3k+2$
$(1/2)\pi$	$\hat{C}_4$	$(-1)^{l/2}, \text{ even } l$ $(-1)^{(l-1)/2}, \text{ odd } l$

Then the standard form of the character table is arranged in Table 8.13.

Let us suppose that within an initial group G_0 the state vectors corresponding to the degenerate energy level E are transformed according to the irreducible representation Γ . When the symmetry descent occurs to a subgroup G , the degenerate level E is split into the levels $E_1, E_2, \dots, E_n$, each corresponding to the representations $\Gamma_1, \Gamma_2, \dots, \Gamma_n$ of the subgroup G

$$E(\Gamma) \xrightarrow{G_0 \rightarrow G} \begin{cases} E_1(\Gamma_1) \\ E_2(\Gamma_2) \\ \dots \\ E_n(\Gamma_n) \end{cases}$$

TABLE 8.13

Character table of the rotation group R_3

R_3	$\hat{E}$	$\hat{C}_2$	$\hat{C}_3$	$\hat{C}_4$
$s (l=0)$	1	1	1	1
$p (l=1)$	3	-1	0	1
$d (l=2)$	5	1	-1	-1
$f (l=3)$	7	-1	1	-1

The irreducible representation Γ of the group $\mathbf{G}_0$ appears in the subgroup $\mathbf{G}$ to be reducible; thus a decomposition into a set of irreducible representations is possible

$$\Gamma(\mathbf{G}) \rightarrow \sum_{i=1} n_i \Gamma_i$$

The decomposition of the reducible representation into irreducible ones proceeds through the *reduction formula*

$$n_i = \frac{1}{g(\mathbf{G})} \sum_{\text{all } \hat{R}} \chi_{\Gamma}(\hat{R}) \cdot \chi_{\Gamma_i}(\hat{R})$$

where $g(\mathbf{G})$ is the order of the subgroup $\mathbf{G}$; the summation runs over all symmetry operations common for the group $\mathbf{G}_0$ and its subgroup $\mathbf{G}$.

The application of the reduction formula is exemplified by the decomposition of the D_2 representation of the group $\mathbf{R}_3$ in terms of the irreducible representations of the cubic group $\mathbf{O}$ which has a character table according to Table 8.14.

Now the appearances of the individual irreducible representations are evaluated according to a reduction formula of the form

$$n(\Gamma_i) = \frac{1}{24} \left[\chi_{\Gamma}(\hat{E}) \cdot \chi_{\Gamma_i}(\hat{E}) + \chi_{\Gamma}(\hat{C}_4) \cdot 6\chi_{\Gamma_i}(\hat{C}_4) \right. \\ \left. + \chi_{\Gamma}(\hat{C}_4^2) \cdot 3\chi_{\Gamma_i}(\hat{C}_4^2) + \chi_{\Gamma}(\hat{C}_3) \cdot 8\chi_{\Gamma_i}(\hat{C}_3) + \chi_{\Gamma}(\hat{C}_2) \cdot 6\chi_{\Gamma_i}(\hat{C}_2) \right]$$

yielding

$$n(A_1) = \frac{1}{24} [5 \cdot 1 + (-1) \cdot 6 \cdot 1 + 1 \cdot 3 \cdot 1 + (-1) \cdot 8 \cdot 1 + 1 \cdot 6 \cdot 1] = 0$$

TABLE 8.14
Character table of the cubic group $\mathbf{O}$

$\mathbf{O}$	$\hat{E}$	$6\hat{C}_4$	$3\hat{C}_4^2$	$8\hat{C}_3$	$6\hat{C}_2$
A_1	1	1	1	1	1
A_2	1	-1	1	1	-1
E	2	0	2	-1	0
T_1	3	1	-1	0	-1
T_2	3	-1	-1	0	1

and analogously

$$n(A_2) = 0$$

$$n(E_2) = 1$$

$$n(T_1) = 0$$

$$n(T_2) = 1$$

The result is that the representation D_2 of the group $\mathbf{R}_3$ is decomposed into irreducible representations of the group $\mathbf{O}$ as follows

$$D_2 \xrightarrow{\mathbf{R}_3 \rightarrow \mathbf{O}} D_E + D_{T_2}$$

This result can be interpreted in the way that the five-fold degenerate d -level ($l = 2$) of a free atom is split, in the case of cubic symmetry, into a doubly degenerate level E and a triply degenerate level T_2 . Another important result of great interest is

$$D_3 \xrightarrow{\mathbf{R}_3 \rightarrow \mathbf{O}} D_{A_2} + D_{T_1} + D_{T_2}$$

which means that the seven-fold degenerate level ($l = 3$) of a free atom is split into a non-degenerate level A_2 and two triply degenerate levels T_1 and T_2 . These results are valid both for the one-electron states of atoms and for many-electron states (terms). Since the ground state terms of the electron configurations d^n are either ${}^mD$ ($L = 2$) or ${}^mF$ ($L = 3$), then the above-derived splitting scheme within the group $\mathbf{O}$ is complete when the ground terms are concerned. The splitting of states for some groups is listed in Table 8.15.

8.2.4 Irreducible tensors

For further consideration, let us remember that the expression

$$\hat{T}_{k,m} = r^k Y_{k,m}(\vartheta, \varphi)$$

in fact represents the m th component of an irreducible tensor operator of rank k . Then the crystal field potential can be viewed as a linear combination of irreducible tensors

$$V(\vec{r}) = \sum_{k=0}^{\infty} \sum_{m=-k}^{+k} A_{k,m} \hat{T}_{k,m}(\vec{r})$$

TABLE 8.15
Splitting of one-electron levels in crystal fields of different symmetry

Level	O	T _d	O _h	D _{4h}	D _{2h}	D ₃	C _{4v}	C _{2v}
<i>s</i>	A_1	A_1	A_{1g}	A_{1g}	A_1	A_1	A_1	A_1
<i>p</i>	T_1	T_2	T_{1u}	$A_{2u} + E_u$	$B_2 + E$	$A_2 + E$	$A_1 + E$	$A_1 + B_1 + B_2$
<i>d</i>	E	E	E_g	$A_{1g} + B_{1g}$	$A_1 + B_1$	E	$A_1 + B_1$	$2A_1$
	T_2	T_2	T_{2g}	$B_{2g} + E_g$	$B_2 + E$	$A_1 + E$	$B_2 + E$	$A_1 + B_1 + B_2$
<i>f</i>	A_2	A_2	A_{2u}	B_{1u}	$A_1 + A_2$	A_2	B_2	A_2
	T_1	T_2	T_{1u}	$A_{1u} + E_u$	$+B_2 + 2E$	$A_2 + E$	$A_1 + E$	$A_1 + B_1 + B_2$
	T_2	T_1	T_{2u}	$B_{2u} + E_u$		$A_1 + E$	$B_1 + E$	$A_1 + B_1 + B_2$
<i>g</i>	A_1	A_1	A_{1g}	A_{1g}	$2A_1 + A_2$	A_1	A_1	A_1
	E	E	E_g	$A_{1g} + B_{1g}$	$+B_1 + B_2$	E	$A_1 + B_1$	$2A_1$
	T_1	T_1	T_{1g}	$A_{2g} + E_g$	$+2E$	$A_2 + E$	$A_2 + E$	$A_2 + B_1 + B_2$
	T_2	T_2	T_{2g}	$B_{2g} + E_g$		$A_1 + E$	$B_2 + E$	$A_2 + B_1 + B_2$
<i>h</i>	E	E	E_u	$A_{1u} + B_{1u}$	$A_1 + A_2 + B_1$	E	$A_2 + B_2$	$2A_2$
	$2T_1$	$2T_2$	$2T_{1u}$	$2(A_{2u} + E_u)$	$+2B_2 + 3E$	$2(A_2 + E)$	$2(A_1 + E)$	$2(A_1 + B_1 + B_2)$
	T_2	T_1	T_{2u}	$B_{2u} + E_u$		$A_1 + E$	$B_1 + E$	$A_1 + B_1 + B_2$
<i>i</i>	A_1	A_1	A_{1g}	A_{1g}	$2A_1 + A_2$	A_1	A_1	A_1
	A_2	A_2	A_{2g}	B_{1g}	$+2B_1 + 2B_2$	A_2	B_1	A_1
	E	E	E_g	$A_{1g} + B_{1g}$	$+3E$	E	$A_1 + B_1$	$2A_1$
	T_1	T_1	T_{1g}	$A_{2g} + E_g$		$A_2 + E$	$A_2 + E$	$B_1 + A_2 + B_2$
	$2T_2$	$2T_2$	$2T_{2g}$	$2(B_{2g} + E_g)$		$2(A_1 + E)$	$2(B_2 + E)$	$2(B_1 + A_2 + B_2)$

As already noted, the crystal field potential should be invariant under all the transformations of the symmetry point group. This means that it is transformed according to the totally symmetric representation (A_1) of the group $\mathbf{G}$. The spherical tensor component $\hat{T}_{k,m}$ appears within the crystal field potential when the decomposition of the irreducible representations D_k of the rotation group $\mathbf{R}_3$ in terms of irreducible representations Γ_i of the point group $\mathbf{G}$ contains the totally symmetric representation A_1

$$D_k \xrightarrow{\mathbf{R}_3 \rightarrow \mathbf{G}} \sum_i \Gamma_i = A_1 + \dots$$

Otherwise, the components $\hat{T}_{k,m}$ cannot form a linear combination invariant under the symmetry operations of the group $\mathbf{G}$.

The generation of functions which transform according to the irreducible representations of the symmetry point group is a more difficult task. It is based on the following steps [8].

1. The irreducible representation D_l of the rotation group $\mathbf{R}_3$ is decomposed into a sum of irreducible representations Γ_i of the point group $\mathbf{G}$, using the reduction formula.
2. The operations $\hat{R}$ of the point group $\mathbf{G}$ are expressed through a set of Euler angles (α, β, γ) ; the sequence of the Euler rotations is:
 - (a) rotation about the z -axis through an angle $0 \leq \gamma < 2\pi$;
 - (b) rotation about the y -axis through an angle $0 \leq \beta < \pi$;
 - (c) rotation about the z -axis through an angle $0 \leq \alpha < 2\pi$.
3. The results of the action of the operations $\hat{R}(\alpha\beta\gamma)$ on the set of spherical harmonic functions (representing basis elements of the reducible representation within the subgroup $\mathbf{G}$) are obtained as follows

$$\hat{R}(\alpha\beta\gamma)Y_{l,m} = \sum_{m'=-l}^{+l} [D_l(\alpha\beta\gamma)]_{m',m} Y_{l,m'}$$

where the $2l+1$ dimensional transformation matrix has the elements

$$\begin{aligned} [D_l(\alpha\beta\gamma)]_{m',m} &= \int Y_{l,m'}^* \hat{R} Y_{l,m} dV \\ &= \sum_{\kappa=\kappa_{\min}}^{\kappa_{\max}} (-1)^\kappa \frac{[(l+m)!(l-m)!(l+m')!(l-m')!]^{1/2}}{(l-m'-\kappa)!(l+m-\kappa)!\kappa!(\kappa+m'-l)!} \\ &\quad \times [\cos(\beta/2)]^{2l-m-m'-2\kappa} [\sin(\beta/2)]^{2\kappa+m'-m} \exp(im'\alpha + im\gamma) \end{aligned}$$

with

$$\kappa_{\min} = \max\{0, l - m'\}$$

$$\kappa_{\max} = \min\{l - m', l + m\}$$

4. The functions $|\Gamma_i, \gamma_i\rangle$ transformed according to the irreducible representations Γ_i are calculated with the help of the projection operator defined as

$$\hat{P}(\Gamma, \gamma) = \frac{g(\Gamma)}{g(\mathbf{G})} \sum_{\hat{R}} [D_{\Gamma}(\hat{R})]_{\gamma\gamma}^* \hat{R}$$

where $[D_{\Gamma}(\hat{R})]_{\gamma\gamma}$ is a diagonal element of the transformation matrix of the operation $\hat{R}$ in the irreducible representation Γ . Such a matrix fulfils the general transformation relation

$$\hat{R}|\Gamma, \gamma\rangle = \sum_{\gamma'} [D_{\Gamma}(\hat{R})]_{\gamma\gamma'} |\Gamma, \gamma'\rangle$$

The projection operator leaves unchanged the functions $|\Gamma_i, \gamma_i\rangle$ that constitute the basis of the irreducible representation Γ , i.e.

$$\hat{P}(\Gamma, \gamma)|\Gamma, \gamma\rangle = |\Gamma, \gamma\rangle$$

and annihilates functions belonging to other representations, viz.

$$\hat{P}(\Gamma, \gamma)|\Gamma', \gamma'\rangle = 0$$

Once the basis function of the irreducible representation Γ is determined, the remaining functions are generated through the projection operator

$$\hat{P}(\Gamma, \gamma, \gamma') = \frac{g(\Gamma)}{g(\mathbf{G})} \sum_{\hat{R}} [D_{\Gamma}(\hat{R})]_{\gamma\gamma'}^* \hat{R}$$

as

$$\hat{P}(\Gamma, \gamma', \gamma)|\Gamma, \gamma\rangle = |\Gamma, \gamma'\rangle$$

The above procedure is much simplified when the one-dimensional representation A_1 is involved; all transformation matrices are one-dimensional, equal to 1.

8.2.5. Splitting of d -levels in a weak crystal field

Group theory is capable of predicting the symmetry of the states upon the symmetry descent due to the crystal field. However, it is incapable of predicting either the sign or the magnitude of the splitting. For this purpose the eigenvalue problem should be solved. When the crystal field operator is taken as a (small) perturbation acting on the free-atom terms, we speak about the weak crystal field. Then the energy levels are determined by first-order perturbation theory for degenerate states by solving the secular equation in the basis set of the term functions $|I\rangle = |L, M_L, S, M_S\rangle$ as follows

$$\det\{v_{IJ} - \delta_{IJ}\varepsilon\} = 0$$

For the simplest case of a one-electron configuration d^1 the term functions are identical with the d -orbitals, and thus the formulae for the pertinent matrix elements listed in Table 8.10 are directly applicable. Then the 5×5 secular determinant is solved. For the case of an octahedral complex the matrix elements of the crystal field potential in the basis set of spherical harmonic functions $Y_{l,m}$ form the matrix

$$\mathbf{v} = E_0 \mathbf{I} + \frac{\Delta}{10} \begin{pmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{pmatrix}$$

where we use the substitutions

$$E_0 = 6qF_0(R)$$

and

$$\Delta \equiv 10Dq = \frac{5}{3}qF_4(R)$$

The roots of the secular equation become

$$\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = E_0 - \frac{4}{10}\Delta = q\left[6F_0(R) - \frac{2}{3}F_4(R)\right]$$

$$\varepsilon_4 = \varepsilon_5 = E_0 + \frac{6}{10}\Delta = q[6F_0(R) + F_4(R)]$$

These roots span the irreducible representations T_{2g} and E_g of the octahedral group O_h . The same result is obtained when, from the basis set functions, the combinations transforming according to the irreducible representations of the octahedral group are formed

$$|T_{2g}, 1\rangle = -\frac{i}{\sqrt{2}}(Y_{2,2} - Y_{2,-2}) = d_{xy}$$

$$|T_{2g}, 2\rangle = -\frac{1}{\sqrt{2}}(Y_{2,1} - Y_{2,-1}) = d_{xz}$$

$$|T_{2g}, 3\rangle = \frac{i}{\sqrt{2}}(Y_{2,1} + Y_{2,-1}) = d_{yz}$$

$$|E_g, 1\rangle = Y_{2,0} = d_{z^2}$$

$$|E_g, 2\rangle = \frac{1}{\sqrt{2}}(Y_{2,2} + Y_{2,-2}) = d_{x^2-y^2}$$

In such a basis set the above Hamiltonian matrix is already diagonal.

For a many-electron system the matrix elements between the term functions should be combined via the matrix elements over the one-electron functions. For example, the matrix elements of the crystal field potential over the functions of the ^3F term of the electron configuration d^2 are

$$v = 2E_0 I + \frac{\Delta}{10} \begin{pmatrix} -3 & 0 & 0 & 0 & \sqrt{15} & 0 & 0 \\ 0 & 7 & 0 & 0 & 0 & -5 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & \sqrt{15} \\ 0 & 0 & 0 & -6 & 0 & 0 & 0 \\ \sqrt{15} & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & -5 & 0 & 0 & 0 & 7 & 0 \\ 0 & 0 & \sqrt{15} & 0 & 0 & 0 & -3 \end{pmatrix}$$

They yield the following roots of the secular equation

$$\varepsilon_3(A_{1g}) = 2E_0 + \frac{6}{5}\Delta = q[12F_0(R) + 2F_4(R)]$$

$$\varepsilon_{2,4,5}(T_{2g}) = 2E_0 + \frac{1}{5}\Delta = q[12F_0(R) + \frac{1}{3}F_4(R)]$$

$$\varepsilon_{1,6,7}(T_{1g}) = 2E_0 - \frac{3}{5}\Delta = q[12F_0(R) - 4F_4(R)]$$

The splitting of other atomic terms due to the crystal field potential of the given symmetry (group) can be evaluated in an analogous way [9]. The results for octahedral and tetrahedral fields are collected in Table 8.16.

From the above formulae it is evident that the splitting of an atomic term is a linear function of the crystal field strength parameter Δ . For larger values of Δ , however, the energies of certain states originating in different atomic terms tend to cross over. For example, the states $T_{1g}({}^3F)$ and $T_{1g}({}^3P)$ of the electron configuration d^2 approach each other at the higher Δ . In such a case the approximation of the weak crystal field loses its battle and the correct treatment is represented by the intermediate crystal field.

8.2.6 Equivalent operator treatment

We have already seen that the crystal field potential can be rather simply expressed through a set of radial parameters and the irreducible tensor operators $\hat{T}_{k,m}$ which refer to a certain, symmetry-predetermined combination of spherical harmonic functions (see Table 8.12). Such an expression can be written in several equivalent forms

TABLE 8.16
Energy levels of free ions in weak octahedral and tetrahedral crystal fields

O_h	T_d	Atomic term	Split term	$d_L d_S$	Energy
d^1	d^9	${}^2D$	${}^2E_g$	4	$+(6/10)\Delta$
			${}^2T_{2g}$	6	$-(4/10)\Delta$
d^2	d^8	${}^3F$	${}^3A_{2g}$	3	$+(12/10)\Delta$
			${}^3T_{2g}$	9	$+(2/10)\Delta$
			${}^3T_{1g}$	9	$-(6/10)\Delta$
d^3	d^7	${}^4F$	${}^4T_{1g}$	12	$+(6/10)\Delta$
			${}^4T_{2g}$	12	$-(2/10)\Delta$
			${}^4A_{2g}$	4	$-(12/10)\Delta$
d^4	d^6	${}^5D$	${}^5T_{2g}$	15	$+(4/10)\Delta$
			${}^5E_g$	10	$-(6/10)\Delta$
d^5	d^5	${}^6S$	${}^6A_{1g}$	6	0
d^6	d^4	${}^5D$	${}^5E_g$	10	$+(6/10)\Delta$
			${}^5T_{2g}$	15	$-(4/10)\Delta$
d^7	d^3	${}^4F$	${}^4A_{2g}$	4	$+(12/10)\Delta$
			${}^4T_{2g}$	12	$+(2/10)\Delta$
			${}^4T_{1g}$	12	$-(6/10)\Delta$
d^8	d^2	${}^3F$	${}^3T_{1g}$	9	$+(6/10)\Delta$
			${}^3T_{2g}$	9	$-(2/10)\Delta$
			${}^3A_{2g}$	3	$-(12/10)\Delta$
d^9	d^1	${}^2D$	${}^2T_{2g}$	6	$+(4/10)\Delta$
			${}^2E_g$	4	$-(6/10)\Delta$

$$\begin{aligned}
V(\vec{r}) &= \sum_{k=0,2,4,6} \sum_{m=-k}^{+k} A_{k,m} r^k Y_{k,m}(\vartheta, \varphi) \\
&= \sum_{k=0,2,4,6} \sum_{m=-k}^{+k} A'_{k,m} r^k \hat{C}_{k,m}(\vartheta, \varphi) \\
&= \sum_{k=0,2,4,6} \sum_{m=-k}^{+k} A_{k,m} \hat{T}_{k,m}(\vec{r}) \\
&= \sum_{k=0,2,4,6} \sum_{m=0}^{+k} A''_{k,m} P_{k,m}(x, y, z) \\
&= \sum_{k=0,2,4,6} \sum_{m=0}^{+k} B_k^m \hat{O}_k^m(\hat{J}_z, \hat{J}_{\pm})
\end{aligned}$$

Here $Y_{k,m}$ are the spherical harmonic functions; $\hat{C}_{k,m} = \sqrt{4\pi/(2k+1)} Y_{k,m}$ is the Racah tensor operator; $\hat{T}_{k,m} = r^k Y_{k,m}$ is the irreducible tensor operator; $P_{k,m}$ (not to be confused with the Legendre polynomials) are unnormalised homogeneous polynomials of Cartesian coordinates proportional to the function $r^k(Y_{k,m} + Y_{k,-m})$; $\hat{O}_k^m$ are referred to as *equivalent operators* which are constructed of only the angular momentum operators.

The passage from the spherical harmonic functions and/or their combinations to the equivalent operators is based on the Wigner–Eckart theorem and consequently on the replacement theorem. The reduction of a matrix element to the reduced matrix element and a Clebsch–Gordan coefficient

$$\langle jm | \hat{T}_{k,n} | jm' \rangle = \frac{1}{\sqrt{2j+1}} \langle jm' kn | jm \rangle \langle j || \hat{T}_k || j \rangle$$

and a similar reduction

$$\langle jm | \hat{O}_k^n | jm' \rangle = \frac{1}{\sqrt{2j+1}} \langle jm' kn | jm \rangle \langle j || \hat{O}_k || j \rangle$$

make it possible to write the proportionality

$$\langle jm | \hat{T}_{k,n} | jm' \rangle = \alpha(k, j) \langle jm | \hat{O}_k^n | jm' \rangle$$

with the proportionality factor

$$\alpha(k, j) = \frac{\langle j || \hat{T}_k || j \rangle}{\langle j || \hat{O}_k || j \rangle}$$

Therefore, instead of the irreducible tensor components, a proper combination of the angular momentum operators ($\hat{J}_z, \hat{J}_+, \hat{J}_-$) is applicable. However, the expansion coefficients (the potential constants) need to be redefined to account for the proportionality factor $\alpha(k, j)$. A set of equivalent operators is compiled in Table 8.17. It is quite practical to handle the equivalent operators since they can be easily constructed by matrix multiplications with the help of computers.

The shift (raising and lowering) operators have their Cartesian analogues as follows

$$\frac{1}{2}(\hat{J}_+^2 + \hat{J}_-^2) = \hat{J}_x^2 - \hat{J}_y^2$$

$$\frac{1}{2}(\hat{J}_+^3 + \hat{J}_-^3) = \hat{J}_x^3 - \hat{J}_x\hat{J}_y^2 - \hat{J}_y\hat{J}_x^2\hat{J}_y - \hat{J}_y^2\hat{J}_x$$

$$\begin{aligned} \frac{1}{2}(\hat{J}_+^4 + \hat{J}_-^4) = & \hat{J}_x^4 + \hat{J}_y^4 - \hat{J}_x^2\hat{J}_y^2 - \hat{J}_y^2\hat{J}_x^2 - \hat{J}_x\hat{J}_y^2\hat{J}_x - \hat{J}_y\hat{J}_x^2\hat{J}_y \\ & - \hat{J}_x\hat{J}_y\hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x\hat{J}_y\hat{J}_x \end{aligned}$$

The crystal field potential expressed in terms of the equivalent operators adopts quite a simple form. For example, when the d -electrons are involved, the crystal field potential for the octahedral system becomes expressed as

$$V(\mathbf{O}_h) = B_4(\hat{O}_4^0 + 5\hat{O}_4^4)$$

The constant term $B_0^0\hat{O}_0^0$ was omitted since it affects only the zero point of energy. In treating this prescription quantitatively we need to specify the angular momentum and its matrices. For example, for the ${}^2D$ term there is $L = 2$ and thus

$$\begin{aligned} \hat{L}_z = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -2 \end{pmatrix}, \quad \hat{L}_+ = \begin{pmatrix} 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{6} & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\ \hat{L}_- = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{6} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix} \end{aligned}$$

so that the crystal field operator becomes

$$\hat{V}(\mathbf{O}_h) = B_4(35\hat{L}_z^4 - 155\hat{L}_z^2 + 72\hat{I}) + 5B_4(1/2)(\hat{L}_+^4 + \hat{L}_-^4)$$

TABLE 8.17
Equivalent operators [10, 11]

$\hat{O}_2^0 = 3\hat{J}_z^2[\hbar^{-2}] - J(J+1)$
$\hat{O}_2^1 = \frac{1}{4}[\hat{J}_z(\hat{J}_+ + \hat{J}_-) + (\hat{J}_+ + \hat{J}_-)\hat{J}_z][\hbar^{-2}]$
$\hat{O}_2^2 = \frac{1}{2}(\hat{J}_+^2 + \hat{J}_-^2)[\hbar^{-2}]$
$\hat{O}_4^0 = 35\hat{J}_z^4[\hbar^{-4}] + [-30J(J+1) + 25]\hat{J}_z^2[\hbar^{-2}] - 6J(J+1) + 3J^2(J+1)^2$
$\hat{O}_4^1 = \frac{1}{4}\{[7\hat{J}_z^2[\hbar^{-2}] - 3J(J+1) - 1]\hat{J}_z(\hat{J}_+ + \hat{J}_-) + (\hat{J}_+ + \hat{J}_-)\hat{J}_z[7\hat{J}_z^2[\hbar^{-2}] - 3J(J+1) - 1]\}[\hbar^{-2}]$
$\hat{O}_4^2 = \frac{1}{4}\{[7\hat{J}_z^2[\hbar^{-2}] - J(J+1) - 5](\hat{J}_+^2 + \hat{J}_-^2) + (\hat{J}_+^2 + \hat{J}_-^2)[7\hat{J}_z^2[\hbar^{-2}] - J(J+1) - 5]\}[\hbar^{-2}]$
$\hat{O}_4^3 = \frac{1}{4}[\hat{J}_z(\hat{J}_+^3 + \hat{J}_-^3) + (\hat{J}_+^3 + \hat{J}_-^3)\hat{J}_z][\hbar^{-4}]$
$\hat{O}_4^4 = \frac{1}{2}(\hat{J}_+^4 + \hat{J}_-^4)[\hbar^{-4}]$
$\hat{O}_6^0 = 231\hat{J}_z^6[\hbar^{-6}] + [-315J(J+1) + 735]\hat{J}_z^4[\hbar^{-4}] + [105J^2(J+1)^2 - 525J(J+1) + 294]\hat{J}_z^2[\hbar^{-2}] - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1)$
$\hat{O}_6^1 = \frac{1}{4}\{[35\hat{J}_z^4[\hbar^{-4}] - (30J(J+1) - 15)\hat{J}_z^2[\hbar^{-2}] + (5J^2(J+1)^2 - 10J(J+1) + 12)]\hat{J}_z(\hat{J}_+ + \hat{J}_-)$ $+ (\hat{J}_+ + \hat{J}_-)\hat{J}_z[35\hat{J}_z^4[\hbar^{-4}] - (30J(J+1) - 15)\hat{J}_z^2[\hbar^{-2}] + (5J^2(J+1)^2 - 10J(J+1) + 12)]\}[\hbar^{-2}]$
$\hat{O}_6^2 = \frac{1}{4}\{[33\hat{J}_z^4[\hbar^{-4}] - (18J(J+1) + 123)\hat{J}_z^2[\hbar^{-2}] + J^2(J+1)^2 + 10J(J+1) + 102](\hat{J}_+^2 + \hat{J}_-^2)$ $+ (\hat{J}_+^2 + \hat{J}_-^2)[33\hat{J}_z^4[\hbar^{-4}] - (18J(J+1) + 123)\hat{J}_z^2[\hbar^{-2}] + J^2(J+1)^2 + 10J(J+1) + 102)]\}[\hbar^{-2}]$
$\hat{O}_6^3 = \frac{1}{4}\{[11\hat{J}_z^2[\hbar^{-2}] - 3J(J+1) - 59]\hat{J}_z(\hat{J}_+^3 + \hat{J}_-^3) + (\hat{J}_+^3 + \hat{J}_-^3)\hat{J}_z[11\hat{J}_z^2[\hbar^{-2}] - 3J(J+1) - 59]\}[\hbar^{-4}]$
$\hat{O}_6^4 = \frac{1}{4}\{[11\hat{J}_z^2[\hbar^{-2}] - J(J+1) - 38](\hat{J}_+^4 + \hat{J}_-^4) + (\hat{J}_+^4 + \hat{J}_-^4)[11\hat{J}_z^2[\hbar^{-2}] - J(J+1) - 38]\}[\hbar^{-4}]$
$\hat{O}_6^5 = \frac{1}{4}[\hat{J}_z(\hat{J}_+^5 + \hat{J}_-^5) + (\hat{J}_+^5 + \hat{J}_-^5)\hat{J}_z][\hbar^{-6}]$
$\hat{O}_6^6 = \frac{1}{2}(\hat{J}_+^6 + \hat{J}_-^6)[\hbar^{-6}]$

Here $\hat{I}$ is the 5×5 unit matrix. The matrix multiplication (which is easy with the help of computers) yields

$$\begin{aligned}\hat{V}(\mathbf{O}_h) &= B_4 \begin{pmatrix} 12 & 0 & 0 & 0 & 0 \\ 0 & -48 & 0 & 0 & 0 \\ 0 & 0 & 72 & 0 & 0 \\ 0 & 0 & 0 & -48 & 0 \\ 0 & 0 & 0 & 0 & 12 \end{pmatrix} + 5B_4 \begin{pmatrix} 0 & 0 & 0 & 0 & 12 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 12 & 0 & 0 & 0 & 0 \end{pmatrix} \\ &= 12B_4 \begin{pmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{pmatrix}\end{aligned}$$

which is exactly the same result as that obtained by the more laborious treatment above.

The departure from octahedral symmetry is described by an enlargement of the crystal field potential for lower symmetry terms. A tetragonal distortion is described by the potential

$$\hat{V}(\mathbf{D}_{4h}) = B_4(\hat{O}_4^0 + 5\hat{O}_4^4) + B_{2D}^0\hat{O}_2^2 + B_{4D}^0\hat{O}_4^0$$

and a trigonal distortion by

$$\hat{V}(\mathbf{D}_{3d}) = (-2/3)B_4(\hat{O}_4^0 + 20\sqrt{2}\hat{O}_4^3) + B_{2D}^0\hat{O}_2^2 + B_{4D}^0\hat{O}_4^0$$

Using the corresponding matrix products of the angular momentum operators, one gets

$$\begin{aligned}\hat{V}(\mathbf{D}_{4h}) &= 12B_4 \begin{pmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{pmatrix} + B_{2D}^0 \begin{pmatrix} 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 3 & 0 \\ \sqrt{6} & 0 & 0 & 0 & \sqrt{6} \\ 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \end{pmatrix} \\ &\quad + 12B_{4D}^0 \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}\end{aligned}$$

The tetragonal distortion of an octahedral pattern is a frequent case of interest and the following potential constants are often used

$$a = 120B_4$$

$$D = 3B_{2D}^0$$

$$F = 180B_{4D}^0$$

Although analytic expressions for the potential constants exist, they are rarely calculated directly. The covalency degree, uncertainties of effective ligand charges and other conceptual drawbacks make such an approach problematic. The potential constants are more often taken as free parameters of the theory which enter the final formulae of electron spectroscopy, electron spin resonance and magnetochemistry. The potential constants in different representations of the crystal field potential obey simple proportionality relationships which can be found in special monographs [10–13]. For example, the potential expressed through the Racah operators

$$V(\mathbf{D}_4) = \alpha r^2 \hat{C}_{2,0} + \beta r^4 \hat{C}_{4,0} + \gamma r^4 (\hat{C}_{4,4} + \hat{C}_{4,-4})/\sqrt{2}$$

has the potential constants related to the crystal field splitting parameters as follows

$$\alpha \langle r^2 \rangle = -7Ds$$

$$\beta \langle r^4 \rangle = 21(Dq - Dt)$$

$$\gamma \langle r^4 \rangle = 3\sqrt{35}Dq$$

One form of the crystal field operator involves the homogeneous polynomials $P_{k,m}(x, y, z)$ such as

$$P_4 = P_{4,0} + 5P_{4,4} = 20 \left(x^4 + y^4 + z^4 - \frac{3}{5}r^4 \right)$$

and

$$P_6 = P_{6,0} - 21P_{6,4} = -14 \cdot 16 \left\{ x^6 + y^6 + z^6 + \frac{15}{4}(x^4y^2 + y^4x^2 + x^4z^2 + z^4x^2 + y^4z^2 + z^4y^2) - \frac{15}{14}r^6 \right\}$$

Then for cubic groups it holds true that

$$V'(\mathbf{O}_h, \dots) = A_4P_4 + A_6P_6$$

with the potential constants listed in Table 8.18.

TABLE 8.18

Potential constants $A_i/(e^2/4\pi\epsilon_0)q_L^0$

	Octahedron	Cube	Tetrahedron
A_4	$(7/16)R_L^{-5}$	$-(7/8)R_L^{-5}$	$-(7/16)R_L^{-5}$
A_6	$(3/64)R_L^{-7}$	$(1/9)R_L^{-7}$	$(1/18)R_L^{-7}$

The matrix elements of interest can be replaced by those of the corresponding equivalent operators. These are [10]:

(a) for a single electron

$$\langle l, m_l | P_{k,m}(\vec{r}) | l, m_l' \rangle = \langle l \| a_k \| l \rangle \langle l^k \rangle \langle l, m_l | \hat{O}_k^m(\vec{l}) | l, m_l' \rangle$$

with

$$\langle l \| a_2 \| l \rangle = -\frac{2}{(2l-1)(2l+3)}$$

$$\langle l \| a_4 \| l \rangle = \frac{6}{(2l-1)(2l-3)(2l+3)(2l+5)}$$

$$\langle l \| a_6 \| l \rangle = -\frac{20}{(2l-1)(2l-3)(2l-5)(2l+3)(2l+5)(2l+7)}$$

(b) for term functions (applicable for a weak crystal field, usually for the ground states of 3d elements obeying Hund's rules)

$$\left\langle L, M_L \left| \sum_i^n P_{k,m}(\vec{r}_i) \right| L, M_L' \right\rangle = \langle L \| a_k \| L \rangle \langle l^k \rangle \langle L, M_L | \hat{O}_k^m(\vec{L}) | L, M_L' \rangle$$

with

$$\langle L \| a_2 \| L \rangle = \pm \frac{2l+1-4S}{2L-1} \langle l \| a_2 \| l \rangle = \mp \frac{2(2l+1-4S)}{(2l-1)(2l+3)(2L-1)}$$

$$\langle L \| a_4 \| L \rangle = \langle L \| a_2 \| L \rangle 3 \frac{3(l-1)(l+2) - 7(l-2S)(l+1-2S)}{2(2l-3)(2l+5)(L-1)(2L-3)}$$

where the upper sign is valid for a shell less than half full and the lower sign for a shell more than half full;

- (c) for multiplet functions (applicable for a very weak crystal field, usually for the ground states of $4f$ elements)

$$\left\langle J, M_J \left| \sum_i^n P_{k,m}(\vec{r}_i) \right| J, M'_J \right\rangle = \langle J \| a_k \| J \rangle \langle r^k \rangle \left\langle J, M_J \left| \hat{O}_k^m(\vec{J}) \right| J, M'_J \right\rangle$$

with the potential constants proportional to the reduced matrix elements of the irreducible tensor operator

$$\langle J \| a_k \| J \rangle \approx \frac{1}{\sqrt{2J+1}} \langle J \| \hat{T}_k \| J \rangle$$

Since an analogous replacement holds true

$$\langle L, S \| a_k \| L, S \rangle \approx \frac{1}{\sqrt{2L+1}} \langle L, S \| \hat{T}_k \| L, S \rangle$$

and a recoupling with the help of the $6j$ -symbols is possible

$$\langle J \| \hat{T}_k \| J \rangle = (-1)^{L+S+J+k} (2J+1) \left\{ \begin{matrix} J & k & J \\ L & S & L \end{matrix} \right\} \langle L, S \| \hat{T}_k \| L, S \rangle$$

then a closed-form relationship is obtained

$$\langle J \| a_k \| J \rangle = (-1)^{L+S+J+k} \sqrt{\frac{2J+1}{2L+1}} \left\{ \begin{matrix} J & k & J \\ L & S & L \end{matrix} \right\} \langle L, S \| a_k \| L, S \rangle$$

The introduced potential constants are presented in Table 8.19.

For the ${}^3F$ term of the electron configuration d^2 the angular momentum is $L = 3$ and thus the crystal field potential for the octahedral symmetry becomes expressed as follows

$$\begin{aligned} V(\mathbf{O}_h) &= A_4 P_4 = \frac{e^2}{4\pi\epsilon_0} q_L^0 (7/16) R_L^{-5} (P_{4,0} + 5P_{4,4}) \\ &= \frac{e^2}{4\pi\epsilon_0} q_L^0 (7/16) R_L^{-5} \langle r^4 \rangle \left\langle {}^3F(d^2) \| a_4 \| {}^3F(d^2) \right\rangle (\hat{O}_4^0 + 5\hat{O}_4^4) \\ &= \frac{e^2}{4\pi\epsilon_0} q_L^0 (7/16) R_L^{-5} \langle r^4 \rangle (-2/315) \left\{ 35\hat{L}_z^4 [\hbar^{-4}] - 335\hat{L}_z^2 [\hbar^{-2}] \right. \\ &\quad \left. + 360\hat{I} + 5\frac{1}{2}(\hat{L}_+^4 + \hat{L}_-^4) [\hbar^{-4}] \right\} \end{aligned}$$

TABLE 8.19
Multiplicative factors of the crystal field potential

Orbital	$\langle l \ a_2 \ l \rangle$	$\langle l \ a_4 \ l \rangle$	$\langle l \ a_6 \ l \rangle$
p	$-2/5$	0	0
d	$-2/21$	$2/63$	0
f	$-2/45$	$\frac{2}{11 \cdot 45}$	$-\frac{4}{11 \cdot 13 \cdot 27}$

Term	$\langle L \ a_2 \ L \rangle$	$\langle L \ a_4 \ L \rangle$
$^2D(d^1)$	$-2/21$	$2/63$
$^3F(d^2)$	$-2/105$	$-2/315$
$^4F(d^3)$	$2/105$	$2/315$
$^5D(d^4)$	$2/21$	$-2/63$
$^6S(d^5)$	0	0
$^5D(d^6)$	$-2/21$	$2/63$
$^4F(d^7)$	$-2/105$	$-2/315$
$^3F(d^8)$	$2/105$	$2/315$
$^2D(d^9)$	$2/21$	$-2/63$

Multiplet	$\langle J \ a_2 \ J \rangle$	$\langle J \ a_4 \ J \rangle$	$\langle J \ a_6 \ J \rangle$
$^2F_{5/2}(f^1)$	$-\frac{2}{5 \cdot 7}$	$\frac{2}{3^2 \cdot 5 \cdot 7}$	0
$^3H_4(f^2)$	$-\frac{2^2 \cdot 13}{3^2 \cdot 5^2 \cdot 11}$	$-\frac{2^2}{3^2 \cdot 5^2 \cdot 11^2}$	$\frac{2^4 \cdot 17}{3^4 \cdot 5 \cdot 7 \cdot 11^2 \cdot 13}$
$^4I_{9/2}(f^3)$	$-\frac{7}{3^2 \cdot 11^2}$	$-\frac{2^3 \cdot 17}{3^3 \cdot 11^3 \cdot 13}$	$-\frac{5 \cdot 17 \cdot 19}{3^3 \cdot 7 \cdot 11^3 \cdot 13^2}$
$^5I_4(f^4)$	$\frac{2 \cdot 7}{3 \cdot 5 \cdot 11^2}$	$\frac{2^3 \cdot 7 \cdot 17}{3^3 \cdot 5 \cdot 11^3 \cdot 13}$	$\frac{2^3 \cdot 17 \cdot 19}{3^3 \cdot 7 \cdot 11^3 \cdot 13^2}$
$^6H_{5/2}(f^5)$	$\frac{13}{3^3 \cdot 5 \cdot 7}$	$\frac{2 \cdot 13}{3^3 \cdot 5 \cdot 7 \cdot 11}$	0
$^7F_0(f^6)$	0	0	0
$^8S_{7/2}(f^7)$	0	0	0
$^7F_6(f^8)$	$-\frac{1}{3^2 \cdot 11}$	$\frac{2}{3^3 \cdot 5 \cdot 11^2}$	$-\frac{1}{3^4 \cdot 7 \cdot 11^2 \cdot 13}$
$^6H_{15/2}(f^9)$	$-\frac{2}{3^2 \cdot 5 \cdot 7}$	$-\frac{2^3}{3^3 \cdot 5 \cdot 7 \cdot 11 \cdot 13}$	$\frac{2^2}{3^3 \cdot 7 \cdot 11^2 \cdot 13^2}$
$^5I_8(f^{10})$	$-\frac{1}{2 \cdot 3^2 \cdot 5^2}$	$-\frac{1}{2 \cdot 3 \cdot 5 \cdot 7 \cdot 11 \cdot 13}$	$-\frac{5}{3^3 \cdot 7 \cdot 11^2 \cdot 13^2}$
$^4I_{15/2}(f^{11})$	$\frac{2^2}{3^2 \cdot 5^2 \cdot 7}$	$\frac{2}{3^2 \cdot 5 \cdot 7 \cdot 11 \cdot 13}$	$\frac{2^3}{3^3 \cdot 7 \cdot 11^2 \cdot 13^2}$
$^3H_6(f^{12})$	$\frac{1}{3^2 \cdot 11}$	$\frac{2^3}{3^4 \cdot 5 \cdot 11^2}$	$-\frac{5}{3^4 \cdot 7 \cdot 11^2 \cdot 13}$
$^2F_{7/2}(f^{13})$	$\frac{2}{3^2 \cdot 7}$	$-\frac{2}{3 \cdot 5 \cdot 7 \cdot 11}$	$\frac{2^2}{3^3 \cdot 7 \cdot 11 \cdot 13}$

Taking into account the angular momentum matrices ($\hat{L}_z, \hat{L}_+, \hat{L}_-$) we arrive at the expression

$$V(\mathbf{O}_h) = \frac{e^2}{4\pi\epsilon_0} q_L^0 (7/16) R_L^{-5} \langle r^4 \rangle (-2/315)(60)$$

$$\begin{pmatrix} 3 & 0 & 0 & 0 & \sqrt{15} & 0 & 0 \\ 0 & -7 & 0 & 0 & 0 & 5 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & \sqrt{15} \\ 0 & 0 & 0 & 6 & 0 & 0 & 0 \\ \sqrt{15} & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 5 & 0 & 0 & 0 & -7 & 0 \\ 0 & 0 & \sqrt{15} & 0 & 0 & 0 & 3 \end{pmatrix}$$

with the multiplicative factor in front of the matrix equal to

$$K = -(1/6) R_L^{-5} \langle r^4 \rangle = -\Delta/10$$

This matrix can be rearranged into a block diagonal form and consequently the secular equation is split into a set of equations of lower dimensions

$$\det \begin{pmatrix} 3K - \epsilon & \sqrt{15}K \\ \sqrt{15}K & 1K - \epsilon \end{pmatrix} = 0$$

$$\det \begin{pmatrix} 1K - \epsilon & \sqrt{15}K \\ \sqrt{15}K & 3K - \epsilon \end{pmatrix} = 0$$

$$\det \begin{pmatrix} -7K - \epsilon & 5K \\ 5K & -7K - \epsilon \end{pmatrix} = 0$$

$$\det(6K - \epsilon) = 0$$

The resulting eigenvalues are identical to those already presented for the splitting of the ${}^3F(d^2)$ term. A great advantage of the present approach is that the matrix elements of the crystal field operator between the many-electron wave functions are easily generated without knowledge of the explicit form of the determinantal wave functions.

In treating the 4f-systems the coupling through the crystal field between two multiplets is important; in this case the method of the operator equivalents is not applicable and the correct treatment needs the direct application of the Wigner-Eckart theorem for the reduction of the matrix element

$$\langle L, S, J, M_J | \hat{T}_{k,m} | L, S, J', M_J' \rangle = \frac{1}{\sqrt{2J+1}} \langle J', M_J', k, m | J, M_J \rangle \langle J || \hat{T}_k || J' \rangle$$

with the reduced matrix element expressed via a recoupling formula

$$\begin{aligned} \langle J \| \hat{T}_k \| J' \rangle &= (-1)^{L+S+J'+k} \sqrt{2J+1} \sqrt{2J'+1} \\ &\times \left\{ \begin{matrix} J & k & J' \\ L' & S & L \end{matrix} \right\} \langle L, S \| \hat{T}_k \| L', S \rangle \end{aligned}$$

8.3 MAGNETIC PROPERTIES OF FREE IONS

8.3.1 Spin Hamiltonian

The Hamiltonian that describes the interaction of the single magnetic centre with the external magnetic field involves the orbital Zeeman and the spin Zeeman terms

$$\hat{H}^Z = \mu_B \vec{B} \cdot (\vec{L} + g_e \vec{S}) [\hbar^{-1}]$$

This can be enriched by the operator of the spin-orbit coupling and eventually by the operator of the hyperfine (electron-nuclear) interaction

$$\begin{aligned} \hat{H}' &= \hat{H}^Z + \lambda \vec{L} \cdot \vec{S} [\hbar^{-2}] + A \vec{I} \cdot \vec{S} [\hbar^{-2}] \\ &= \mu_B \vec{B} \cdot (\vec{L} + g_e \vec{S}) [\hbar^{-1}] + \lambda \vec{L} \cdot \vec{S} [\hbar^{-2}] + A \vec{I} \cdot \vec{S} [\hbar^{-2}] \end{aligned}$$

It is assumed that the state vectors are represented by orthonormal kets of spatial variables, viz. $|K\rangle = |\alpha, L, M_L\rangle$. In terms of perturbation theory the first-order “energy” correction is

$$\begin{aligned} \hat{H}^{(1)} &= \langle 0 | \hat{H}' | 0 \rangle = (\mu_B g_e \vec{B} + [\hbar^{-1}] A \vec{I}) \cdot \vec{S} \langle 0 | 0 \rangle [\hbar^{-1}] \\ &\quad + (\mu_B \vec{B} + [\hbar^{-1}] \lambda \vec{S}) \cdot \langle 0 | \vec{L} | 0 \rangle [\hbar^{-1}] \end{aligned}$$

Here the second term vanishes since the angular momentum operator acting on the ground state vector yields

$$\langle 0 | \vec{L} | 0 \rangle = a \langle 0 | K \rangle = 0$$

The second-order “energy” correction is given by the standard formula

$$\hat{H}^{(2)} = - \sum_{K \neq 0} \frac{\langle 0 | \hat{H}' | K \rangle \langle K | \hat{H}' | 0 \rangle}{E_K - E_0}$$

and since

$$\begin{aligned} \langle 0 | \hat{H}' | K \rangle &= (\mu_B \vec{B} + [\hbar^{-1}] \lambda \vec{S}) \cdot \langle 0 | \vec{L} | K \rangle [\hbar^{-1}] \\ &\quad + (\mu_B g_e \vec{B} \cdot \vec{S} + [\hbar^{-1}] A \vec{I} \cdot \vec{S}) \langle 0 | K \rangle [\hbar^{-1}] \end{aligned}$$

one gets

$$\hat{H}^{(2)} = - \sum_{K \neq 0} \frac{[(\mu_B \vec{B} + [\hbar^{-1}] \lambda \vec{S}) \cdot \langle 0 | \vec{L} | K \rangle][(\mu_B \vec{B} + [\hbar^{-1}] \lambda \vec{S}) \cdot \langle K | \vec{L} | 0 \rangle][\hbar^{-2}]}{E_K - E_0}$$

After introducing the *A*-tensor as follows

$$A_{ab} = - \sum_{K \neq 0} \frac{\langle 0 | \hat{L}_a | K \rangle \langle K | \hat{L}_b | 0 \rangle}{E_K - E_0} [\hbar^{-2}], \quad [\text{energy}^{-1}]$$

we can write

$$\hat{H}^{(2)} = (\mu_B \vec{B} + \lambda \vec{S} [\hbar^{-1}]) \cdot \vec{\bar{A}} \cdot (\mu_B \vec{B} + \lambda \vec{S} [\hbar^{-1}])$$

(One should be careful in defining the sign of the *A*-tensor since the opposite sign can be met in literature [10].) The overall result of perturbation theory up to the second order can be written in the form

$$\begin{aligned} \hat{H}^S &= \hat{H}^{(1)} + \hat{H}^{(2)} = \sum_a \sum_b \{ \mu_B^2 A_{ab} B_a B_b + \mu_B B_a (g_e \delta_{ab} + 2\lambda A_{ab}) \hat{S}_b [\hbar^{-1}] \\ &\quad + A \hat{I}_a \hat{S}_b \delta_{ab} [\hbar^{-2}] + \lambda^2 A_{ab} \hat{S}_a \hat{S}_b [\hbar^{-2}] \} \end{aligned}$$

or

$$\hat{H}^S = -\frac{1}{2} \vec{B} \cdot \vec{\bar{\kappa}} \cdot \vec{B} + \mu_B \vec{B} \cdot \vec{\bar{g}} \cdot \vec{S} [\hbar^{-1}] + A \vec{I} \cdot \vec{S} [\hbar^{-2}] - \frac{1}{2} \vec{S} \cdot \vec{\bar{D}} \cdot \vec{S} [\hbar^{-2}]$$

where we introduce the *κ*-tensor (reduced, temperature-independent paramagnetic susceptibility tensor) as

$$-\frac{1}{2} \kappa_{ab}^{\text{para}} = \mu_B^2 A_{ab}, \quad [\text{energy} \cdot \text{induction}^{-2}]$$

the *g*-tensor (magnetogyric ratio tensor) as

$$g_{ab} = g_e \delta_{ab} + 2\lambda A_{ab}, \quad [\text{dimensionless}]$$

and the *D*-tensor (spin–spin interaction tensor) as

$$-\frac{1}{2}D_{ab} = \lambda^2 A_{ab} = D'_{ab}, \quad [\text{energy}]$$

The operator $\hat{H}^S$ is termed the *spin Hamiltonian*: it acts only on the spin kets $|S, M_S\rangle$. It produces eigenvalues identical with those produced by the perturbation operator $\hat{H}'$ acting on the full set of variables $|\alpha, L, M_L, S, M_S\rangle$.

The above form of the spin Hamiltonian is common in electron spin resonance. In magnetochemistry the hyperfine interaction is neglected and the temperature-independent paramagnetic term can be omitted (this can be included in the empirical correction of experimental data, together with the diamagnetic term).

8.3.2 Curie law

Let us investigate the situation of having an orbitally non-degenerate atomic term ^{2S+1}S or a molecular state ^{2S+1}A and ^{2S+1}B , respectively. In the absence of thermally accessible excited states the only contribution to the spin Hamiltonian is an isotropic (spin) Zeeman term

$$\hat{H}^{\text{mg}} = \mu_B g_e B_z \hat{S}_z [\hbar^{-1}]$$

With the kets $|i\rangle = |S, M_S\rangle$ this produces the eigenvalues

$$\varepsilon_i = \mu_B g_e B_z M_S$$

Then the molar magnetisation is given through the Brillouin function (introduced in Section 6.1) as

$$M = (N_A \mu_B g_e S) \mathcal{B}_S(\eta)$$

for the argument

$$\eta = \frac{\mu_B g_e B_z}{kT}$$

For small arguments ($\eta \ll 1$, small fields, high temperature) an expansion of the Brillouin function is possible

$$\mathcal{B}_S(\eta) \approx \frac{S+1}{3} \eta$$

and then the magnetisation becomes a linear function of the field

$$M = (N_A \mu_B g_e S) \frac{S+1}{3} \frac{\mu_B g_e \mu_0 H_z}{kT}$$

Consequently the molar magnetic susceptibility obeys the *Curie law*

$$\bar{\chi}_{\text{mol}} = \frac{M}{H_z} = \frac{N_A \mu_0 \mu_B^2}{k} \frac{S(S+1)}{3} \frac{g_e^2}{T}$$

After introducing the constant

$$C_0 = \frac{N_A \mu_0 \mu_B^2}{k}$$

and the Curie constant

$$C = C_0 \frac{S(S+1)}{3} g_e^2$$

we get the common form of the Curie law

$$\bar{\chi}_{\text{mol}} = \frac{C}{T}$$

The behaviour of the magnetisation versus the magnetic field is displayed in Fig. 8.1.

Another elegant derivation of the Curie law is based on the van Vleck formula (introduced in Section 6.1). The Zeeman coefficients for this particular case are

i	$\varepsilon_i^{(0)}$	$\varepsilon_i^{(1)}$	$\varepsilon_i^{(2)}$
M_S	0	$\mu_B g_e M_S$	0

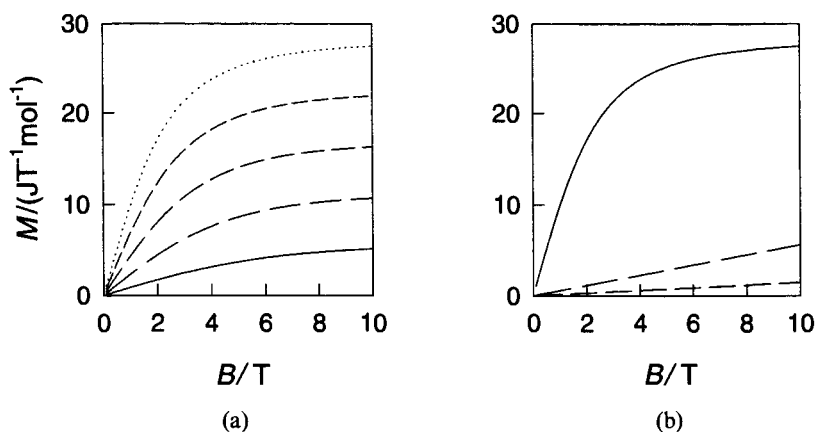


Fig. 8.1. Molar magnetisation versus magnetic field for paramagnets: (a) for $T = 4.2 \text{ K}$ individual curves correspond to $S = 1/2$ (solid), 1 (long dashed), $3/2$ (medium dashed), 2 (short dashed) and $5/2$ (dotted); (b) for $S = 5/2$ individual curves correspond to $T = 4.2 \text{ K}$ (solid), 77 K (long dashed) and 300 K (medium dashed).

and, after substituting them into the van Vleck formula, one gets

$$\bar{\chi}_{\text{mol}} = N_A \mu_0 \frac{\sum_{M_S=-S}^{+S} \frac{(\mu_B g_e M_S)^2}{kT} \exp(0)}{\sum_{M_S=-S}^{+S} \exp(0)}$$

With the help of the sum

$$\sum_{M_S=-S}^{+S} (M_S)^2 = \frac{S(S+1)(2S+1)}{3}$$

we get the Curie law

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2 g_e^2 S(S+1)(2S+1)}{k T} \frac{1}{2S+1} = C_0 \frac{S(S+1) g_e^2}{3 T}$$

Obedience to the Curie law implies that the product function

$$(\bar{\chi}_{\text{mol}} T) = C$$

versus T is a straight line with zero slope. The theoretical “spin-only” values of the Curie constant are given in Table 8.20 together with some other useful numbers.

The effective magnetic moment is introduced as follows

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_{\text{eff}}^2}{3kT}$$

TABLE 8.20
Curie parameters

S	$C (\text{m}^3 \text{mol}^{-1} \text{K})$	$C (\text{cm}^3 \text{mol}^{-1} \text{K})$	μ_{eff}/μ_B	$(\chi_{\text{mol}} T)/C_0$
1/2	4.714	0.375	1.73	1
1	12.571	1.000	2.83	2.667
3/2	23.571	1.876	3.87	5
2	37.713	3.001	4.90	8
5/2	54.999	4.377	5.92	11.667
3	75.427	6.002	6.93	16
7/2	98.998	7.878	7.94	21

so that

$$\mu_{\text{eff}} = \sqrt{\frac{3k}{N_A \mu_0}} \chi_{\text{mol}} T$$

and this (spin-only value) is equal to

$$\mu_{\text{eff}}/\mu_B = g_e \sqrt{S(S+1)}$$

When the linear approximation to the Brillouin function is not fulfilled, then the mean magnetic susceptibility $\bar{\chi} = M/H$ should be substituted by a differential magnetic susceptibility

$$\tilde{\chi} = \frac{\partial M}{\partial H} = \mu_0 \frac{\partial M}{\partial B}$$

This is evidenced from Fig. 8.2 where the correct value of the magnetic susceptibility is

$$\tilde{\chi}_{\text{mol}} = C_0 \frac{g_e^2}{T} \left\{ (S + 1/2)^2 \left[1 - \left(\frac{\exp(x) + \exp(-x)}{\exp(x) - \exp(-x)} \right)^2 \right] - \frac{1}{4} \left[1 - \left(\frac{\exp(y) + \exp(-y)}{\exp(y) - \exp(-y)} \right)^2 \right] \right\}$$

for the arguments

$$x = (S + 1/2) \frac{g_e \mu_B B}{kT}$$

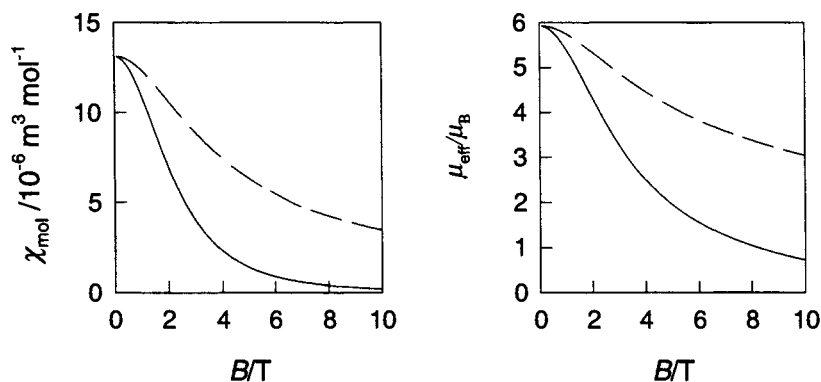


Fig. 8.2. Correct (solid line, based on the differential susceptibility) and approximate (dashed line, based on the mean susceptibility) functions for an $S = 5/2$ paramagnet at $T = 4.2 \text{ K}$.

and

$$y = \frac{1}{2} \frac{g_e \mu_B B}{kT}$$

8.4 ZERO-FIELD SPLITTING

8.4.1 Zero-field energy

The Hamiltonian that accounts for spin–spin interaction in the simplest form is

$$\hat{H}^{\text{zfs}} = \sum_a \sum_b D'_{ab} \hat{S}_a \hat{S}_b [\hbar^{-2}]$$

Assuming that the coordinate axes are identical with the principal axes of the D -tensor, only the diagonal elements contribute

$$\hat{H}^{\text{zfs}} = \sum_a D'_{aa} \hat{S}_a^2 [\hbar^{-2}] = (D'_{xx} \hat{S}_x^2 + D'_{yy} \hat{S}_y^2 + D'_{zz} \hat{S}_z^2) [\hbar^{-2}]$$

By introducing new parameters

$$D = \frac{1}{2} (-D'_{xx} - D'_{yy} + 2D'_{zz})$$

$$E = \frac{1}{2} (D'_{xx} - D'_{yy})$$

$$K = \frac{1}{3} (D'_{xx} + D'_{yy} + D'_{zz})$$

the equivalent form of the $\hat{H}^{\text{zfs}}$ operator is

$$\hat{H}^{\text{zfs}} = \left[D(\hat{S}_z^2 - \frac{1}{3} \hat{S}^2) + E(\hat{S}_x^2 - \hat{S}_y^2) + K \hat{S}^2 \right] [\hbar^{-2}]$$

(a simple substitution of parameters serves as a proof). Notice that the D and E parameters remain unchanged when the same constant term is added (subtracted) to the diagonal elements of the D -tensor. On the other hand, we know that in terms of the equivalent operators it holds true that

$$\hat{H}^{\text{zfs}} = B_0^0 \hat{O}_0^0 + B_2^0 \hat{O}_2^0 + B_2^2 \hat{O}_2^2$$

with

$$\hat{O}_0^0 = S(S+1)$$

$$\hat{O}_2^0 = 3\hat{S}_z^2[\hbar^{-2}] - S(S+1)$$

$$\hat{O}_2^2 = (\hat{S}_x^2 - \hat{S}_y^2)[\hbar^{-2}] = \frac{1}{2}(\hat{S}_+^2 + \hat{S}_-^2)[\hbar^{-2}]$$

Then

$$D = 3B_2^0$$

$$E = B_2^2$$

and

$$K = -B_0^0$$

The constant term $K\hat{S}^2$ can be deleted from further consideration since it uniformly shifts all the energy levels.

The omission of the constant term, in fact, corresponds to the subtraction of one-third of the trace of the D -tensor from the diagonal elements

$$\tilde{D}_{ab} = D'_{ab} - \frac{1}{3}(D'_{xx} + D'_{yy} + D'_{zz})\delta_{ab}$$

Consequently the (diagonal) D -tensor becomes traceless

$$\tilde{D}_{xx} + \tilde{D}_{yy} + \tilde{D}_{zz} = 0$$

for

$$\hat{H}^{\text{zfs}} = (\tilde{D}_{xx}\hat{S}_x^2 + \tilde{D}_{yy}\hat{S}_y^2 + \tilde{D}_{zz}\hat{S}_z^2)[\hbar^{-2}]$$

Now, the D -tensor components and the zero-field splitting parameters are interrelated through

$$D = \frac{3}{2}\tilde{D}_{zz} = -\frac{3}{2}(\tilde{D}_{xx} + \tilde{D}_{yy})$$

$$E = \frac{1}{2}(\tilde{D}_{xx} - \tilde{D}_{yy})$$

and

$$\tilde{D}_{xx} = -\frac{1}{3}D + E$$

$$\tilde{D}_{yy} = -\frac{1}{3}D - E$$

$$\tilde{D}_{zz} = \frac{2}{3}D$$

It is customary [14] to assign the three principal values of the D -tensor in such a way that the following relations are fulfilled

$$|\tilde{D}_{zz}| \geq |\tilde{D}_{yy}| \geq |\tilde{D}_{xx}|$$

Consequently the asymmetry parameter

$$\eta = \frac{3E}{D} = \frac{\tilde{D}_{xx} - \tilde{D}_{yy}}{\tilde{D}_{zz}}$$

is restricted to the range

$$0 \leq \eta \leq 1$$

Nevertheless, a different convention [15] assumes that

$$\check{D}_{xx} = -\frac{1}{3}D - E$$

$$\check{D}_{yy} = -\frac{1}{3}D + E$$

$$\check{D}_{zz} = \frac{2}{3}D$$

and introduces a new parameter

$$\lambda = \frac{E}{D} = \frac{\check{D}_{yy} - \check{D}_{xx}}{3\check{D}_{zz}}$$

restricted to

$$-\frac{1}{3} \leq \lambda \leq +\frac{1}{3}$$

With this fixation E is always positive and thus the sign of λ determines the sign of D and vice versa.

With the help of the angular momentum matrices (Appendix 2) it is easy to construct the zero-field splitting Hamiltonian matrix for the given value of S (Table 8.21).

TABLE 8.21
Matrices of the zero-field splitting Hamiltonian

Matrix $\langle M_S \hat{H}^{\text{zfs}} M'_S \rangle$	Eigenvalues
$S = 1/2$ $\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$	
$S = 1$ $\begin{pmatrix} (1/3)D & 0 & E \\ 0 & -(2/3)D & 0 \\ E & 0 & (1/3)D \end{pmatrix}$	$\varepsilon_1 = -(2/3)D$ $\varepsilon_2 = (1/3)D + E$ $\varepsilon_3 = (1/3)D - E$
$S = 3/2$ $\begin{pmatrix} D & 0 & \sqrt{3}E & 0 \\ 0 & -D & 0 & \sqrt{3}E \\ \sqrt{3}E & 0 & -D & 0 \\ 0 & \sqrt{3}E & 0 & D \end{pmatrix}$	$\varepsilon_1 = \varepsilon_2$ $= -\sqrt{D^2 + 3E^2}$ $\varepsilon_3 = \varepsilon_4$ $= +\sqrt{D^2 + 3E^2}$
$S = 2$ $\begin{pmatrix} 2D & 0 & \sqrt{6}E & 0 & 0 \\ 0 & -D & 0 & 3E & 0 \\ \sqrt{6}E & 0 & -2D & 0 & \sqrt{6}E \\ 0 & 3E & 0 & -D & 0 \\ 0 & 0 & \sqrt{6}E & 0 & 2D \end{pmatrix}$	$\varepsilon_1 = -D - 3E$ $\varepsilon_2 = -D + 3E$ $\varepsilon_3 = 2D$ $\varepsilon_4 = -2\sqrt{D^2 + 3E^2}$ $\varepsilon_5 = +2\sqrt{D^2 + 3E^2}$
$S = 5/2^a$ $\begin{pmatrix} (10/3)D & 0 & \sqrt{10}E & 0 & 0 & 0 \\ 0 & -(2/3)D & 0 & \sqrt{18}E & 0 & 0 \\ \sqrt{10}E & 0 & -(8/3)D & 0 & \sqrt{18}E & 0 \\ 0 & \sqrt{18}E & 0 & -(8/3)D & 0 & \sqrt{10}E \\ 0 & 0 & \sqrt{18}E & 0 & -(2/3)D & 0 \\ 0 & 0 & 0 & \sqrt{10}E & 0 & (10/3)D \end{pmatrix}$	$\varepsilon_1 = \varepsilon_2 = -2D\alpha$ $\times \cos[(\pi - \arccos \beta)/3]$ $\varepsilon_3 = \varepsilon_4 = -2D\alpha$ $\times \cos[(\pi + \arccos \beta)/3]$ $\varepsilon_5 = \varepsilon_6 = 2D\alpha$ $\times \cos[(\arccos \beta)/3]$

^a Goniometric solution of a cubic equation for $\alpha = \sqrt{28(1 + 3E^2/D^2)}/9$ and $\beta = 80(1 - 9E^2/D^2)/(3\alpha)^3$.

In the absence of the external magnetic field the $\hat{H}^{\text{zfs}}$ term is the only perturbation that influences the magnetic energy levels (except in the case of $S = 1/2$ for which this vanishes). Then the energy levels in the zero magnetic field are obtained by solving the secular equation

$$\det \left\{ \left\langle M_S \right| \hat{H}^{\text{zfs}} \left| M'_S \right\rangle - \delta_{M_S, M'_S} \varepsilon \right\} = 0$$

The corresponding eigenvalues are listed in Table 8.21 when the analytic solution exists.

The effect of the D and E parameters on energy levels is displayed in Figs. 8.3 and 8.4.

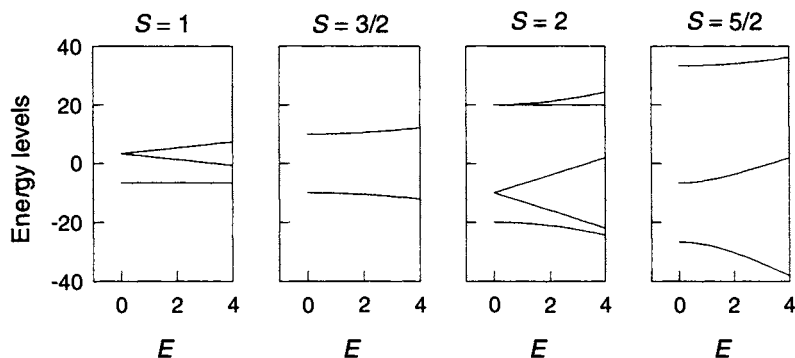


Fig. 8.3. Energy levels of $S = 1, 3/2, 2$ and $5/2$ paramagnets split in the zero field; $D = 10$ (arbitrary units).

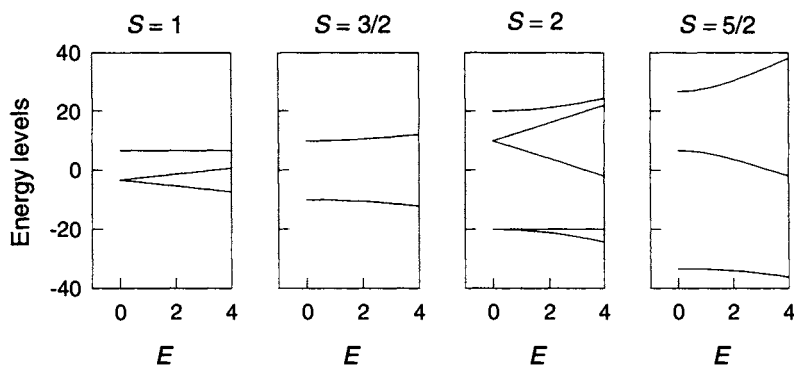


Fig. 8.4. Energy levels of $S = 1, 3/2, 2$ and $5/2$ paramagnets split in the zero field; $D = -10$ (arbitrary units).

8.4.2 Splitting in the magnetic field

The presence of the magnetic field is covered by the following form of the Hamiltonian

$$\hat{H}^{\text{mg}} = \hat{H}^{\text{zfs}} + \hat{H}^{\text{Z}}$$

where the (spin) Zeeman term is given as

$$\hat{H}^{\text{Z}} = (g_x \mu_{\text{B}} B_x \hat{S}_x + g_y \mu_{\text{B}} B_y \hat{S}_y + g_z \mu_{\text{B}} B_z \hat{S}_z) [\hbar^{-1}]$$

The matrices for individual spin components are presented in Appendix 2. Then the energy levels are obtained as eigenvalues of the secular equation

$$\det \left\{ \langle M_S | \hat{H}^{\text{mg}} | M'_S \rangle - \varepsilon_{i,a} \delta_{M_S, M'_S} \right\} = 0$$

for individual Cartesian directions ($a = x, y, z$).

8.4.3 Axial component

Let us first assume the case of $E = 0$ (only axial anisotropy, no rhombic anisotropy). Then analytic solutions of the secular equations exist; these are collected in Table 8.22.

In order to follow the procedure in more detail the case of $S = 1$ will serve as an example. The magnetic Hamiltonian in the parallel direction ($\parallel, z$) has the following matrix elements

$$\langle M_S | \hat{H}_z^{\text{mg}} | M'_S \rangle = \begin{pmatrix} (1/3)D & 0 & 0 \\ 0 & -(2/3)D & 0 \\ 0 & 0 & (1/3)D \end{pmatrix} + G_{\parallel} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

with

$$G_{\parallel} = g_{\parallel} \mu_{\text{B}} B_{\parallel}$$

and its eigenvalues are straightforward due to the absence of the off-diagonal matrix elements

$$\varepsilon_{1,\parallel} = (1/3)D + G_{\parallel}$$

$$\varepsilon_{2,\parallel} = (-2/3)D$$

$$\varepsilon_{3,\parallel} = (1/3)D - G_{\parallel}$$

TABLE 8.22

Eigenvalues of the magnetic Hamiltonian matrices for $E = 0$ shifted to an appropriate zero level

	M_S	Parallel ($\parallel$) $G_{\parallel} = g_{\parallel}\mu_B B_{\parallel}$	Perpendicular ($\perp$) $G_{\perp} = g_{\perp}\mu_B B_{\perp}$	Approximate ($\perp$) ^a
$S = 1$	+1	$D + G_{\parallel}$	$[D + (D^2 + 4G_{\perp}^2)^{1/2}]/2$	$D + G_{\perp}^2/D$
	-1	$D - G_{\parallel}$	D	D
	0	0	$[D - (D^2 + 4G_{\perp}^2)^{1/2}]/2$	$-G_{\perp}^2/D$
$S = 3/2$	+3/2	$2D + (3/2)G_{\parallel}$	$D + G_{\perp}/2 + [D^2 + G_{\perp}^2 - DG_{\perp}]^{1/2}$	$2D + (3/8)G_{\perp}^2/D$
	-3/2	$2D - (3/2)G_{\parallel}$	$D - G_{\perp}/2 + [D^2 + G_{\perp}^2 + DG_{\perp}]^{1/2}$	$2D + (3/8)G_{\perp}^2/D$
	+1/2	$(1/2)G_{\parallel}$	$D + G_{\perp}/2 - [D^2 + G_{\perp}^2 - DG_{\perp}]^{1/2}$	$G_{\perp} - (3/8)G_{\perp}^2/D$
	-1/2	$-(1/2)G_{\parallel}$	$D - G_{\perp}/2 - [D^2 + G_{\perp}^2 + DG_{\perp}]^{1/2}$	$-G_{\perp} - (3/8)G_{\perp}^2/D$
$S = 2$	+2	$4D + 2G_{\parallel}$	$[5D + (9D^2 + 4G_{\perp}^2)^{1/2}]/2$	$4D + (1/3)G_{\perp}^2/D^b$
	-2	$4D - 2G_{\parallel}$		$4D + (1/3)G_{\perp}^2/D^b$
	+1	$D + G_{\parallel}$		$D + (7/6)G_{\perp}^2/D^b$
	-1	$D - G_{\parallel}$		$D + (7/6)G_{\perp}^2/D^b$
	0	0	$[5D - (9D^2 + 4G_{\perp}^2)^{1/2}]/2$	$-3G_{\perp}^2/D^b$
$S = 5/2$	+5/2	$6D + (5/2)G_{\parallel}$		$6D + (5/16)G_{\perp}^2/D^b$
	-5/2	$6D - (5/2)G_{\parallel}$		$6D + (5/16)G_{\perp}^2/D^b$
	+3/2	$2D + (3/2)G_{\parallel}$		$2D + (11/16)G_{\perp}^2/D^b$
	-3/2	$2D - (3/2)G_{\parallel}$		$2D + (11/16)G_{\perp}^2/D^b$
	+1/2	$(1/2)G_{\parallel}$		$(3/2)G_{\perp} - G_{\perp}^2/D^{b,c}$
	-1/2	$-(1/2)G_{\parallel}$		$-(3/2)G_{\perp} - G_{\perp}^2/D^{b,c}$

^aRestriction: $D \gg g_{\perp}\mu_B B_{\perp}$; $g_{\perp}^2 = g_x^2 = g_y^2$; $g_{\parallel}^2 = g_z^2$.

^bApproximate eigenvalues from second-order perturbation theory.

^cThe first-order perturbation theory requires a diagonalisation of the submatrix having degenerate diagonal elements.

These energy levels can be shifted to an appropriate zero level since only the energy differences will affect the Boltzmann population, not their absolute values. After a shift by $(2/3)D$ we get

$$\varepsilon_{1,\parallel} = D + G_{\parallel}$$

$$\varepsilon_{2,\parallel} = 0$$

$$\varepsilon_{3,\parallel} = D - G_{\parallel}$$

The shift of energy levels can be done before solving the secular equation by subtracting the same increment from the diagonal elements.

The magnetic Hamiltonian in the perpendicular direction ($\perp$, x) has the following matrix elements

$$\begin{aligned} \langle M_S | \hat{H}_x^{\text{mg}} | M'_S \rangle &= \begin{pmatrix} (1/3)D & 0 & 0 \\ 0 & -(2/3)D & 0 \\ 0 & 0 & (1/3)D \end{pmatrix} \\ &+ G_{\perp} \begin{pmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{pmatrix} \end{aligned}$$

with

$$G_{\perp} = g_{\perp} \mu_B B_{\perp}$$

which after the shift becomes

$$\begin{aligned} \langle M_S | \hat{H}_x^{\text{mg}} | M'_S \rangle &+ (2/3)D \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ &= \begin{pmatrix} D & (1/\sqrt{2})G_{\perp} & 0 \\ (1/\sqrt{2})G_{\perp} & 0 & (1/\sqrt{2})G_{\perp} \\ 0 & (1/\sqrt{2})G_{\perp} & D \end{pmatrix} \end{aligned}$$

The secular determinant is

$$\det \begin{pmatrix} D - \varepsilon & (1/\sqrt{2})G_{\perp} & 0 \\ (1/\sqrt{2})G_{\perp} & 0 - \varepsilon & (1/\sqrt{2})G_{\perp} \\ 0 & (1/\sqrt{2})G_{\perp} & D - \varepsilon \end{pmatrix} = 0$$

and after its expansion an algebraic equation of the third order arises

$$(D - \varepsilon)(-\varepsilon)(D - \varepsilon) - 2(D - \varepsilon)[(1/\sqrt{2})G_{\perp}]^2 = 0$$

with the following roots representing the set of (shifted) eigenvalues

$$\varepsilon_{1,\perp} = \frac{1}{2}[D + (D^2 + 4G_{\perp}^2)^{1/2}]$$

$$\varepsilon_{2,\perp} = \frac{1}{2}[D - (D^2 + 4G_{\perp}^2)^{1/2}]$$

$$\varepsilon_{3,\perp} = D$$

The magnetic Hamiltonian in the second perpendicular direction ($\perp$, y) is complex Hermitian

$$\begin{aligned} \langle M_S | \hat{H}_y^{\text{mg}} | M'_S \rangle = & \begin{pmatrix} (1/3)D & 0 & 0 \\ 0 & -(2/3)D & 0 \\ 0 & 0 & (1/3)D \end{pmatrix} \\ & + G_{\perp} i \begin{pmatrix} 0 & -1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & -1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{pmatrix} \end{aligned}$$

yielding the secular equation

$$\det \begin{pmatrix} D - \varepsilon & -i(1/\sqrt{2})G_{\perp} & 0 \\ i(1/\sqrt{2})G_{\perp} & 0 - \varepsilon & -i(1/\sqrt{2})G_{\perp} \\ 0 & i(1/\sqrt{2})G_{\perp} & D - \varepsilon \end{pmatrix} = 0$$

This has exactly the same set of eigenvalues as we already obtained for the x -direction.

The above three secular equations can be combined into a single

$$\det \begin{pmatrix} 1 \cdot G_z + D - \varepsilon & (1/\sqrt{2})G_- & 0 \\ (1/\sqrt{2})G_+ & 0 - \varepsilon & (1/\sqrt{2})G_- \\ 0 & (1/\sqrt{2})G_+ & -1 \cdot G_z + D - \varepsilon \end{pmatrix} = 0$$

where the Zeeman parameters are

$$G_z = g_z \mu_B B l_z$$

$$G_{\pm} = G_x \pm iG_y = \mu_B B (g_x l_x \pm i g_y l_y)$$

with l_x , l_y and l_z representing the direction cosines for the vector $\vec{B}$ relative to the symmetry axes.

The next case of $S = 3/2$ starts from the secular equation

$$\det \begin{pmatrix} (3/2)G_z + 2D - \varepsilon & (\sqrt{3}/2)G_- & 0 & 0 \\ (\sqrt{3}/2)G_+ & (1/2)G_z + 0 - \varepsilon & 1 \cdot G_- & 0 \\ 0 & 1 \cdot G_+ & -(1/2)G_z + 0 - \varepsilon & (\sqrt{3}/2)G_- \\ 0 & 0 & (\sqrt{3}/2)G_+ & -(3/2)G_z + 2D - \varepsilon \end{pmatrix} = 0$$

the case of $S = 2$ from the equation

$$\det \begin{pmatrix} 2G_z + 4D - \varepsilon & 1 \cdot G_- & 0 & 0 & 0 \\ 1 \cdot G_+ & G_z + D - \varepsilon & (\sqrt{6}/2)G_- & 0 & 0 \\ 0 & (\sqrt{6}/2)G_+ & 0 - \varepsilon & (\sqrt{6}/2)G_- & 0 \\ 0 & 0 & (\sqrt{6}/2)G_+ & -G_z + D - \varepsilon & 1 \cdot G_- \\ 0 & 0 & 0 & 1 \cdot G_+ & -2G_z + 4D - \varepsilon \end{pmatrix} = 0$$

and finally the case of $S = 5/2$ from the equation

$$\det \begin{pmatrix} (5/2)G_z + 6D - \varepsilon & (\sqrt{5}/2)G_- & 0 \\ (\sqrt{5}/2)G_+ & (3/2)G_z + 2D - \varepsilon & (\sqrt{8}/2)G_- \\ 0 & (\sqrt{8}/2)G_+ & (1/2)G_z - \varepsilon \\ 0 & 0 & (\sqrt{9}/2)G_+ \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ (\sqrt{9}/2)G_- & 0 & 0 \\ -(1/2)G_z - \varepsilon & (\sqrt{8}/2)G_- & 0 \\ (\sqrt{8}/2)G_+ & -(3/2)G_z + 2D - \varepsilon & (\sqrt{5}/2)G_- \\ 0 & (\sqrt{5}/2)G_+ & -(5/2)G_z + 6D - \varepsilon \end{pmatrix} = 0$$

According to Table 8.22 the eigenvalues of the magnetic Hamiltonian matrices are simple analytic functions for the case of $E = 0$. Their dependence upon the magnetic field is presented in Figs. 8.5 and 8.6. It can be seen that the energy levels in the parallel direction vary strictly linearly with the field strength. In the perpendicular direction a quadratic dependence is clearly visible for lower fields; at higher fields, however, the dependence tends to be linear.

The square roots present in the analytic formulae for the eigenvalues in the perpendicular direction can be further expanded by utilising the formula

$$\sqrt{1+x} = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \dots$$

viz.

$$\begin{aligned} [D + (D^2 + 4G_\perp^2)^{1/2}]/2 &= \frac{D}{2} + \frac{D}{2} \left[1 + \frac{4G_\perp^2}{D^2} \right]^{1/2} \\ &\approx \frac{D}{2} + \frac{D}{2} \left[1 + \frac{1}{2} \frac{4G_\perp^2}{D^2} + \dots \right] = D + \frac{G_\perp^2}{D} + O_3(G) \end{aligned}$$

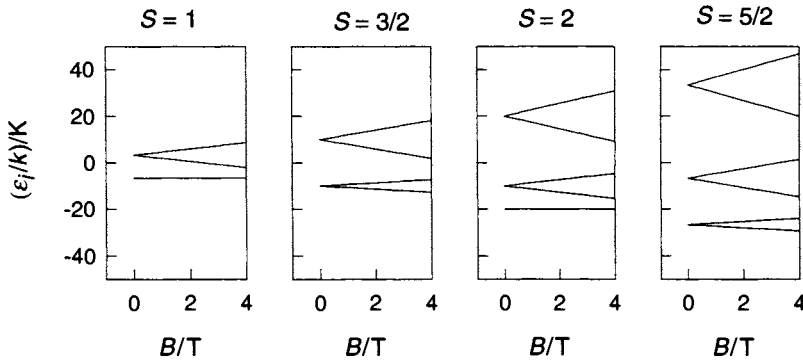


Fig. 8.5. Energy levels of zero-field splitting systems ($D/k = 10 \text{ K}$, $E = 0$) in the parallel ($\parallel$, z) direction.

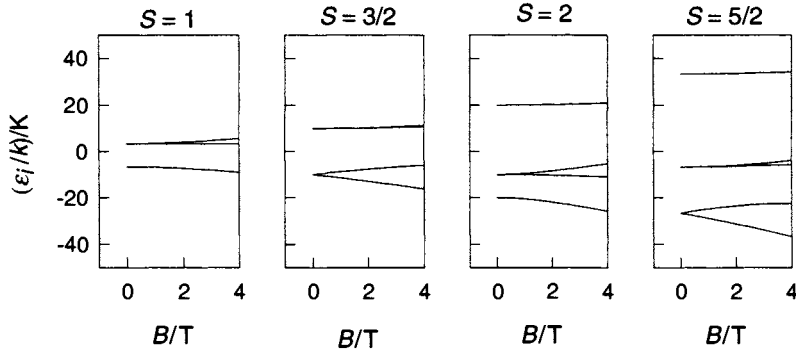


Fig. 8.6. Energy levels of zero-field splitting systems ($D/k = 10 \text{ K}$, $E = 0$) in the perpendicular ($\perp$, x, y) direction.

but

$$\begin{aligned}
 D + G_{\perp}/2 + [D^2 + G_{\perp}^2 - DG_{\perp}]^{1/2} &= D + \frac{G_{\perp}}{2} + D \left[1 + \frac{G_{\perp}^2 - DG_{\perp}}{D^2} \right]^{1/2} \\
 &\approx D + \frac{G_{\perp}}{2} + D \left[1 + \frac{1}{2} \frac{G_{\perp}^2 - DG_{\perp}}{D^2} - \frac{1}{8} \left(\frac{G_{\perp}^2 - DG_{\perp}}{D^2} \right)^2 + \dots \right] \\
 &= 2D + \frac{3}{8} \frac{G_{\perp}^2}{D} + O_3(G)
 \end{aligned}$$

This allows to us write approximate formulae where terms proportional to B^2 appear. Such expressions are particularly useful in applying the van Vleck equation since the identification of the van Vleck coefficients is an easy task.

However, one should be careful in this procedure since the expansion is applicable only when $x \ll 1$ which is equivalent to the restriction

$$D \gg g_{\perp} \mu_B B_{\perp}$$

Numerically this means that

$$(D/k)[\text{K}] \gg 2.0 \times (9.3 \times 10^{-24} \text{J T}^{-1}) / (1.4 \times 10^{-23} \text{J K}^{-1}) \times B[\text{T}]$$

Otherwise the formulae diverge.

For higher orders analytic solutions of the secular equation are not accessible; in such a case the approximate solutions can be found by applying second-order perturbation theory

$$\varepsilon_i = H_{ii}^{(0)} + H_{ii}^{(1)} + \sum_{j \neq i} \frac{H_{ij}^2}{H_{ii}^{(0)} - H_{jj}^{(0)}} + \dots$$

The zero-field energy is

$$H_{ii}^{(0)} = \varepsilon_M^{(0)} = D[M^2 - S(S+1)/3]$$

For the perpendicular direction the second-order coefficient becomes

$$\begin{aligned} \varepsilon_{M,\perp}^{(2)} &= - \sum_{M' \neq M} \frac{(\mu_B g_{\perp} \langle SM' | \hat{S}_x | SM \rangle)^2}{\varepsilon_{M'}^{(0)} - \varepsilon_M^{(0)}} \\ &= - \sum_{M' \neq M} \frac{(\mu_B g_{\perp} \langle SM' | (\hat{S}_+ + \hat{S}_-)/2 | SM \rangle)^2}{\varepsilon_{M'}^{(0)} - \varepsilon_M^{(0)}} \\ &= -(\mu_B g_{\perp})^2 \left\{ \frac{(S-M)(S+M+1)}{4D(1+2M)} \delta_{M',M+1} \right. \\ &\quad \left. + \frac{(S+M)(S-M+1)}{4D(1-2M)} \delta_{M',M-1} \right\} = (\mu_B g_{\perp})^2 \frac{M^2 + S(S+1)}{2(4M^2 - 1)D} \end{aligned}$$

Prior to the second order, the first-order perturbation theory requires a diagonalisation of the 2×2 submatrix having degenerate diagonal elements (Kramers ions, $M = \pm 1/2$)

$$\begin{aligned}
\varepsilon_{M=\pm 1/2, \perp}^{(1)} &= \pm \left\langle SM' \left| \mu_{\text{B}} g_{\perp} (\hat{S}_{+} + \hat{S}_{-})/2 \right| SM \right\rangle \\
&= \pm \mu_{\text{B}} g_{\perp} \frac{1}{2} [(S + 1/2)(S - 1/2 + 1)]^{1/2} = \pm \mu_{\text{B}} g_{\perp} (S + 1/2)/2 \\
\varepsilon_{M=\pm 1/2, \perp}^{(2)} &= -(\mu_{\text{B}} g_{\perp})^2 \left\{ \frac{(S \mp M)(S \pm M + 1)}{4D(1 \pm 2M)} \right\} \\
&= -(\mu_{\text{B}} g_{\perp})^2 \frac{(S - 1/2)(S + 3/2)}{8D}
\end{aligned}$$

8.4.4 Rhombic component

The involvement of the E parameter is a rather more complex task. The structure of the secular equation does not allow a splitting into the blocks of dimension 2 or 3 so that, in general, an analytic solution does not exist. The eigenvalues for the given set of parameters (D , E and gB) are obtained numerically. Standard diagonalisation routines can be used for this purpose.

Normally it is assumed that the zero-field splitting parameters obey a relationship

$$|D| \geq 3E \geq 0$$

Otherwise one can interchange the cartesian axes (which cannot influence the properties of the system) but the above relationship is still fulfilled [14]. The data displayed in Figs. 8.7 and 8.8 were generated for values which are close to the limiting case.

8.4.5 Axial magnetic anisotropy

The most frequent treatment is that the components of the magnetic susceptibility are derived for the case of $D \neq 0$ and $E = 0$ by utilising the van Vleck equation. For this purpose we need the van Vleck coefficients as they result from the approximate expansion of magnetic energy levels. Based on Table 8.22, the non-zero van Vleck coefficients are arranged in Table 8.23; notice that

$$\varepsilon_{i,||}^{(2)} = 0$$

holds true for zero-field splitting systems.

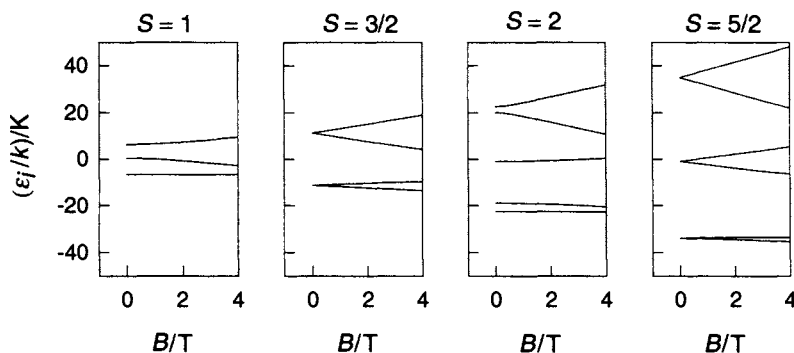


Fig. 8.7. Energy levels of zero-field splitting systems ($D/k = 10$ K and $E/k = 3$ K) in the parallel direction.

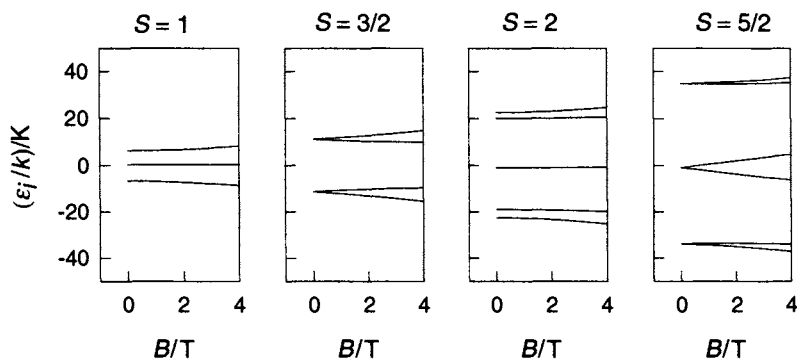


Fig. 8.8. Energy levels of zero-field splitting systems ($D/k = 10$ K and $E/k = 3$ K) in the perpendicular direction.

With the van Vleck coefficients determined, their substitution into the van Vleck equation yields the analytic formulae for the parallel and perpendicular components of the magnetic susceptibility, respectively (Table 8.24). However, one should keep in mind the above-mentioned restriction under which the expansion of the square roots is applicable.

By the help of formulae for the magnetic susceptibility a modelling of important magnetochemical curves, like χ_a versus T , $(\chi_a T)$ versus T , χ_{av} versus T , $(\chi_{av} T)$ versus T and μ_{eff} versus T , is possible. Some results are presented in Figs. 8.9 and 8.10.

It can be seen that the $(\chi_{av} T)$ versus T curves are nearly linear with the zero slope at a higher temperature. With lowering of temperature these exhibit a drop: the greater $|D|$, the higher the temperature at which the turning is evident. It should be noted that the curves $(\chi_{av} T)$ versus T are rather insensitive to the sign of the D -parameter and therefore it is problematic to establish the sign of the D -parameter from the powder sample data only. By

TABLE 8.23

Van Vleck coefficients for zero-field splitting systems ($E = 0$)

	M_S	$\varepsilon_i^{(0)}$	$\varepsilon_{i,\parallel}^{(1)}/\mu_B$	$\varepsilon_{i,\perp}^{(1)}/\mu_B$	$\varepsilon_{i,\perp}^{(2)}/\mu_B^2$
$S = 1$	+1	D	$+g_{\parallel}$	0	$+g_{\perp}^2/D$
	-1	D	$-g_{\parallel}$	0	0
	0	0	0	0	$-g_{\perp}^2/D$
$S = 3/2$	+3/2	$2D$	$+(3/2)g_{\parallel}$	0	$+(3/8)g_{\perp}^2/D$
	-3/2	$2D$	$-(3/2)g_{\parallel}$	0	$+(3/8)g_{\perp}^2/D$
	+1/2	0	$+(1/2)g_{\parallel}$	$+g_{\perp}$	$-(3/8)g_{\perp}^2/D$
	-1/2	0	$-(1/2)g_{\parallel}$	$-g_{\perp}$	$-(3/8)g_{\perp}^2/D$
$S = 2$	+2	$4D$	$+2g_{\parallel}$	0	$+(1/3)g_{\perp}^2/D$
	-2	$4D$	$-2g_{\parallel}$	0	$+(1/3)g_{\perp}^2/D$
	+1	D	$+g_{\parallel}$	0	$+(7/6)g_{\perp}^2/D$
	-1	D	$-g_{\parallel}$	0	$+(7/6)g_{\perp}^2/D$
	0	0	0	0	$-3g_{\perp}^2/D$
$S = 5/2$	+5/2	$6D$	$+(5/2)g_{\parallel}$	0	$+(5/16)g_{\perp}^2/D$
	-5/2	$6D$	$-(5/2)g_{\parallel}$	0	$+(5/16)g_{\perp}^2/D$
	+3/2	$2D$	$+(3/2)g_{\parallel}$	0	$+(11/16)g_{\perp}^2/D$
	-3/2	$2D$	$-(3/2)g_{\parallel}$	0	$+(11/16)g_{\perp}^2/D$
	+1/2	0	$+(1/2)g_{\parallel}$	$+(3/2)g_{\perp}$	$-g_{\perp}^2/D$
	-1/2	0	$-(1/2)g_{\parallel}$	$-(3/2)g_{\perp}$	$-g_{\perp}^2/D$

TABLE 8.24

Formulae for the susceptibility components of a zero-field splitting system ($E = 0$)^a

$S = 1$	$\chi_{\parallel} = (C_0 g_{\parallel}^2/T)[2 \exp(-x)]/[1 + 2 \exp(-x)]$ $\chi_{\perp} = (C_0 g_{\perp}^2/T)(2/x)[1 - \exp(-x)]/[1 + 2 \exp(-x)]$
$S = 3/2$	$\chi_{\parallel} = (C_0 g_{\parallel}^2/T)(1/4)[1 + 9 \exp(-2x)]/[1 + \exp(-2x)]$ $\chi_{\perp} = (C_0 g_{\perp}^2/T)\{1 + (3/4x)[1 - \exp(-2x)]\}/[1 + \exp(-2x)]$
$S = 2$	$\chi_{\parallel} = (C_0 g_{\parallel}^2/T)[2 \exp(-x) + 8 \exp(-4x)]/[1 + 2 \exp(-x) + 2 \exp(-4x)]$ $\chi_{\perp} = (C_0 g_{\perp}^2/T)\{(6/x)[1 - \exp(-x)] + (4/3x)[\exp(-x) - \exp(-4x)]\}/[1 + 2 \exp(-x) + 2 \exp(-4x)]$
$S = 5/2$	$\chi_{\parallel} = (C_0 g_{\parallel}^2/4T)[1 + 9 \exp(-2x) + 25 \exp(-6x)]/[1 + \exp(-2x) + \exp(-6x)]$ $\chi_{\perp} = (C_0 g_{\perp}^2/4T)\{9 + (8/x)[1 - \exp(-2x)] + (5/2x)[\exp(-2x) - \exp(-6x)]\}/[1 + \exp(-2x) + \exp(-6x)]$

^aSubstitution: $x = D/kT$; restriction: $D \gg G_{\perp} \mu_B B_{\perp}$.

measuring the oriented single crystals, however, the sign of the D -parameter is well determined.

In order to understand completely the behaviour of the χT (or μ_{eff}) curve a more detailed analysis is possible. The contribution of a given energy level to

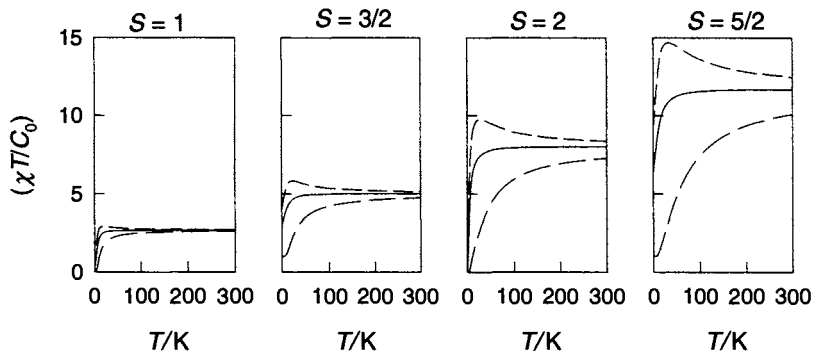


Fig. 8.9. Magnetic susceptibility components for zero-field splitting systems; $D/k = 20$ K; long dashed— $\chi_{||}$, short dashed— $\chi_{\perp}$, solid— χ_{av} .

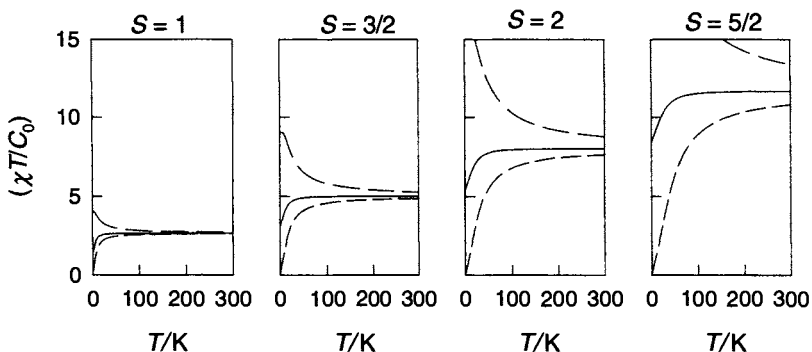


Fig. 8.10. Magnetic susceptibility components for zero-field splitting systems; $D/k = -20$ K; long dashed— $\chi_{||}$, short dashed— $\chi_{\perp}$, solid— χ_{av} .

the magnetic susceptibility is expressed via the van Vleck equation as follows

$$\chi_{i,a} = N_A \mu_0 \left\{ \frac{[\varepsilon_{i,a}^{(1)}]^2}{kT} - 2\varepsilon_{i,a}^{(2)} \right\} P_i = \frac{C_0}{T} \left\{ \frac{[\varepsilon_{i,a}^{(1)}]^2}{\mu_B} - 2kT \frac{\varepsilon_{i,a}^{(2)}}{\mu_B^2} \right\} P_i$$

and the Boltzmann probability factors are

$$P_i = \frac{\exp(-\varepsilon_i^{(0)}/kT)}{\sum_j \exp(-\varepsilon_j^{(0)}/kT)}$$

Then it holds true that

$$\chi_{i,av} = \frac{1}{3}(\chi_{||} + 2\chi_{\perp}) = \frac{1}{3} \frac{C_0}{T} \left\{ \frac{[\varepsilon_{i,||}^{(1)}]^2}{\mu_B} + 2 \frac{[\varepsilon_{i,\perp}^{(1)}]^2}{\mu_B} - 4kT \frac{\varepsilon_{i,\perp}^{(2)}}{\mu_B^2} \right\} P_i$$

For example, for an $S = 3/2$ system the Boltzmann probabilities of individual M_S spin states are

$$P_{\pm 1/2} = \frac{1}{2 + 2 \exp(-2x)}$$

$$P_{\pm 3/2} = \frac{\exp(-2x)}{2 + 2 \exp(-2x)}$$

with $x = D/kT$. Then the contributions of individual spin states to the molar magnetic susceptibility can be found as

$$\chi_{\pm 1/2} = \frac{1}{3} \frac{C_0}{T} [(1/4)g_{\parallel}^2 + 2g_{\perp}^2(1 + 3/4x)]P_{\pm 1/2}$$

$$\chi_{\pm 3/2} = \frac{1}{3} \frac{C_0}{T} [(9/4)g_{\parallel}^2 + 2g_{\perp}^2(-3/4x)]P_{\pm 3/2}$$

so that the average susceptibility is

$$\begin{aligned} \chi_{\text{av}} = & \frac{1}{3} \frac{C_0}{T} [(1/4)g_{\parallel}^2 + 2g_{\perp}^2(1 + 3/4x)]2P_{\pm 1/2} \\ & + \frac{1}{3} \frac{C_0}{T} [(9/4)g_{\parallel}^2 + 2g_{\perp}^2(-3/4x)]2P_{\pm 3/2} \end{aligned}$$

The corresponding plots are in Fig. 8.11 for such a set of parameters ($D, g_{\parallel}, g_{\perp}$) as is responsible for the occurrence of a maximum on the $(\chi_{\text{av}}T)$ versus T curve. For $D < 0$ the ground state is $M_S = \pm 3/2$ and it is the only state populated near $T = 0$, giving rise to some magnetic moment.

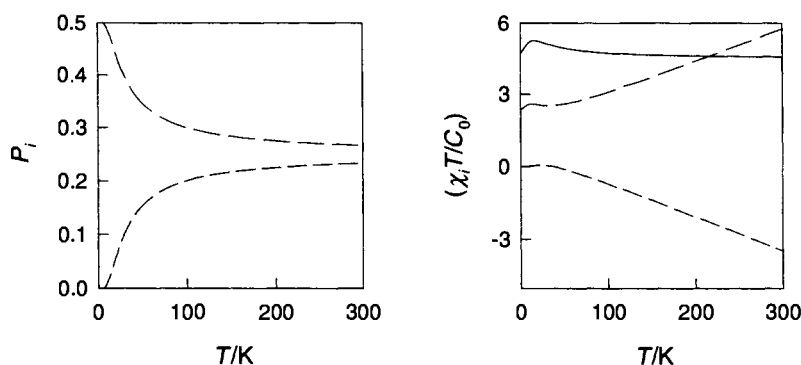


Fig. 8.11. Decomposition of the magnetic susceptibility into the contributions of individual states for an $S = 3/2$ system: $D/k = -20$ K, $g_{\parallel} = 2.5$, $g_{\perp} = 1.5$; long dashed— $M_S = \pm 3/2$, short dashed— $M_S = \pm 1/2$, solid— $(\chi_{\text{av}}T)$.

With a temperature drift this state becomes depopulated in favour of the $M_S = \pm 1/2$ state which is less magnetically productive. Consequently the total susceptibility is reduced so that a maximum on the $(\chi_{av}T)$ versus T curve can appear.

The susceptibility contributions of individual states derived for the remaining spin cases are collected in Table 8.25.

8.4.6 Rhombic magnetic anisotropy

The involvement of the E -parameter is complicated by the absence of analytic formulae for the corresponding energy levels

$$\varepsilon_{i,a} = f(D, E, g_a, B_a)$$

Numerical solutions of the secular equations, nevertheless, exist and thus some more complex procedures outlined in Section 6.1 can be applied to obtain the magnetic susceptibility components

$$\chi_a = f(D, E, g_a; T)$$

A few analytical solutions for eigenvalues are listed in Table 8.26.

8.4.7 Magnetisation of a zero-field splitting system

For a low temperature and high fields the zero-field splitting systems are no longer linear magnetics. The thermal energy kT is of the order of the

TABLE 8.25

Formulae for the susceptibility contributions of zero-field splitting systems

$S = 1$	$\chi_0 = (1/3)(C_0/T)[4g_{\perp}^2(1/x)]/[1 + 2 \exp(-x)]$ $\chi_{+1} = (1/3)(C_0/T)[g_{\parallel}^2 + 4g_{\perp}^2(1/x)] \exp(-x)/[1 + 2 \exp(-x)]$ $\chi_{-1} = (1/3)(C_0/T)g_{\parallel}^2 \exp(-x)/[1 + 2 \exp(-x)]$
$S = 3/2$	$\chi_{\pm 1/2} = (1/3)(C_0/T)[g_{\parallel}^2(1/4) + 2g_{\perp}^2(1 + 3/4x)]/[2 + 2 \exp(-2x)]$ $\chi_{\pm 3/2} = (1/3)(C_0/T)[g_{\parallel}^2(9/4) + 2g_{\perp}^2(-3/4x)] \exp(-2x)/[2 + 2 \exp(-2x)]$
$S = 2$	$\chi_0 = (1/3)(C_0/T)[12g_{\perp}^2/x]/[1 + 2 \exp(-x) + 2 \exp(-4x)]$ $\chi_{\pm 1} = (1/3)(C_0/T)[g_{\parallel}^2 + g_{\perp}^2(-14/3x)] \exp(-x)/[1 + 2 \exp(-x) + 2 \exp(-4x)]$ $\chi_{\pm 2} = (1/3)(C_0/T)[4g_{\parallel}^2 + g_{\perp}^2(-4/3x)] \exp(-4x)/[1 + 2 \exp(-x) + 2 \exp(-4x)]$
$S = 5/2$	$\chi_{\pm 1/2} = (1/3)(C_0/T)[g_{\parallel}^2(1/4) + 2g_{\perp}^2(9/4 + 2/x)]/[2 + 2 \exp(-2x) + 2 \exp(-6x)]$ $\chi_{\pm 3/2} = (1/3)(C_0/T)[g_{\parallel}^2(9/4) + 2g_{\perp}^2(-11/8x)] \exp(-2x)/[2 + 2 \exp(-2x) + 2 \exp(-6x)]$ $\chi_{\pm 5/2} = (1/3)(C_0/T)[g_{\parallel}^2(25/4) + 2g_{\perp}^2(-5/8x)] \exp(-6x)/[2 + 2 \exp(-2x) + 2 \exp(-6x)]$

TABLE 8.26

Analytical expressions for the exact eigenvalues of zero-field splitting systems [14, 17]

Spin	Direction	Shifted eigenvalues
$S = 1$	z	$D + (E^2 + G_z^2)^{1/2}$
		0
		$D - (E^2 + G_z^2)^{1/2}$
	x	$D + E$
		$(D - E)/2 - [(D - E)^2/4 + G_x^2]^{1/2}$
		$(D - E)/2 + [(D - E)^2/4 + G_x^2]^{1/2}$
$S = 3/2$	z	$(D + E)/2 + [(D + E)^2/4 + G_z^2]^{1/2}$
		$(D + E)/2 - [(D + E)^2/4 + G_z^2]^{1/2}$
		$D - E$
	x	$D + G_z/2 + [(D + G_z)^2 + 3E^2]^{1/2}$
		$D - G_z/2 + [(D - G_z)^2 + 3E^2]^{1/2}$
		$D + G_z/2 - [(D + G_z)^2 + 3E^2]^{1/2}$
		$D - G_z/2 - [(D - G_z)^2 + 3E^2]^{1/2}$
	y	$D + G_x/2 + [(D - G_x/2)^2 + 3(E + G_x/2)^2]^{1/2}$
		$D - G_x/2 + [(D + G_x/2)^2 + 3(E - G_x/2)^2]^{1/2}$
		$D + G_x/2 - [(D - G_x/2)^2 + 3(E + G_x/2)^2]^{1/2}$
		$D - G_x/2 - [(D + G_x/2)^2 + 3(E - G_x/2)^2]^{1/2}$
	y	$D + G_y/2 + [(D - G_y/2)^2 + 3(E - G_y/2)^2]^{1/2}$
		$D - G_y/2 + [(D + G_y/2)^2 + 3(E + G_y/2)^2]^{1/2}$
		$D + G_y/2 - [(D - G_y/2)^2 + 3(E - G_y/2)^2]^{1/2}$
		$D - G_y/2 - [(D + G_y/2)^2 + 3(E + G_y/2)^2]^{1/2}$

magnetic energy and of the zero-field splitting energy

$$D \approx g\mu_B B \approx kT$$

and thus a more fundamental treatment is required.

Let us consider an $S = 2$ system under the constraint of $E = 0$. The energy levels (Table 8.22) can be substituted into the partition function so that

$$\begin{aligned}
 Z_{||} = \sum_{i=1}^5 \exp(-\varepsilon_{i,||}/kT) &= \exp(0) + \exp[-(D + \gamma B)/kT] \\
 &+ \exp[-(D - \gamma B)/kT] + \exp[-(4D + 2\gamma B)/kT] \\
 &+ \exp[-(4D - 2\gamma B)/kT]
 \end{aligned}$$

with

$$\gamma \equiv g_{||}\mu_B$$

Then the molar magnetisation is

$$\begin{aligned} M_{||} &= N_A kT \left(\frac{\partial \ln Z_{||}}{\partial B} \right)_T \\ &= N_A \frac{\gamma}{Z_{||}} \{ -\exp[-(D + \gamma B)/kT] + \exp[-(D - \gamma B)/kT] \\ &\quad - 2\exp[-(4D + 2\gamma B)/kT] + 2\exp[-(4D - 2\gamma B)/kT] \} \end{aligned}$$

No expansions of the exponentials are permitted. The approximation for the mean susceptibility

$$\bar{\chi}_{||} = \mu_0 \frac{M_{||}}{B}$$

can violate and a more laborious derivation of the differential magnetic susceptibility formula is necessary

$$\begin{aligned} \tilde{\chi}_{||} &= \mu_0 \frac{\partial M_{||}}{\partial B} \\ &= N_A \mu_0 \gamma \frac{\partial}{\partial B} \frac{1}{Z_{||}} \{ \exp[(D + \gamma B)/kT] - \exp[(D - \gamma B)/kT] \\ &\quad + 2\exp[(4D + 2\gamma B)/kT] - 2\exp[(4D - 2\gamma B)/kT] \} \end{aligned}$$

yielding

$$\begin{aligned} \tilde{\chi}_{||} &= \frac{C_0}{T} \frac{g_{||}^2}{Z_{||}^2} \{ Z_{||} \{ \exp[-(D + \gamma B)/kT] + \exp[-(D - \gamma B)/kT] \\ &\quad + 4\exp[-(4D + 2\gamma B)/kT] + 4\exp[-(4D - 2\gamma B)/kT] \} \\ &\quad - \{ -\exp[-(D + \gamma B)/kT] + \exp[-(D - \gamma B)/kT] \\ &\quad - 2\exp[-(4D + 2\gamma B)/kT] + 2\exp[-(4D - 2\gamma B)/kT] \}^2 \} \end{aligned}$$

These formulae can be written in the form

$$\begin{aligned} M_{||} &= N_A \mu_B \frac{g_{||}}{Z_{||}} T_1 \\ \tilde{\chi}_{||} &= \frac{C_0}{T} \frac{g_{||}^2}{Z_{||}^2} (Z_{||} T_2 - T_1^2) \end{aligned}$$

with

$$\begin{aligned} T_1 &= -\exp[-(D + \gamma B)/kT] + \exp[-(D - \gamma B)/kT] \\ &\quad - 2\exp[-(4D + 2\gamma B)/kT] + 2\exp[-(4D - 2\gamma B)/kT] \end{aligned}$$

and

$$T_2 = \exp[-(D + \gamma B)/kT] + \exp[-(D - \gamma B)/kT] \\ + 4 \exp[-(4D + 2\gamma B)/kT] + 4 \exp[-(4D - 2\gamma B)/kT]$$

The magnetisation formula has been used to generate the curves displayed in Fig. 8.12. It can be seen that some abrupt steps appear at the magnetisation curve. These are less pronounced, or even disappear, when the temperature is high enough. The individual steps correspond to a change of the ground state due to magnetic perturbation: $M_S = 0$ is the ground state below the first critical field B_{c1} ; above it $M_S = -1$ becomes the ground state until the second critical field B_{c2} is reached. Above it $M_S = -2$ adopts the role of the ground state.

The terms of the magnetisation and magnetic susceptibility are listed in Table 8.27 for the remaining spin cases and displayed in Figs. 8.13 and 8.14.

From Fig. 8.13 it can be seen that the resolution of the steps on the magnetisation curve depends upon the balance between T , B and D . For fixed T and low D no resolution is observed. With increasing D the steps become clearly visible at higher fields.

Fig. 8.14 brings evidence that zero-field splitting systems at a low temperature ($T = 4.2$ K) do not behave like linear magnetics: the magnetic susceptibility is a field-dependent quantity which, for higher D , is not a monotonic but an oscillating function.

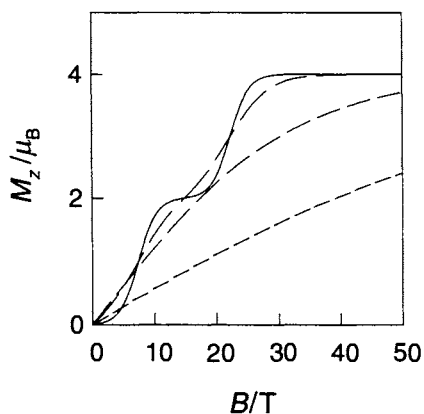


Fig. 8.12. Parallel magnetisation per atom versus magnetic field for an $S = 2$ zero-field splitting system: $D/k = 1$ K; individual curves correspond to $T = 2$ K (solid), 4.2 K (long dashed), 20 K (medium dashed) and 77 K (short dashed).

TABLE 8.27

Terms of parallel magnetisation and magnetic susceptibility for zero-field splitting systems ($E = 0$)

$Z_{ }$	T_1	T_2
$S = 1$		
$1 + \exp[-(D + \gamma B)/kT]$	$-\exp[-(D + \gamma B)/kT]$	$\exp[-(D + \gamma B)/kT]$
$+ \exp[-(D - \gamma B)/kT]$	$+ \exp[-(D - \gamma B)/kT]$	$+ \exp[-(D - \gamma B)/kT]$
$S = 3/2$		
$\exp[-(+\gamma B/2)/kT]$	$-(1/2)\exp[-(+\gamma B/2)/kT]$	$(1/4)\exp[-(+\gamma B/2)/kT]$
$+ \exp[-(-\gamma B/2)/kT]$	$+ (1/2)\exp[-(-\gamma B/2)/kT]$	$+ (1/4)\exp[-(-\gamma B/2)/kT]$
$+ \exp[-(2D + \gamma B3/2)/kT]$	$-(3/2)\exp[-(2D + \gamma B3/2)/kT]$	$+ (9/4)\exp[-(2D + \gamma B3/2)/kT]$
$+ \exp[-(2D - \gamma B3/2)/kT]$	$+ (3/2)\exp[-(2D - \gamma B3/2)/kT]$	$+ (9/4)\exp[-(2D - \gamma B3/2)/kT]$
$S = 2$		
$1 + \exp[-(D + \gamma B)/kT]$	$-\exp[-(D + \gamma B)/kT]$	$\exp[-(D + \gamma B)/kT]$
$+ \exp[-(D - \gamma B)/kT]$	$+ \exp[-(D - \gamma B)/kT]$	$+ \exp[-(D - \gamma B)/kT]$
$+ \exp[-(4D + 2\gamma B)/kT]$	$-2\exp[-(4D + 2\gamma B)/kT]$	$+ 4\exp[-(4D + 2\gamma B)/kT]$
$+ \exp[-(4D - 2\gamma B)/kT]$	$+ 2\exp[-(4D - 2\gamma B)/kT]$	$+ 4\exp[-(4D - 2\gamma B)/kT]$
$S = 5/2$		
$\exp[-(+\gamma B/2)/kT]$	$-(1/2)\exp[-(+\gamma B/2)/kT]$	$(1/4)\exp[-(+\gamma B/2)/kT]$
$+ \exp[-(-\gamma B/2)/kT]$	$+ (1/2)\exp[-(-\gamma B/2)/kT]$	$+ (1/4)\exp[-(-\gamma B/2)/kT]$
$+ \exp[-(2D + \gamma B3/2)/kT]$	$-(3/2)\exp[-(2D + \gamma B3/2)/kT]$	$+ (9/4)\exp[-(2D + \gamma B3/2)/kT]$
$+ \exp[-(2D - \gamma B3/2)/kT]$	$+ (3/2)\exp[-(2D - \gamma B3/2)/kT]$	$+ (9/4)\exp[-(2D - \gamma B3/2)/kT]$
$+ \exp[-(6D + \gamma B5/2)/kT]$	$-(5/2)\exp[-(6D + \gamma B5/2)/kT]$	$+ (25/4)\exp[-(6D + \gamma B5/2)/kT]$
$+ \exp[-(6D - \gamma B5/2)/kT]$	$+ (5/2)\exp[-(6D - \gamma B5/2)/kT]$	$+ (25/4)\exp[-(6D - \gamma B5/2)/kT]$

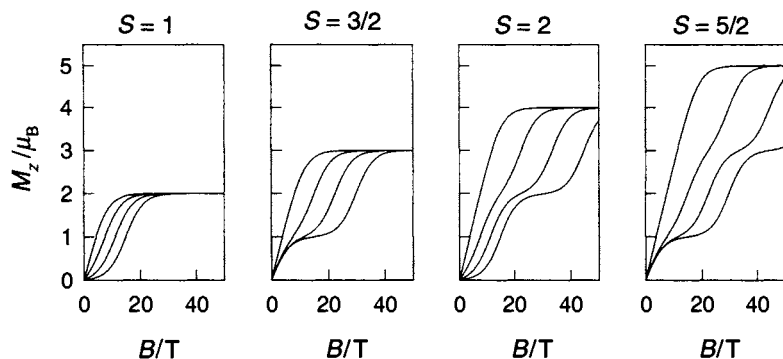


Fig. 8.13. Parallel magnetisation per atom versus magnetic field for zero-field splitting systems: $T = 4.2$ K; $D/k = 5, 10, 15$ and 20 K.

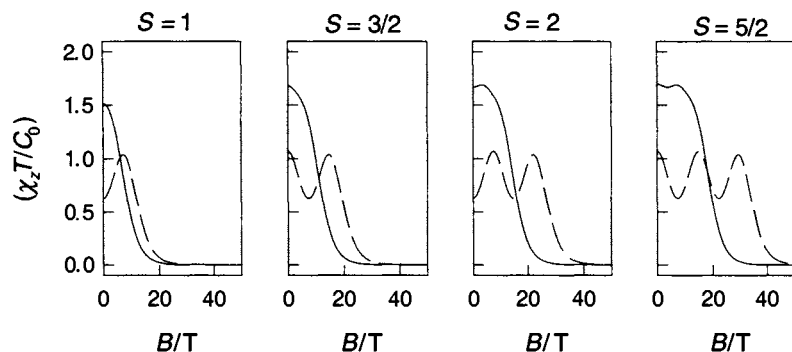


Fig. 8.14. Parallel differential susceptibility function for zero-field splitting systems: $T = 4.2$ K; $D/k = 5$ (solid) and 10 K (dashed).

The magnetisation and magnetic susceptibility in the perpendicular direction can be treated in a similar way but, owing to square roots in the eigenvalue expressions, the final formulae will be more complex.

Let us assume an $S = 3/2$ system as an example. The partition function in the perpendicular direction is defined with the help of the exact eigenvalues listed in Table 8.26. Then the corresponding magnetisation becomes as given in Table 8.28. The formula for M_y differs from that for M_x only in some signs. The averaged magnetisation is

$$M_{\text{av}} = \frac{1}{3}(M_x + M_y + M_z)$$

These formulae have been applied in Fig. 8.15.

TABLE 8.28

Exact magnetisation formulae for an $S = 3/2$ system

$$M_z = -\frac{1}{2} \frac{N_A \mu_B g_z}{Z_z} \left\{ \begin{aligned} &+ \exp\{-[+G_z/2 + \sqrt{(D + G_z)^2 + 3E^2}]/kT\} \{+1 + [+2(D + G_z)]/\sqrt{(D + G_z)^2 + 3E^2}\} \\ &+ \exp\{-[-G_z/2 + \sqrt{(D - G_z)^2 + 3E^2}]/kT\} \{-1 + [-2(D - G_z)]/\sqrt{(D - G_z)^2 + 3E^2}\} \\ &+ \exp\{-[+G_z/2 - \sqrt{(D + G_z)^2 + 3E^2}]/kT\} \{+1 - [+2(D + G_z)]/\sqrt{(D + G_z)^2 + 3E^2}\} \\ &+ \exp\{-[-G_z/2 - \sqrt{(D - G_z)^2 + 3E^2}]/kT\} \{-1 - [-2(D - G_z)]/\sqrt{(D - G_z)^2 + 3E^2}\} \end{aligned} \right\}$$

$$M_x = -\frac{1}{2} \frac{N_A \mu_B g_x}{Z_x} \left\{ \begin{aligned} &+ \exp\{-[+G_x/2 + \sqrt{(D - G_x/2)^2 + 3(E + G_x/2)^2}]/kT\} \\ &\times \{+1 + [-(D - G_x/2) + 3(E + G_x/2)]/\sqrt{(D - G_x/2)^2 + 3(E + G_x/2)^2}\} \\ &+ \exp\{-[-G_x/2 + \sqrt{(D + G_x/2)^2 + 3(E - G_x/2)^2}]/kT\} \\ &\times \{-1 + [(D + G_x/2) - 3(E - G_x/2)]/\sqrt{(D + G_x/2)^2 + 3(E - G_x/2)^2}\} \\ &+ \exp\{-[+G_x/2 - \sqrt{(D - G_x/2)^2 + 3(E + G_x/2)^2}]/kT\} \\ &\times \{+1 - [-(D - G_x/2) + 3(E + G_x/2)]/\sqrt{(D - G_x/2)^2 + 3(E + G_x/2)^2}\} \\ &+ \exp\{-[-G_x/2 - \sqrt{(D + G_x/2)^2 + 3(E - G_x/2)^2}]/kT\} \\ &\times \{-1 - [(D + G_x/2) - 3(E - G_x/2)]/\sqrt{(D + G_x/2)^2 + 3(E - G_x/2)^2}\} \end{aligned} \right\}$$

$$M_y = -\frac{1}{2} \frac{N_A \mu_B g_y}{Z_y} \left\{ \begin{aligned} &+ \exp\{-[+G_y/2 + \sqrt{(D - G_y/2)^2 + 3(E - G_y/2)^2}]/kT\} \\ &\times \{+1 + [-(D - G_y/2) - 3(E - G_y/2)]/\sqrt{(D - G_y/2)^2 + 3(E - G_y/2)^2}\} \\ &+ \exp\{-[-G_y/2 + \sqrt{(D + G_y/2)^2 + 3(E + G_y/2)^2}]/kT\} \\ &\times \{-1 + [(D + G_y/2) + 3(E + G_y/2)]/\sqrt{(D + G_y/2)^2 + 3(E + G_y/2)^2}\} \\ &+ \exp\{-[+G_y/2 - \sqrt{(D - G_y/2)^2 + 3(E - G_y/2)^2}]/kT\} \\ &\times \{+1 - [-(D - G_y/2) - 3(E - G_y/2)]/\sqrt{(D - G_y/2)^2 + 3(E - G_y/2)^2}\} \\ &+ \exp\{-[-G_y/2 - \sqrt{(D + G_y/2)^2 + 3(E + G_y/2)^2}]/kT\} \\ &\times \{-1 - [(D + G_y/2) + 3(E + G_y/2)]/\sqrt{(D + G_y/2)^2 + 3(E + G_y/2)^2}\} \end{aligned} \right\}$$

TABLE 8.28

Exact magnetisation formulae for an $S = 3/2$ system (*contd.*)

$$\begin{aligned}
 Z_z &= \exp\{-[+G_z/2 + \sqrt{(D + G_z)^2 + 3E^2}]/kT\} \\
 &\quad + \exp\{-[-G_z/2 + \sqrt{(D - G_z)^2 + 3E^2}]/kT\} \\
 &\quad + \exp\{-[+G_z/2 - \sqrt{(D + G_z)^2 + 3E^2}]/kT\} \\
 &\quad + \exp\{-[-G_z/2 - \sqrt{(D - G_z)^2 + 3E^2}]/kT\} \\
 \\
 Z_x &= \exp\{-[+G_x/2 + \sqrt{(D - G_x/2)^2 + 3(E + G_x/2)^2}]/kT\} \\
 &\quad + \exp\{-[-G_x/2 + \sqrt{(D + G_x/2)^2 + 3(E - G_x/2)^2}]/kT\} \\
 &\quad + \exp\{-[+G_x/2 - \sqrt{(D - G_x/2)^2 + 3(E + G_x/2)^2}]/kT\} \\
 &\quad + \exp\{-[-G_x/2 - \sqrt{(D + G_x/2)^2 + 3(E - G_x/2)^2}]/kT\} \\
 \\
 Z_y &= \exp\{-[+G_y/2 + \sqrt{(D - G_y/2)^2 + 3(E - G_y/2)^2}]/kT\} \\
 &\quad + \exp\{-[-G_y/2 + \sqrt{(D + G_y/2)^2 + 3(E + G_y/2)^2}]/kT\} \\
 &\quad + \exp\{-[+G_y/2 - \sqrt{(D - G_y/2)^2 + 3(E - G_y/2)^2}]/kT\} \\
 &\quad + \exp\{-[-G_y/2 - \sqrt{(D + G_y/2)^2 + 3(E + G_y/2)^2}]/kT\}
 \end{aligned}$$

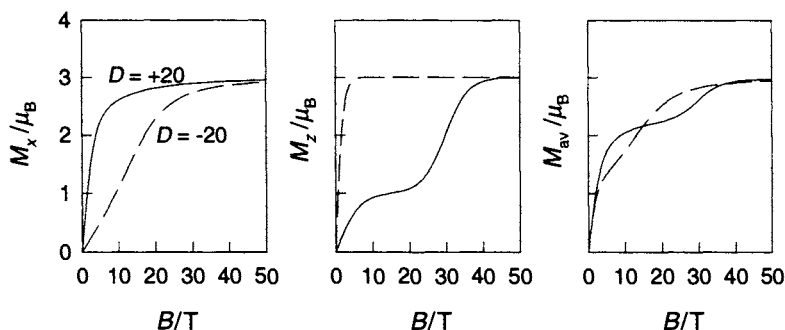


Fig. 8.15. Parallel, perpendicular and averaged magnetisation for an $S = 3/2$ zero-field splitting system: $D/k = 20$ K (solid) and -20 K (dashed), $E = 0$, $T = 4.2$ K.

8.4.8 Higher-order terms

A more general form of the zero-field splitting operator is

$$\hat{H}^{\text{zfs}} = \sum_{k=0} \sum_{m=0}^k B_k^m \hat{O}_k^m$$

where only even terms ($k = 0, 2, 4$ and 6) can contribute. The maximum power is determined by the value of the spin number since the restrictions are:

$$k \leq 2 \text{ for } S = 1 \text{ and } 3/2$$

$$k \leq 4 \text{ for } S = 2 \text{ and } 5/2$$

$$k \leq 6 \text{ for } S = 3 \text{ and } 7/2$$

Now we can see that for $S \geq 2$, in addition to the second-order equivalent operators, the fourth-order equivalent operators can contribute. These, in fact, correspond to higher-order spin-spin interaction—a biquadratic spin-spin interaction, like

$$\hat{H}^{\text{bq}} = b(\hat{S} \cdot \hat{S})^2$$

8.4.9 Splitting in cubic symmetry

In the case of perfect octahedral symmetry the biquadratic term is

$$\begin{aligned} \hat{H}^{\text{bq}} &= B_4^0 \hat{O}_4^0 + B_4^4 \hat{O}_4^4 = B_4(\hat{O}_4^0 + 5\hat{O}_4^4) \\ &= \frac{1}{6}a \left\{ (\hat{S}_x^4 + \hat{S}_y^4 + \hat{S}_z^4)[\hbar^{-4}] - \frac{1}{5}S(S+1)(3S^2 + 3S - 1) \right\} \end{aligned}$$

with the relationship among the Hamiltonian parameters as follows

$$a = 120B_4 = 120B_4^0 = 24B_4^4$$

The corresponding matrix elements for $S = 5/2$ are

$$\langle M_S | \hat{H}^{\text{bq}} | M'_S \rangle = \begin{pmatrix} (1/2)a & 0 & 0 & 0 & (\sqrt{5}/2)a & 0 \\ 0 & -(3/2)a & 0 & 0 & 0 & (\sqrt{5}/2)a \\ 0 & 0 & a & 0 & 0 & 0 \\ 0 & 0 & 0 & a & 0 & 0 \\ (\sqrt{5}/2)a & 0 & 0 & 0 & -(3/2)a & 0 \\ 0 & (\sqrt{5}/2)a & 0 & 0 & 0 & (1/2)a \end{pmatrix}$$

giving the zero-field eigenvalues

$$\varepsilon_{1,2} = -2a$$

$$\varepsilon_{3,4,5,6} = a$$

The separation of the quartet state from the ground doublet is

$$\Delta\varepsilon = 3a$$

Such a result is correct from the viewpoint of the double group theory: the group $\mathbf{O}'$ can have only the doubly degenerate Γ_7 or quadruply degenerate Γ_8 irreducible representations. The above result is well fulfilled either for perfect octahedral symmetry or for perfect tetrahedral symmetry of the coordination polyhedron.

However, one can pass from the fourfold axis coordinate system (the z -axis being coincident with the $\hat{C}_4$ rotational axis) to a threefold one where

$$\hat{H}^{\text{bq}} = -\frac{2}{3}B_4(\hat{O}_4^0 + 20\sqrt{2}\hat{O}_4^3)$$

and

$$\frac{1}{6}a = -\frac{40}{3}B_4^0 = -\frac{800\sqrt{2}}{3}B_4^3$$

hold true. Then the matrix elements are

$$\langle M_S | \hat{H}^{\text{bq}} | M'_S \rangle = \begin{pmatrix} -(1/3)a & 0 & 0 & -(\sqrt{20}/3)a & 0 & 0 \\ 0 & a & 0 & 0 & 0 & 0 \\ 0 & 0 & -(2/3)a & 0 & 0 & (\sqrt{20}/3)a \\ -(\sqrt{20}/3)a & 0 & 0 & -(2/3)a & 0 & 0 \\ 0 & 0 & 0 & 0 & a & 0 \\ 0 & 0 & (\sqrt{20}/3)a & 0 & 0 & -(1/3)a \end{pmatrix}$$

and they yield exactly the same eigenvalues as before.

The addition of the Zeeman term along either the fourfold or the threefold axis leads to the eigenvalues listed in Table 8.29. The expansion of the square roots, for instance

$$\begin{aligned} [(a \pm 2G)^2 + (5/4)a^2]^{1/2} &= \frac{3}{2}a \left[1 + 16 \frac{\pm aG + G^2}{9a^2} \right]^{1/2} \\ &\approx \frac{3}{2}a \left[1 + \frac{1}{2} \left(16 \frac{\pm aG + G^2}{9a^2} \right) - \frac{1}{8} \left(16 \frac{\pm aG + G^2}{9a^2} \right)^2 + \dots \right] \\ &= \frac{3}{2}a \pm \frac{4}{3}G + \frac{20}{27} \frac{G^2}{a} + O_3(G) \end{aligned}$$

yields approximate expressions for the energy levels, assuming that the magnetic field is much lower than the cubic zero-field splitting parameter

$$G_{\parallel} = \mu_B g_{\parallel} B \ll a$$

Figure 8.16 brings information of how the energy levels are split under the influence of the magnetic field. As a consequence of cubic symmetry the energy levels in the perpendicular direction should be the same as in the parallel direction and the g -values isotropic.

8.4.10 Splitting in non-cubic symmetry

In the case of non-cubic symmetry of the coordination polyhedron, but close to the cubic one, the zero-field splitting Hamiltonian adopts the form of [10]

(a) (nearly) tetragonal symmetry

$$\hat{H}^{\text{zfs}(4)} = B_2^0 \hat{O}_2^0 + (B_2^2 \hat{O}_2^2) + B_4^0 \hat{O}_4^0 + B_4^2 (\hat{O}_4^0 + 5\hat{O}_4^4)$$

TABLE 8.29

Energy levels for a cubic system for $S = 5/2$ [10]^a

Magnetic field	Exact energy	Approximate energy
(a) along a fourfold axis	$\pm(1/2)G_{\parallel} + a$ $(1/2)(\pm G_{\parallel} - a) + [(a \pm 2G_{\parallel})^2 + (5/4)a^2]^{1/2}$ $(1/2)(\pm G_{\parallel} - a) - [(a \pm 2G_{\parallel})^2 + (5/4)a^2]^{1/2}$	$a \pm (1/2)G_{\parallel}$ $a \pm (11/6)G_{\parallel} + (20/27)(G_{\parallel}^2/a)$ $-2a \pm (5/6)G_{\parallel} - (20/27)(G_{\parallel}^2/a)$
(b) along a threefold axis	$\pm(3/2)G_{\parallel} + a$ $\pm G_{\parallel} - (1/2)a + (1/6)[(a \pm 9G_{\parallel})^2 + 80a^2]^{1/2}$ $\pm G_{\parallel} - (1/2)a - (1/6)[(a \pm 9G_{\parallel})^2 + 80a^2]^{1/2}$	$a \pm (3/2)G_{\parallel}$ $a \pm (7/6)G_{\parallel} + (20/27)(G_{\parallel}^2/a)$ $-2a \pm (5/6)G_{\parallel} - (20/27)(G_{\parallel}^2/a)$

^aFor $a \gg \mu_B g_{\parallel} B$.

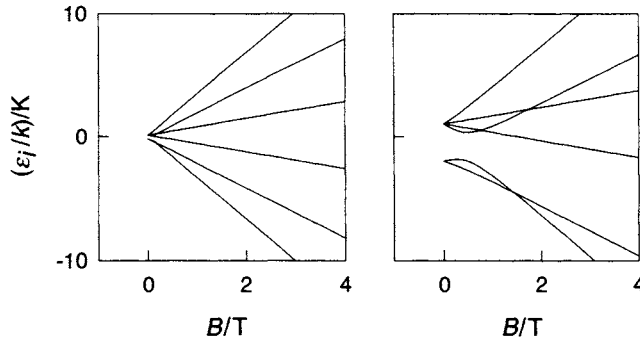


Fig. 8.16. Exact energy levels of an $S = 5/2$ system in cubic symmetry: $a/k = 0.1$ K (left) and 1 K (right).

(b) (nearly) trigonal symmetry

$$\hat{H}^{\text{zfs}(4)} = B_2^0 \hat{O}_2^0 + (B_2^2 \hat{O}_2^2) + B_4^0 \hat{O}_4^0 - \frac{2}{3} B_4 (\hat{O}_4^0 + \sqrt{800} \hat{O}_4^3)$$

which is equivalent to the form

$$\begin{aligned} \hat{H}^{\text{zfs}(4)} = & D\{\hat{S}_z^2[\hbar^{-2}] - \frac{1}{3}S(S+1)\} + E(\hat{S}_x^2 - \hat{S}_y^2)[\hbar^{-2}] \\ & + \frac{1}{6}a\{(\hat{S}_\xi^4 + \hat{S}_\eta^4 + \hat{S}_\zeta^4)[\hbar^{-4}] - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)\} \\ & + \frac{1}{180}F\{35\hat{S}_z^4[\hbar^{-4}] - 30S(S+1)\hat{S}_z^2[\hbar^{-2}] + 25\hat{S}_z^2[\hbar^{-2}] \\ & - 6S(S+1) + 3S^2(S+1)^2\} \end{aligned}$$

Here the ξ , η and ζ axes are the fourfold axes for the cubic part of the crystal field. The z -axis is chosen along either the tetragonal axis (when x , y and z coincide with ξ , η and ζ) or the trigonal $[111]$ axis of the crystal. The Hamiltonian parameters are interrelated through

$$a = 120B_4$$

$$D = 3B_2^0$$

$$E = B_2^2$$

$$F = 180B_4^0$$

(One must be careful of definitions of the Hamiltonian parameters in comparing different sources since other notations can be met in literature.) The F -term enters only the diagonal matrix elements; the a -term enters the off-diagonal matrix elements, being shifted by four positions from the diagonal ones. A full zero-field splitting matrix for $S = 5/2$ and tetragonal symmetry becomes

$$\hat{H}^{\text{zfs}(4)} = \begin{pmatrix} (10/3)D & 0 & \sqrt{10}E & 0 & (\sqrt{5}/2)a & 0 \\ + (1/2)a' & - (2/3)D & 0 & \sqrt{18}E & 0 & (\sqrt{5}/2)a \\ 0 & - (3/2)a' & - (8/3)D + a' & 0 & \sqrt{18}E & 0 \\ \sqrt{10}E & 0 & 0 & - (8/3)D + a' & 0 & \sqrt{10}E \\ 0 & \sqrt{18}E & 0 & 0 & - (2/3)D & 0 \\ (\sqrt{5}/2)a & 0 & \sqrt{18}E & 0 & - (3/2)a' & (10/3)D \\ 0 & (\sqrt{5}/2)a & 0 & \sqrt{10}E & 0 & + (1/2)a' \end{pmatrix}$$

with

$$a' = a + (2/3)F$$

The energy levels (for $E = 0$) are compiled in Table 8.30.

The g -values of the overall spin Hamiltonian should keep the axial symmetry: $g_z = g_{\parallel}$ and $g_x = g_y = g_{\perp}$.

The second relevant case of $S = 2$ is of lower interest since the orbital contribution (e.g. in high-spin Fe(II) complexes) dominates.

TABLE 8.30

Zero-field energy levels for an $S = 5/2$ system in the combined effect of cubic splitting and tetragonal and/or trigonal distortion [10]

Lowered symmetry	Exact energy levels
(a) tetragonal distortion (D_{4h})	$a' - (8/3)D$ $-(1/2)a' + (4/3)D + [(a' + 2D)^2 + (5/4)a^2]^{1/2}$ $-(1/2)a' + (4/3)D - [(a' + 2D)^2 + (5/4)a^2]^{1/2}$ with $a' = a + (2/3)F$
(b) trigonal distortion (D_3)	$a'' - (2/3)D$ $-(1/2)a'' + (1/3)D + (1/6)[(a'' + 18D)^2 + 80a^2]^{1/2}$ $-(1/2)a'' + (1/3)D - (1/6)[(a'' + 18D)^2 + 80a^2]^{1/2}$ with $a'' = a - F$

8.4.11 *A*-tensor

The *A*-tensor, already introduced, represents a contribution of the angular momentum in second-order perturbation theory to the set of magnetic parameters. In the rigorous treatment the magnetic parameters are expressed as follows:

(1) the reduced magnetic susceptibility tensor

$$-\frac{1}{2}\kappa_{ab}^{\text{para}} = -\sum_{K \neq 0} \frac{X_a^{0K} X_b^{K0}}{E_K - E_0}$$

(2) the differential magnetogyric-ratio tensor

$$\Delta g_{ab} = -S_a^{-1} \sum_{K \neq 0} \frac{Y_a^{0K} X_b^{K0}}{E_K - E_0} - S_b^{-1} \sum_{K \neq 0} \frac{X_a^{0K} Y_b^{K0}}{E_K - E_0}$$

(3) the spin-spin interaction tensor

$$-\frac{1}{2}D_{ab} = -S_a^{-1} S_b^{-1} \sum_{K \neq 0} \frac{Y_a^{0K} Y_b^{K0}}{E_K - E_0}$$

with

$$X_a^{AB} = \mu_B [\hbar^{-1}] \left\langle \Psi_A \left| \sum_{i=1}^n \hat{l}_{Gia} \right| \Psi_B \right\rangle$$

where the position of the *i*th electron refers to a common gauge origin, and

$$Y_a^{AB} = \left\langle \Psi_A \left| \sum_{i=1}^n \xi_N(r_{Ni}) \hat{l}_{Nia} \hat{s}_{ia} \right| \Psi_B \right\rangle [\hbar^{-2}]$$

where the position of the *i*th electron refers to the *N*th nucleus.

Let us assume a mononuclear complex with the gauge origin coinciding with the central atom. Then one can introduce a molecular *A*-tensor as follows

$$A_{ab}^{\text{mol}} = -\sum_{K \neq 0} \frac{\langle 0 | \hat{L}_a | K \rangle \langle K | \hat{L}_b | 0 \rangle}{E_K - E_0} [\hbar^{-2}]$$

with

$$\langle A | \hat{L}_a | B \rangle = \left\langle \Psi_A \left| \sum_{i=1}^n \hat{L}_{Nia} \right| \Psi_B \right\rangle$$

For a single heavy centre with the kets restricted to a single atomic term there is

$$Y_a^{AB} = \langle \Psi_A | \lambda (\vec{L} \cdot \vec{S})_a | \Psi_B \rangle [\hbar^{-2}]$$

where a spin-orbit splitting parameter λ occurs. Then

$$S_a^{-1} Y_a^{AB} = \lambda \langle A | \hat{L}_a | B \rangle [\hbar^{-1}]$$

The above assumptions imply that the set of magnetic parameters becomes expressed as follows

$$-\frac{1}{2} \kappa_{ab}^{\text{para}} = \mu_B^2 A_{ab}^{\text{at}}$$

$$\Delta g_{ab} = 2\lambda A_{ab}^{\text{at}}$$

and

$$-\frac{1}{2} D_{ab} = \lambda^2 A_{ab}^{\text{at}} = D'_{ab}$$

The traceless D -tensor is introduced by subtracting one-third of the trace of the D -tensor; hence

$$\tilde{D}_{aa} = D'_{aa} - t\delta_{aa}$$

with

$$t = \frac{1}{3} \text{Tr}(\tilde{D}) = \frac{1}{3} (D'_{xx} + D'_{yy} + D'_{zz}) = \frac{1}{3} \lambda^2 (A_{xx} + A_{yy} + A_{zz})$$

Then the axial zero-field splitting parameter is expressed as follows

$$D = \frac{3}{2} \tilde{D}_{zz} = \lambda^2 \left[A_{zz} - \frac{1}{2} (A_{xx} + A_{yy}) \right]$$

and the rhombic zero-field splitting parameter as

$$E = \frac{1}{2} (\tilde{D}_{xx} - \tilde{D}_{yy}) = \frac{1}{2} \lambda^2 (A_{xx} - A_{yy})$$

The g -tensor components become

$$g_{aa} = g_e + 2\lambda A_{aa}$$

and the κ -tensor components are

$$\kappa_{aa}^{\text{para}} = -2\mu_B^2 A_{aa}$$

The temperature-independent paramagnetic term is

$$\begin{aligned}\chi^{\text{TIP}} &= \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}) \\ &= N_A \mu_0 \frac{1}{3}(\kappa_{xx} + \kappa_{yy} + \kappa_{zz}) \\ &= -N_A \mu_0 \mu_B^2 \frac{2}{3}(A_{xx} + A_{yy} + A_{zz})\end{aligned}$$

(Note that a different sign of the A -tensor and different definitions of the parameters D and E can be met in the literature.)

On the basis of the above relationships one can conclude that the three principal components of the A -tensor can be used to express the complete set of magnetic parameters that describes zero-field splitting in mononuclear complexes, i.e. g_{xx} , g_{yy} , g_{zz} , D and E . In addition, they define the temperature-independent paramagnetic term χ^{TIP} . Therefore it is possible to reconstruct the components of the A -tensor having the set of magnetic parameters determined from an appropriate fit of experimental data. However, an opposite procedure is possible: to consider the components of the A -tensor as the principal quantities which determine the ZFS parameters. Then one can consider A_{xx} , A_{yy} , A_{zz} and λ as a set of free parameters subjected to optimisation. In performing such a procedure, the following optimisation scheme can be followed.

1. A trial set of $(A_{xx}, A_{yy}, A_{zz}, \lambda)$ is used to evaluate the set of magnetic parameters $(g_{xx}, g_{yy}, g_{zz}, D, E)$.
2. The spin Hamiltonian matrices $\mathbf{H}_a$ are constructed from the $(g_{xx}, g_{yy}, g_{zz}, D, E)$ set and the “working” values of B_m . Atomic units (hartree) are an appropriate system of units for this purpose.
3. For a series of B_m values the eigenvalues $\varepsilon_{ia}(B_m)$ are found by diagonalising the spin Hamiltonian matrices. From the field dependence of energy levels:
 - (a) either the van Vleck coefficients result,
 - (b) or the microscopic magnetic moments μ_{ia} are evaluated.

4. Consequently the magnetic susceptibility is evaluated either via the van Vleck formula (mean magnetic susceptibility) or by differentiating the molar magnetisation (differential magnetic susceptibility).
5. The (powder) averaged magnetic susceptibility is corrected for the temperature-independent paramagnetic term

$$\chi_{\text{av}}^{\text{Calc.}} = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}) + \chi^{\text{TIP}}$$

6. A proper error functional is constructed of calculated and experimental data (the latter corrected for underlying diamagnetism) and subjected to minimisation.

The set of optimised parameters (A_{xx} , A_{yy} , A_{zz} , λ) can be considered:

- (a) either as a final set,
- (b) or as a first appropriate estimate for the set of magnetic parameters (g_{xx} , g_{yy} , g_{zz} , D , E) and χ^{TIP} , being refined by subsequent optimisation.

8.4.12 Measurements of zero-field splitting parameters

The temperature variation of the powder sample magnetic susceptibility reflects the integral effect of the g -values and zero-field splitting parameters (D , E , a , F). However, several other techniques allow us to measure these parameters directly:

- (a) magnetic anisotropy measurements on single crystals,
- (b) magnetisation measurements,
- (c) far-infrared spectroscopy,
- (d) calorimetric measurements on Schottky anomalies,
- (e) electron spin resonance,
- (f) inelastic neutron scattering.

Magnetic anisotropy measurements on oriented single crystals are capable of distinguishing the parallel and perpendicular magnetic susceptibilities [18]. Such measurements were done, for instance, for $[\text{C}(\text{NH}_2)_3]\text{V}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ salt between 1.5 and 20 K [19, 20]. It was found that on lowering the temperature the perpendicular component of the magnetic susceptibility increases whereas the parallel component passes through a maximum at ca 4 K and then turns to zero. Such a situation provides evidence that $D > 0$. More experimental data are collected in Table 8.31.

Magnetisation measurements at low temperature are capable of identifying the steps on the magnetisation curve (see Fig. 8.13) which directly reflect the magnitude of D . The condition is $D > 0$ since in this case the zero-field ground state is the component of the lowest spin projection; this is being altered by a component of the higher spin projection on increasing the field.

TABLE 8.31

Selected experimental data on the axial zero-field splitting parameter D

System	(D/hc) (cm ⁻¹) ^a	Ref.
V(III), $> d^2$, $S = 1$		
[C(NH ₂) ₃]V(SO ₄) ₂ · 6H ₂ O	3.79	[19, 20]
Cs ₃ VCl ₆ · 4H ₂ O	8.05	[21, 22]
[V(acac) ₃]	7.7	[23]
[V(urea) ₆](ClO ₄) ₃	5.86	[24]
Cr(III), d^3 , $S = 3/2$		
[Cr(NH ₃) ₆](ClO ₄) ₂ Br · CsBr	0.18	[25]
Fe(III), d^5 , $S = 5/2$		
[Fe(TPP)Cl]	5.9	[26]
[Fe(acac) ₃]	-0.11	[27]
Fe(II), d^6 , $S = 2$		
FeSiF ₆ · 6H ₂ O	12.2	[28, 29]
Co(II), d^7 , $S = 3/2$		
HgCo(NCS) ₄	10.6	[30]
[Co(Et ₄ dien)Cl ₂]	42-56	[31]
Ni(II), d^8 , $S = 1$		
[Ni(C ₆ H ₅ NO) ₆](ClO ₄) ₂	4.35	[32]
[NiSnCl ₆] · 6H ₂ O	0.40	[33]

^a (D/k) (K) = 0.6950(D/hc) (cm⁻¹).

Such experiments were done in high (pulsed) fields, for instance, for FeSiF₆ · 6H₂O [28, 29].

Far-infrared spectroscopy [34] is another technique capable of measuring the energy gap—the zero-field splitting parameter D .

Calorimetric measurements on Schottky anomalies are reviewed elsewhere [50].

Electron spin resonance (electron paramagnetic resonance) is a spectroscopic method that measures differences between magnetic energy levels. This is the principal difference with respect to magnetic susceptibility measurements which accounts for the Boltzmann occupation of all energy levels. The fundamental resonance condition is

$$\Delta E = h\nu = g_{||}\mu_B B_z$$

Here ν is a (fixed) frequency of the microwave source (e.g. ca 9 GHz at X-band, 35 GHz at Q-band). The spectrum is taken as a first derivative of the absorption versus the ramping magnetic field B_z . According to the selection rules, only those transitions are observable (intense) for which the change in the quantum number of the projection of the spin angular momentum fulfils the condition

$$\Delta M_S = \pm 1$$

However, a variety of forbidden transitions are frequently observed in certain situations. The structure of the ESR spectrum depends upon [10, 11, 14, 16, 17]

- (1) the g -tensor anisotropy,
- (2) the presence of the hyperfine interaction of the central atom nuclear spin with the electron spin (the A^M -tensor),
- (3) the presence of the super-hyperfine interaction of the ligand donor atom nuclear spins with the electron spin (the A^L -tensors),
- (4) the appearance of satellites among which the forbidden transitions may occur,
- (5) the nuclear quadrupole effects,
- (6) the zero-field splitting,
- (7) the eventual exchange (spin-spin) interactions of the magnetic centres.

Either a manual analysis of the important points of the spectrum or preferably a computer simulation of the entire spectrum is capable of subtracting the magnetic parameters. Let us focus on the determination of the zero-field splitting parameter D on the basis of ESR spectra for a mononuclear transition metal complex.

For an $S = 1$ system (e.g. a complex of Ni^{2+}) with $D = 0$ the Zeeman term makes the energy levels equally spaced. The two allowed ESR transitions occur at the same energy

$$-1 \leftrightarrow 0: \Delta E = h\nu = g_{||}\mu_B B_z$$

$$0 \leftrightarrow +1: \Delta E = h\nu = g_{||}\mu_B B_z$$

so that a single, doubly degenerate line is observed. For $D \neq 0$ the energy levels are modified and consequently two separate lines appear

$$-1 \leftrightarrow 0: \Delta E = h\nu = g_{||}\mu_B B_z - |D|$$

$$0 \leftrightarrow +1: \Delta E = h\nu = g_{||}\mu_B B_z + |D|$$

The inclusion of the rhombic zero-field splitting parameter $E \neq 0$ alters the energy levels and consequently the ESR transitions occur at

$$-1 \leftrightarrow 0: \Delta E = h\nu = g_{||}\mu_B B_z - |D| + E^2/2g_{||}\mu_B B_z$$

$$0 \leftrightarrow +1: \Delta E = h\nu = g_{||}\mu_B B_z + |D| - E^2/2g_{||}\mu_B B_z$$

For an $S = 3/2$ system (e.g. a complex of Co^{2+}) with $D = 0$ only one triply degenerate line is observed at

$$\Delta E = h\nu = g_{||}\mu_B B_z$$

This corresponds to the allowed transitions $-3/2 \leftrightarrow -1/2$, $-1/2 \leftrightarrow +1/2$ and $+1/2 \leftrightarrow +3/2$. For $D \neq 0$, however, the energy levels in zero field are split into two doublets separated by $2D$. The addition of the Zeeman term implies that the allowed transitions occur at the energies

$$-3/2 \leftrightarrow -1/2: \Delta E = h\nu = g_{||}\mu_B B_z - 2|D|$$

$$-1/2 \leftrightarrow +1/2: \Delta E = h\nu = g_{||}\mu_B B_z$$

$$+1/2 \leftrightarrow +3/2: \Delta E = h\nu = g_{||}\mu_B B_z + 2|D|$$

The model ESR spectrum, when the magnetic field is parallel to the axis of quantisation, will have a central absorption band surrounded by two lines at $\pm 2|D|$.

The sign of the D -parameter cannot be determined via this simple experiment; its determination requires variable temperature intensity data. It is important to notice that in the X-band spectrometer, with a frequency of the microwave radiation of some 9 GHz, the absorption occurs at ca $B_z = 0.34$ T and the energy separation involved is approximately 0.3 cm^{-1} . In the Q-band spectrometer the measured energy separation spans the order of 1 cm^{-1} . Therefore ESR absorption cannot take place between those energy levels whose splitting is too large. This can happen with non-Kramers ions ($S = 1$ or 2): the zero-field splitting leaves a spin-singlet ground state.

8.5 ORBITAL ANGULAR MOMENTUM CONTRIBUTION

8.5.1 Magnetic angular momentum

The spin Hamiltonian that accounts for the orbital angular momentum contribution is

$$\hat{H}^S = \mu_B \vec{L} \cdot \vec{B}[\hbar^{-1}] + \mu_B g_e \vec{S} \cdot \vec{B}[\hbar^{-1}] + \lambda \vec{L} \cdot \vec{S}[\hbar^{-2}]$$

where the first term is the orbital Zeeman term, the second the spin Zeeman term and the last the spin-orbit coupling term.

A non-zero contribution of the orbital angular momentum—a *magnetic angular momentum*—requires that the matrix elements of the atomic term functions $|\Psi_i\rangle = |L, M_L, S, M_S\rangle$ are non-zero

$$\langle \Psi_i | \hat{L}_a | \Psi_j \rangle \neq 0$$

To predict this property, group theory is applicable (Table 8.32). The angular momentum operator $\hat{L}_a$ ($a = x, y, z$) has the same transformation properties as the rotation operator $\hat{R}_a$ in the point group characterising the symmetry of the molecule. It transforms as the irreducible representation Γ_a of this group. The above requirement is equivalent to the condition that the direct product of the irreducible representations Γ_i of the wave function (which is a reducible representation Γ_r) contains the irreducible representation of the angular momentum (or rotation) operator Γ_a , viz.

$$\Gamma_i \otimes \Gamma_i = \Gamma_r = \Gamma_a + \dots$$

The involvement of the orbital angular momentum has the following consequences:

- (1) the basis set being considered covers all combinations of orbital and spin wave functions; it results from a direct product of the orbital and spin functions;
- (2) the spin-orbit coupling removes the degenerate $^{2S+1}\Gamma$ state. The Zeeman term may be considered as a perturbation acting on the eigenstates of $\hat{H}^{\text{so}} = \lambda \vec{L} \cdot \vec{S} [\hbar^{-2}]$. This is because the spin-orbit splitting ranges from

TABLE 8.32

Existence of the magnetic angular momentum (MAM) for d^n complexes

d^n	Free ion term	O_h group ^a Config.	Term	MAM	T_d group ^b Config.	Term	MAM
d^1	^2D	t_{2g}^1	$^2T_{2g}$	yes	e^1	^2E	no
d^2	^3F	t_{2g}^2	$^3T_{1g}$	yes	e^2	$^3A_2$	no
d^3	^4F	t_{2g}^3	$^4A_{2g}$	no	$e^2 t_2^1$	$^4T_1$	yes
		—	—	—	e^3	^2E	no
d^4	^5D	$t_{2g}^3 e_g^1$	^5E_g	no	$e^2 t_2^2$	$^5T_2$	yes
		t_{2g}^4	$^3T_{1g}$	yes	e^4	$^1A_1$	no
d^5	^6S	$t_{2g}^3 e_g^2$	$^6A_{1g}$	no	$e^2 t_2^3$	$^6A_1$	no
		t_{2g}^5	$^2T_{2g}$	yes	$e^4 t_2^1$	$^2T_2$	yes
d^6	^5D	$t_{2g}^4 e_g^2$	$^5T_{2g}$	yes	$e^3 t_2^3$	^5E	no
		t_{2g}^6	$^1A_{1g}$	no	$e^4 t_2^2$	$^3T_1$	yes
d^7	^4F	$t_{2g}^5 e_g^2$	$^4T_{1g}$	yes	$e^4 t_2^3$	$^4A_2$	no
		$t_{2g}^6 e_g^1$	^2E_g	no	—	—	—
d^8	^3F	$t_{2g}^6 e_g^2$	$^3A_{2g}$	no	$e^4 t_2^4$	$^3T_1$	yes
d^9	^2D	$t_{2g}^6 e_g^3$	^2E_g	no	$e^4 t_2^5$	$^2T_2$	yes

^a $\Gamma(\vec{L}) = T_{1g}$.^b $\Gamma(\vec{L}) = T_2$.

$\Delta E/hc = 100$ to 500 cm^{-1} whereas for laboratory magnetic fields $\mu_B g_e B/hc \approx 0.5$ to 5 cm^{-1} ;

- (3) the magnetic anisotropy assumes importance and the electronic g -factor becomes replaced by the g -tensor;
- (4) the magnetic susceptibility is a complicated function of magnetic parameters (λ , g -components) and often violates the Curie law, even at a relatively high temperature.

8.5.2 Atomic multiplets

The spin-orbit interaction in free atoms alters the atomic terms $|\Psi_i\rangle = |L, M_L, S, M_S\rangle$ into atomic multiplets, denoted as $|L, S, J, M_J\rangle = |JM\rangle$. The energies of the multiplets are given as follows

$$\begin{aligned} E_0(J) &= \left\langle JM \left| \sum_i \xi \vec{l}_i \cdot \vec{s}_i \right| JM \right\rangle [\hbar^{-2}] = \left\langle JM \left| \lambda \vec{L} \cdot \vec{S} \right| JM \right\rangle [\hbar^{-2}] \\ &= \frac{\lambda}{2} \left\langle JM \left| \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \right| JM \right\rangle [\hbar^{-2}] \\ &= \frac{\lambda}{2} [J(J+1) - L(L+1) - S(S+1)] \end{aligned}$$

where λ (in units of energy) stands for the spin-orbit splitting parameter, constant within a given term. The axis along $\hat{J}_z$ adopts the meaning of the quantisation axis and thus

$$\hat{J}_z |JM\rangle = M |JM\rangle [\hbar]$$

The electronic Zeeman operator

$$\hat{H}^Z = \mu_B \vec{L} \cdot \vec{B} [\hbar^{-1}] + \mu_B g_e \vec{S} \cdot \vec{B} [\hbar^{-1}]$$

has the following diagonal matrix elements

$$E_1(J, M) = \left\langle JM \left| \hat{H}^Z \right| JM \right\rangle$$

With the help of the replacement theorem (Section 1.4) these matrix elements can be replaced by those of the total angular momentum operator

$$\left\langle JM \left| \vec{L} + g_e \vec{S} \right| JM' \right\rangle = g_J \left\langle JM \left| \vec{J} \right| JM' \right\rangle$$

where g_J is a constant for the given J , independent of the projections M or M' . In determining the proportionality constant the Wigner–Eckart theorem can be used, i.e.

$$\langle LSJM | \hat{L}_z | LSJM \rangle = (-1)^{J-M} \begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} \langle LSJ \| \tilde{L} \| LSJ \rangle$$

The $3j$ -symbol is either tabulated or easily evaluable [35]

$$\begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} = (-1)^{J-M} \frac{M}{[J(J+1)(2J+1)]^{1/2}}$$

The reduced matrix element of a vector operator (tensor operator of the first rank) is expressed in terms of the $6j$ -symbol as follows

$$\langle LSJ \| \tilde{L} \| LSJ \rangle = (2J+1)(-1)^{L+S+J+1} \left\{ \begin{matrix} J & 1 & J \\ L & S & L \end{matrix} \right\} \langle L \| \tilde{L} \| L \rangle$$

where

$$\langle L \| \tilde{L} \| L \rangle = [(2L+1)(L+1)L]^{1/2} [\hbar]$$

and

$$\left\{ \begin{matrix} J & 1 & J \\ L & S & L \end{matrix} \right\} = (-1)^{L+S+J+1} \times \frac{2[J(J+1) + L(L+1) - S(S+1)]}{[(2J)(2J+1)(2J+2)(2L)(2L+1)(2L+2)]^{1/2}}$$

Then we arrive at the expression

$$\langle LSJM | \hat{L}_z | LSJM \rangle = \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} M [\hbar]$$

Now, the energy in first-order perturbation theory is

$$\begin{aligned} E_1(J, M) &= \langle JM | \hat{H}^Z | JM \rangle = \mu_B \vec{B} \cdot \langle JM | \vec{L} + g_e \vec{S} | JM \rangle [\hbar^{-1}] \\ &= \mu_B \vec{B} \cdot \langle JM | g_e \vec{J} - (g_e - 1) \vec{L} | JM \rangle [\hbar^{-1}] \\ &\approx \mu_B \vec{B} \cdot \langle JM | 2\vec{J} - \vec{L} | JM \rangle [\hbar^{-1}] \end{aligned}$$

Without loss of generality we take the field parallel to the z -axis

$$\begin{aligned} E_1(J, M) &= \mu_B B_z \langle JM | 2\hat{J}_z - \hat{L}_z | JM \rangle [\hbar^{-1}] \\ &= \mu_B B_z \left[2M - \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} M \right] \end{aligned}$$

and a comparison with

$$E_1(J, M) = \mu_B B_z g_J \langle JM | \hat{J}_z | JM \rangle [\hbar^{-1}] = \mu_B B_z g_J M$$

finally yields the *Landé factor*

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

which can be rewritten as

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} = \frac{3}{2} + \frac{(S+L+1)(S-L)}{2J(J+1)}$$

For some special cases one has

g_J	
$L = 0$	$= g_S = 2$
$S = 0$	$= g_L = 1$
$J = 0$	$= 2 + S = 2 + L$

It should be mentioned that the orbital and spin angular momentum vectors define the electronic magnetic momentum vector

$$\vec{\mu} = -\frac{\partial \varepsilon(J, M)}{\partial B} = -\mu_B (\vec{L} + g_e \vec{S}) [\hbar^{-1}]$$

which is not collinear with the total angular momentum vector

$$\vec{J} = \vec{L} + \vec{S}$$

because of $g_e \neq 1$. Consequently the vector $\vec{\mu}$ exhibits a rapid precession about the direction of $\vec{J}$ and thus only a component of $\vec{\mu}$ along $\vec{J}$ is conserved.

In conclusion, the diagonal matrix elements of the electron Zeeman operator are

$$\langle JM | \hat{H}_z^Z | JM \rangle = \mu_B g_J B_z \langle JM | \hat{J}_z | JM \rangle [\hbar^{-1}] = \mu_B g_J B_z M$$

The off-diagonal matrix elements are calculated with the help of the relationship [6, 12]

$$\begin{aligned} \langle J-1, M | \hat{L}_z | JM \rangle &= \langle J-1 | \vec{L} | J \rangle (-1)^{J-M} \begin{pmatrix} J-1 & 1 & J \\ -M & 0 & M \end{pmatrix} \\ &= - \left\{ \frac{[J^2 - (L-S)^2][(L+S+1)^2 - J^2]}{4J} \right\}^{1/2} \left[\frac{(J+M)(J-M)}{(2J+1)J(2J-1)} \right]^{1/2} [\hbar] \end{aligned}$$

and they are

$$\langle J'M | \hat{H}_z^Z | JM \rangle = \mu_B B_z [2 \langle J'M | \hat{J}_z | JM \rangle - \langle J'M | \hat{L}_z | JM \rangle] [\hbar^{-1}]$$

Since the first term vanishes, the off-diagonal matrix elements are

$$\begin{aligned} \langle J'M | \hat{H}_z^Z | JM \rangle &= -\mu_B B_z \langle J'M | \hat{L}_z | JM \rangle [\hbar^{-1}] \\ &= \mu_B B_z \left\{ \frac{[J^2 - (L-S)^2][(L+S+1)^2 - J^2]}{4J^2(4J^2-1)} \right\}^{1/2} \\ &\quad \times (J^2 - M^2)^{1/2} \end{aligned}$$

for

$$J' = J - 1$$

Depending on the relationships between the energy levels and the thermal energy, several limiting cases can be distinguished:

- (1) wide multiplets,
- (2) narrow multiplets,
- (3) multiplets of intermediate width,
- (4) multiplets with orbital reduction,
- (5) multiplets split by the crystal field of ligands.

These are briefly characterized in Fig. 8.17.

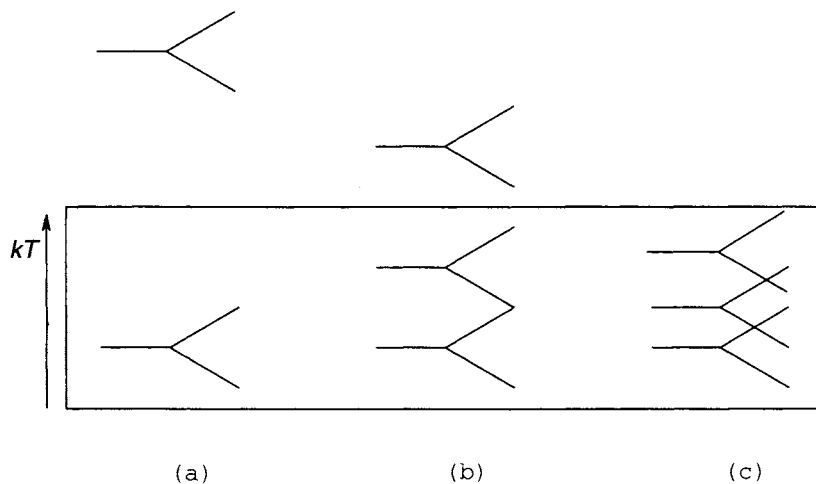


Fig. 8.17. Multiplet width as compared with thermal energy: (a) wide multiplets; (b) multiplets of intermediate width; (c) narrow multiplets.

8.5.3 Wide multiplets

An excited multiplet lies far above the ground one, so that only the energy levels within the ground multiplet are thermally populated. There are $2J + 1$ magnetic levels within a given multiplet of total angular momentum quantum number J . In the magnetic field their energies are given by the electronic Zeeman term as

$$\varepsilon(J, M_J) = \langle JM_J | \hat{H}_z^Z | JM_J \rangle = \mu_B g_J B_z \langle JM_J | \hat{J}_z | JM_J \rangle [\hbar^{-1}] = \mu_B g_J B_z M_J$$

Following the procedure for the derivation of the magnetisation expressed via the Brillouin function (Section 6.1) one obtains

$$M = M_0 \mathcal{B}_J(\eta)$$

with

$$M_0 = N_A \mu_B g_J J$$

and the argument

$$\eta = \frac{g_J \mu_B B_z}{kT}$$

For a small argument of the Brillouin function (when the field B is small and T is high enough) the magnetisation becomes a linear function of the applied field

$$M \approx M_0 \frac{J+1}{3} \eta = \frac{N_A \mu_B^2 g_J^2 J(J+1)}{3kT} B$$

Consequently, the magnetic susceptibility obeys the Curie law of the form

$$\chi = \mu_0 \frac{\partial M}{\partial B} = \frac{N_A \mu_0 \mu_B^2 g_J^2 J(J+1)}{3kT}$$

The above requirements are well fulfilled for Gd(III) and Eu(II) derivatives ($4f^7$ systems, $^8S_{7/2}$ ground state)—Table 8.33. The magnetic susceptibility is isotropic and follows the Curie law for $J = 7/2$.

8.5.4 Narrow multiplets

Let us consider the multiplet of J values whose width is small compared with kT . In this rather hypothetical case the probabilities of occupation of each of the states are all equal. This situation is characterised by the condition

$$E_J^{(0)}/kT \approx 0$$

TABLE 8.33
Properties of some lanthanide ions

$4f^n$	Ion	Ground state	Excited state	$\Delta E/hc$ (cm^{-1})	g_J	ξ/hc (cm^{-1})	$\chi_{\text{mol}} T/C_0$
1	Ce(III)	$^2F_{5/2}$	$^2F_{7/2}$	2200	6/7	640	2.12
2	Pr(III)	$^3H_4$	$^3H_5$	2100	4/5	800	4.26
3	Nd(III)	$^4I_{9/2}$	$^4I_{11/2}$	1900	8/11	900	4.37
4	Pm(III)	$^5I_4$	$^5I_5$	1600	3/5		2.39
5	Sm(III)	$^6H_{5/2}$	$^6H_{7/2}$	1000	2/7	1200	0.23
6	Eu(III)	$^7F_0$	$^7F_1$	300	5	1415	0
7	Gd(III)	$^8S_{7/2}$	$^6P_{7/2}$	30 000	2		21.00
8	Tb(III)	$^7F_6$	$^7F_5$	2000	3/2	1620	31.50
9	Dy(III)	$^6H_{15/2}$	$^6H_{13/2}$	—	4/3	1820	37.78
10	Ho(III)	$^5I_8$	$^5I_7$	—	5/4	2080	37.50
11	Er(III)	$^4I_{15/2}$	$^4I_{13/2}$	6500	6/5	2360	30.61
12	Tm(III)	$^3H_6$	$^3H_5$	—	7/6	2800	19.05
13	Yb(III)	$^2F_{7/2}$	$^2F_{5/2}$	10 000	8/7	2940	6.85

which allows omission of the Boltzmann factors in the van Vleck equation for paramagnetic susceptibility

$$\bar{\chi}_{\text{mol}} = N_A \mu_0 \frac{\sum_{J=|L-S|}^{L+S} \sum_{M=-J}^{+J} \frac{(g_J \mu_B M)^2}{kT} \exp[-E_J^{(0)}/kT]}{\sum_{J=|L-S|}^{L+S} \sum_{M=-J}^{+J} \exp[-E_J^{(0)}/kT]}$$

This relaxes to the form

$$\begin{aligned} \bar{\chi}_{\text{mol}} &= \frac{N_A \mu_0 \mu_B^2}{kT} \frac{\sum_{J=|L-S|}^{L+S} g_J^2 \sum_{M=-J}^{+J} M^2}{\sum_{J=|L-S|}^{L+S} \sum_{M=-J}^{+J} 1} \\ &= \frac{N_A \mu_0 \mu_B^2}{kT} \frac{\sum_{J=|L-S|}^{L+S} \left[\frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right]^2 \frac{J(J+1)(2J+1)}{3}}{\sum_{J=|L-S|}^{L+S} (2J+1)} \end{aligned}$$

which finally yields

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{3kT} [4S(S+1) + L(L+1)]$$

This formula is applicable to a free ion at a sufficiently high temperature.

8.5.5 Multiplets of intermediate width

In this most realistic case the van Vleck formula adopts the form of

$$\bar{\chi}_{\text{mol}} = N_A \mu_0 \frac{\sum_{J=|L-S|}^{L+S} \sum_{M=-J}^{+J} \left[\frac{(E_{J,M}^{(1)})^2}{kT} - 2E_{J,M}^{(2)} \right] \exp[-E_J^{(0)}/kT]}{\sum_{J=|L-S|}^{L+S} \sum_{M=-J}^{+J} \exp[-E_J^{(0)}/kT]}$$

By introducing the particular susceptibility function common for a multiplet

$$\chi_J = N_A \mu_0 \frac{\sum_{M=-J}^{+J} \left[\frac{(E_{J,M}^{(1)})^2}{kT} - 2E_{J,M}^{(2)} \right]}{2J+1}$$

the molar susceptibility becomes expressed as follows

$$\bar{\chi}_{\text{mol}} = \frac{\sum_{J=|L-S|}^{L+S} (2J+1) \chi_J \exp[-E_J^{(0)}/kT]}{\sum_{J=|L-S|}^{L+S} (2J+1) \exp[-E_J^{(0)}/kT]}$$

The zero-order van Vleck coefficients are determined as the relative energies of levels of the $^{2S+1}L_J$ multiplet, as

$$E_J^{(0)} = \frac{\lambda}{2} J(J+1)$$

where we omit the remainder $O = -(\lambda/2)[L(L+1) + S(S+1)]$ which is constant within the term.

The first-order van Vleck coefficients are simply

$$E_{J,M}^{(1)} = \mu_B g_J M$$

and then

$$\sum_{M=-J}^{+J} (E_{J,M}^{(1)})^2 = (\mu_B g_J)^2 \sum_{M=-J}^{+J} M^2 = (\mu_B g_J)^2 \frac{J(J+1)(2J+1)}{3}$$

The determination of the second-order van Vleck coefficients $E_{J,M}^{(2)}$ is the most laborious step. The magnetic field gives rise to matrix elements between the different multiplets of a term: the non-vanishing matrix elements are of the form

$$\begin{aligned} \langle J'M | \hat{H}' | JM \rangle &= \langle J'M | \hat{H}_z^2 | JM \rangle = \mu_B B_z \langle J'M | 2\hat{J}_z - \hat{L}_z | JM \rangle [\hbar^{-1}] \\ &= \mu_B B_z 2M \delta_{J,J'} [\hbar^{-1}] - \mu_B B_z \langle J'M | \hat{L}_z | JM \rangle [\hbar^{-1}] \end{aligned}$$

and can be simply evaluated as follows

$$\begin{aligned}\langle J-1, M | \hat{L}_z | JM \rangle &= \langle J-1 | \vec{L} | J \rangle (J^2 - M^2)^{1/2} \\ &= -(J^2 - M^2)^{1/2} f(SLJ) [\hbar]\end{aligned}$$

with the function

$$f(SLJ) = -\langle J-1 | \vec{L} | J \rangle [\hbar^{-1}] = \left\{ \frac{[J^2 - (L-S)^2][(L+S+1)^2 - J^2]}{4J^2(4J^2 - 1)} \right\}^{1/2}$$

The energy contribution in second-order perturbation theory is

$$\begin{aligned}E_2(J, M) &= -\sum_{j \neq i} \frac{\langle j | \hat{H}' | i \rangle^2}{E_j - E_i} = -\sum_{J' \neq J} \frac{\langle J' M | \hat{H}^Z | JM \rangle^2}{E_0(J') - E_0(J)} \\ &= -(\mu_B B_z)^2 \sum_{J'=J \pm 1} \frac{\langle J' M | \hat{L}_z | JM \rangle^2}{E_0(J') - E_0(J)} [\hbar^{-2}]\end{aligned}$$

With the help of the energy differences

$$E_0(J+1) - E_0(J) = \frac{\lambda}{2}(J+1)(J+2) - \frac{\lambda}{2}J(J+1) = \lambda(J+1)$$

$$E_0(J-1) - E_0(J) = \frac{\lambda}{2}(J-1)J - \frac{\lambda}{2}J(J+1) = -\lambda J$$

and

$$\begin{aligned}\langle J+1, M | \hat{L}_z | JM \rangle &= \langle JM | \hat{L}_z | J+1, M \rangle \\ &= -[(J+1)^2 - M^2]^{1/2} f(SL, J+1) [\hbar]\end{aligned}$$

the second-order van Vleck coefficients result as follows

$$\begin{aligned}E_{J,M}^{(2)} &= -\mu_B^2 \left\{ \frac{\langle J+1 | \vec{L} | J \rangle^2 [(J+1)^2 - M^2]}{\lambda(J+1)} - \frac{\langle J-1 | \vec{L} | J \rangle^2 [J^2 - M^2]}{\lambda J} \right\} [\hbar^{-2}] \\ &= -\mu_B^2 \left\{ \frac{[f(SL, J+1)]^2 [(J+1)^2 - M^2]}{\lambda(J+1)} - \frac{[f(SLJ)]^2 [J^2 - M^2]}{\lambda J} \right\}\end{aligned}$$

These can be further summed up to give

$$\begin{aligned}
 \sum_{M=-J}^{+J} E_{J,M}^{(2)} &= -\mu_B^2 \sum_{M=-J}^{+J} \left\{ \frac{[f(SL, J+1)]^2[(J+1)^2 - M^2]}{\lambda(J+1)} - \frac{[f(SLJ)]^2[J^2 - M^2]}{\lambda J} \right\} \\
 &= -\frac{\mu_B^2}{\lambda} \{ [f(SL, J+1)]^2(J+1) - [f(SLJ)]^2 J \} \left(\sum_{M=-J}^{+J} 1 \right) \\
 &\quad - \frac{\mu_B^2}{\lambda} \left\{ -\frac{[f(SL, J+1)]^2}{J+1} + \frac{[f(SLJ)]^2}{J} \right\} \left(\sum_{M=-J}^{+J} M^2 \right)
 \end{aligned}$$

After simple algebraic manipulations we get

$$\begin{aligned}
 \sum_{M=-J}^{+J} E_{J,M}^{(2)} &= -\frac{\mu_B^2}{3\lambda} (2J+1) 3 \{ [f(SL, J+1)]^2(J+1) - [f(SLJ)]^2 J \} \\
 &\quad - \frac{\mu_B^2}{3\lambda} (2J+1)(J+1)J \left\{ -\frac{[f(SL, J+1)]^2}{J+1} + \frac{[f(SLJ)]^2}{J} \right\} \\
 &= -\frac{\mu_B^2}{3\lambda} (2J+1) \{ [f(SL, J+1)]^2[3(J+1) - J] \\
 &\quad - [f(SLJ)]^2[3J - (J+1)] \} \\
 \sum_{M=-J}^{+J} E_{J,M}^{(2)} &= -\frac{\mu_B^2}{3\lambda} (2J+1) \{ [f(SL, J+1)]^2(2J+3) - [f(SLJ)]^2(2J-1) \}
 \end{aligned}$$

It is understood that $f(SLJ) = 0$ for $J = 0$. A further simplification is obtained when the following identity is utilised

$$\begin{aligned}
 &\{ [f(SL, J+1)]^2(2J+3) - [f(SLJ)]^2(2J-1) \} \\
 &= \frac{[(S+L+1)(S-L)]^2 - [J(J+1)]^2}{[2J(J+1)]^2} \\
 &= (g_J - 1)(g_J - 2)
 \end{aligned}$$

which can be easily proven after insertions for g_J , $f(SLJ)$ and $f(SL, J+1)$. Then the second-order van Vleck coefficients are summed up to

$$\sum_{M=-J}^{+J} E_{J,M}^{(2)} = -\frac{\mu_B^2}{3\lambda} (2J+1)(g_J - 1)(g_J - 2)$$

The derived expressions for the van Vleck coefficients allow us to construct the particular susceptibility function for a multiplet

$$\begin{aligned}
 \chi_J &= N_A \mu_0 \frac{\sum_{M=-J}^{+J} \left[\frac{(E_{J,M}^{(1)})^2}{kT} - 2E_{J,M}^{(2)} \right]}{2J+1} \\
 &= \frac{N_A \mu_0}{2J+1} \left[\frac{1}{kT} \sum_{M=-J}^{+J} (E_{J,M}^{(1)})^2 - 2 \sum_{M=-J}^{+J} E_{J,M}^{(2)} \right] \\
 &= \frac{N_A \mu_0}{2J+1} \left[\frac{\mu_B^2 g_J^2 J(J+1)(2J+1)}{3kT} + 2 \frac{\mu_B^2}{3\lambda} (2J+1)(g_J-1)(g_J-2) \right] \\
 &= \frac{N_A \mu_0 \mu_B^2}{3} \left[\frac{g_J^2}{kT} J(J+1) + \frac{2}{\lambda} (g_J-1)(g_J-2) \right]
 \end{aligned}$$

and the final molar magnetic susceptibility becomes

$$\bar{\chi}_{\text{mol}} = \frac{\sum_{J=|L-S|}^{L+S} (2J+1) \chi_J \exp[-\lambda J(J+1)/2kT]}{\sum_{J=|L-S|}^{L+S} (2J+1) \exp[-\lambda J(J+1)/2kT]}$$

or alternatively

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{3kT} \frac{\sum_{i=|L-S|}^{L+S} a_i (c_i + 2d_i/x) \exp[-b_i x]}{\sum_{i=|L-S|}^{L+S} a_i \exp[-b_i x]}$$

with

$$a_i = 2J + 1$$

$$b_i = \frac{1}{2} J(J+1) - b_1$$

$$c_i = g_J^2 J(J+1)$$

$$d_i = (g_J - 1)(g_J - 2)$$

TABLE 8.34

Terms of the magnetic susceptibility formula for multiplets of intermediate width

Ion	Multiplet	g_J	a_i	b_i	c_i	d_i
Ce(III)	1 $^2F_{5/2}$	6/7	6	0	45/7	+8/49
	2 $^2F_{7/2}$	8/7	8	7/2	144/7	-6/49
Pr(III)	1 $^3H_4$	4/5	9	0	64/5	+6/25
	2 $^3H_5$	31/30	11	5	961/30	-29/900
	3 $^3H_6$	7/6	13	11	343/6	-5/36
Nd(III)	1 $^4I_{9/2}$	8/11	10	0	144/11	+42/121
	2 $^4I_{11/2}$	138/143	12	11/2	4761/143	+740/20 449
	3 $^4I_{13/2}$	72/65	14	12	3888/65	-406/4225
	4 $^4I_{15/2}$	6/5	16	39/2	459/5	-4/25
Pm(III)	1 $^5I_4$	3/5	9	0	36/5	+14/25
	2 $^5I_5$	9/10	11	5	243/10	+11/100
	3 $^5I_6$	15/14	13	11	675/14	-13/196
	4 $^5I_7$	33/28	15	18	1089/14	-115/784
	5 $^5I_8$	5/4	17	26	225/2	-3/16
Sm(III)	1 $^6H_{5/2}$	2/7	6	0	5/7	+60/49
	2 $^6H_{7/2}$	52/63	8	7/2	676/63	+814/3969
	3 $^6H_{9/2}$	106/99	10	8	2809/99	-644/9801
	4 $^6H_{11/2}$	172/143	12	27/2	3796/143	-3306/20 449
	5 $^6H_{13/2}$	50/39	14	20	3125/39	-308/1521
	6 $^6H_{15/2}$	4/3	16	55/2	340/3	-2/9
Eu(III)	1 $^7F_0$	5	1	0	0	+12
	2 $^7F_1$	3/2	3	1	9/2	-1/4
	3 $^7F_2$	3/2	5	3	27/2	-1/4
	4 $^7F_3$	3/2	7	6	27	-1/4
	5 $^7F_4$	3/2	9	10	90/2	-1/4
	6 $^7F_5$	3/2	11	15	135/2	-1/4
	7 $^7F_6$	3/2	13	21	189/2	-1/4
Gd(III)	1 $^8S_{7/2}$	2	8	0	63	0
Tb(III)	1 $^7F_6$	3/2	13	0	189/2	-1/4
	2 $^7F_5$	3/2	11	-6	135/2	-1/4
	3 $^7F_4$	3/2	9	-11	90/2	-1/4
	4 $^7F_3$	3/2	7	-15	27	-1/4
	5 $^7F_2$	3/2	5	-18	27/2	-1/4
	6 $^7F_1$	3/2	3	-20	9/2	-1/4
	7 $^7F_0$	5	1	-21	0	+24
Dy(III)	1 $^6H_{15/2}$	4/3	16	0	340/3	-2/9
	2 $^6H_{13/2}$	50/39	14	-15/2	3125/39	-308/1521
	3 $^6H_{11/2}$	172/143	12	-14	7396/143	-3306/20 449
	4 $^6H_{9/2}$	106/99	10	-39/2	2809/99	-644/9801
	5 $^6H_{7/2}$	52/63	8	-24	676/63	+814/3969
	6 $^6H_{5/2}$	2/7	6	-55/2	5/7	+60/49
Ho(III)	1 $^5I_8$	5/4	17	0	225/2	-3/16
	2 $^5I_7$	33/28	15	-8	1089/14	-115/784
	3 $^5I_6$	15/14	13	-15	675/14	-13/196
	4 $^5I_5$	9/10	11	-21	243/10	+11/100
	5 $^5I_4$	3/5	9	-26	36/5	+14/25

TABLE 8.34

Terms of the magnetic susceptibility formula for multiplets of intermediate width (*contd.*)

Ion	Multiplet	g_J	a_i	b_i	c_i	d_i
Er(III)	1 $^4I_{15/2}$	6/5	16	0	459/5	-4/25
	2 $^4I_{13/2}$	72/65	14	-15/2	3888/65	-406/4225
	3 $^4I_{11/2}$	138/143	12	-14	4761/143	+740/20499
	4 $^4I_{9/2}$	8/11	10	-39/2	144/11	+42/121
Tm(III)	1 $^3H_6$	7/6	13	0	343/6	-5/36
	2 $^3H_5$	31/30	11	-6	961/30	-29/900
	3 $^3H_4$	4/5	9	-11	64/5	+6/25
Yb(III)	1 $^2F_{7/2}$	8/7	8	0	144/7	-6/49
	2 $^2F_{5/2}$	6/7	6	-7/2	45/7	+8/49

and

$$x = \frac{\lambda}{kT} = \pm \frac{\xi}{2S} \frac{1}{kT}$$

where the positive sign applies to the half-filled shells and the negative sign in the opposite case. These constants are collected in Table 8.34.

The representative plots of the product functions $\chi_{\text{mol}}T$ versus the reduced parameter $1/x = kT/\lambda$ are given in Fig. 8.18. The main difference between the left and right parts of Fig. 8.18 lies in the fact that the inverted multiplets (on the right side) have their ground states of maximum J . This results in the high-spin state, which is little affected as the temperature increases.

The real magnetic behaviour of the lanthanide compounds is affected by a magnetic anisotropy which becomes significant upon cooling. Moreover, a reduction of the orbital angular momentum and the crystal field splitting may assume importance.

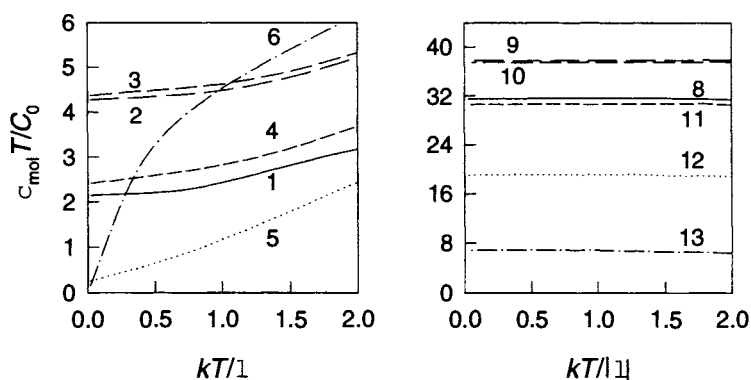


Fig. 8.18. The product function $\chi_{\text{mol}}T$ versus kT/λ for lanthanide trivalent ions: left—less than half-filled shells, right—more than half-filled shells ($\lambda < 0$); numbers correspond to the f^n configuration.

For completeness, Table 8.35 brings data for the susceptibility function of the transition metal ions; these are displayed in Fig. 8.19. However, the crystal field splitting of the energy levels is ultimate for the 3*d*-metal ions so that a more elaborate approach is necessary.

8.5.6 Orbital reduction factor

The experimental data, in accordance with theoretical predictions, show that the orbital angular momentum in real metal complexes is somewhat reduced so that it is legitimate to operate with $\hat{L} \rightarrow \kappa \hat{L}$, $0 < \kappa \leq 1$ being an orbital reduction factor. There are two sources of orbital reduction:

TABLE 8.35

Terms of the magnetic susceptibility formula for multiplets of *dⁿ*-metal ions

Ion	Multiplet	g_J	a_i	b_i	c_i	d_i
d^1	1 $^2D_{3/2}$	4/5	4	0	12/5	+6/25
	2 $^2D_{5/2}$	6/5	6	5/2	63/5	-4/25
d^2	1 $^3F_2$	2/3	5	0	8/3	+4/9
	2 $^3F_3$	13/12	7	3	169/12	-11/144
	3 $^3F_4$	5/4	9	7	125/4	-3/16
d^3	1 $^4F_{3/2}$	2/5	4	0	3/5	+24/5
	2 $^4F_{5/2}$	36/35	6	5/2	324/35	-34/1225
	3 $^4F_{7/2}$	26/21	8	6	169/7	-80/441
	4 $^4F_{9/2}$	4/3	10	21/2	44	-2/9
d^4	1 $^5D_0$	4	1	0	0	+6
	2 $^5D_1$	3/2	3	1	9/2	-1/4
	3 $^5D_2$	3/2	5	3	27/2	-1/4
	4 $^5D_3$	3/2	7	6	27	-1/4
	5 $^5D_4$	3/2	9	10	45	-1/4
d^5	1 $^6S_{5/2}$	2	6	0	35	0
d^6	1 $^5D_4$	3/2	9	0	45	-1/4
	2 $^5D_3$	3/2	7	-4	27	-1/4
	3 $^5D_2$	3/2	5	-7	27/2	-1/4
	4 $^5D_1$	3/2	3	-9	9/2	-1/4
	5 $^5D_0$	4	1	-10	0	+6
d^7	1 $^4F_{9/2}$	4/3	10	0	44	-2/9
	2 $^4F_{7/2}$	26/21	8	-9/2	169/7	-80/441
	3 $^4F_{5/2}$	36/35	6	-8	324/35	-34/1225
	4 $^4F_{3/2}$	2/5	4	-21/2	3/5	+24/25
d^8	1 $^3F_4$	5/4	9	0	125/4	-3/16
	2 $^3F_3$	13/12	7	-4	169/12	-11/144
	3 $^3F_2$	2/3	5	-7	8/3	+4/9
d^9	1 $^2D_{5/2}$	6/5	6	0	63/5	-4/25
	2 $^2D_{3/2}$	4/5	4	-5/2	12/5	+6/25

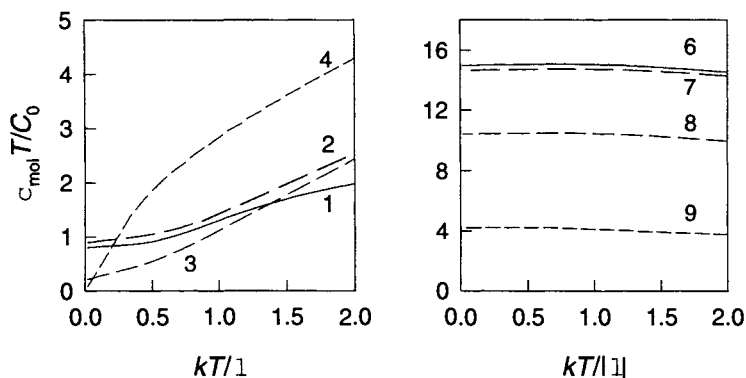


Fig. 8.19. The product function $\chi_{\text{mol}} T$ versus kT/λ for transition metal ions: left—less than half-filled shells, right—more than half-filled shells ($\lambda < 0$); numbers correspond to the d^n configuration.

- (1) covalence, due to bond formation;
- (2) configuration interaction.

In metal complexes a set of molecular orbitals can be written in the form

$$\phi_i = c_i^M d_i^M + c_i^L \chi_i^L$$

where χ_i^L are appropriate symmetry combinations of ligand orbitals (group orbitals), d_i^M being the metal d -orbitals. The LCAO coefficients obey the normalisation condition

$$\begin{aligned} \langle \phi_i | \phi_i \rangle &= (c_i^M)^2 \langle d_i^M | d_i^M \rangle + (c_i^L)^2 \langle \chi_i^L | \chi_i^L \rangle + 2c_i^M c_i^L \langle d_i^M | \chi_i^L \rangle \\ &= (c_i^M)^2 + (c_i^L)^2 + 2c_i^M c_i^L S_{i,i}^{M,L} = 1 \end{aligned}$$

The molecular spin-orbitals

$$\varphi_i = \begin{cases} \phi_i \alpha \\ \phi_i \beta \end{cases}$$

constitute a determinantal wave function

$$|\Psi_\mu\rangle = \hat{A}_n \{\varphi_1(1) \dots \varphi_n(n)\}$$

and thus the integrals of the total angular momentum between the determinantal wave functions are expressed through a sum of one-electron terms

$$\begin{aligned}
\langle \Psi_\mu | \vec{L} | \Psi_\nu \rangle &= \sum_{i=1}^n \langle \Psi_\mu | \vec{l}_i | \Psi_\nu \rangle \\
&= \begin{cases} \sum_{i=1}^n \langle \varphi_i | \vec{l}_i | \varphi_i \rangle & \text{for identical determinants} \\ \langle \varphi_i | \vec{l}_i | \varphi_j \rangle & \text{for determinants differing in one spin-orbital} \end{cases}
\end{aligned}$$

The one-electron integrals are expanded as follows

$$\begin{aligned}
L_{ij,a} &= \langle \phi_i | \hat{l}_{1a} | \phi_j \rangle = c_i^M c_j^M \langle d_i^M | \hat{l}_{1a} | d_j^M \rangle + c_i^M c_j^L \langle d_i^M | \hat{l}_{1a} | \chi_j^L \rangle \\
&\quad + c_i^L c_j^M \langle \chi_i^L | \hat{l}_{1a} | d_j^M \rangle + c_i^L c_j^L \langle \chi_i^L | \hat{l}_{1a} | \chi_j^L \rangle
\end{aligned}$$

To a further approximation we expect the validity

$$c_i^M \approx c_j^M = c^M$$

and

$$c_i^L \approx c_j^L = c^L$$

so that we get

$$L_{ij,a} \approx (c^M)^2 \langle d_i^M | \hat{l}_{1a} | d_j^M \rangle + 2c^M c^L \langle d_i^M | \hat{l}_{1a} | \chi_j^L \rangle + (c^L)^2 \langle \chi_i^L | \hat{l}_{1a} | \chi_j^L \rangle$$

Since the action of the angular momentum operator to a ket $|d_j^M\rangle$ yields a (complex) number ε_j and another ket, say $|d_k^M\rangle$

$$\hat{l}_{1a} |d_j^M\rangle = \varepsilon_j |d_k^M\rangle [\hbar]$$

then

$$L_{ij,a} = \varepsilon_j \left[(c^M)^2 \delta_{i,k} + 2c^M c^L S_{i,k}^{L,M} \right] [\hbar] + (c^L)^2 \langle \chi_i^L | \hat{l}_{1a} | \chi_j^L \rangle$$

The last term can be neglected owing to the combined effect of the small coefficient $(c^L)^2$ and the small integral $\langle \chi_i^L | \hat{l}_{1a} | \chi_j^L \rangle$. Using the normalisation condition for molecular orbitals

$$(c^M)^2 + 2c^M c^L S^{M,L} = 1 - (c^L)^2$$

we arrive at the expression

$$L_{ij,a} = \varepsilon_j [1 - (c^L)^2] [\hbar] = \varepsilon_j \kappa [\hbar]$$

with the *orbital reduction factor*

$$\kappa = [1 - (c^L)^2] \leq 1$$

Now one can see that owing to the covalence effect (the involvement of the ligand orbitals in the molecular orbitals) the angular momentum is reduced to the extent of κ . For the pure metal d -orbitals $\kappa = 1$ holds true (no reduction).

The orbital reduction factor used to be considered as an empirical parameter and the spin Hamiltonian is rewritten in the form

$$\hat{H}^S = \kappa \lambda_0 \vec{L} \cdot \vec{S} [\hbar^{-2}] + \mu_B (\kappa \vec{L} + g_e \vec{S}) \cdot \vec{B} [\hbar^{-1}]$$

where λ_0 is a free-atom (or ion) spin-orbit splitting parameter. Then the actual spin-orbit splitting parameter in a complex is reduced as follows

$$\lambda = \kappa \lambda_0$$

The orbital reduction in metal complexes reaches a value of $\kappa = 0.8$.

8.5.7 CI reduction factor

Within the variational configuration interaction a limited CI expansion is written as follows

$$|\Psi_i\rangle = C_0 |\Phi_0\rangle + C_1 |\Phi_1\rangle$$

and the matrix elements of the angular momentum operator become expressed as

$$L_{ij} = \langle \Psi_i | \vec{L} | \Psi_j \rangle = C_0^2 \langle \Phi_0 | \vec{L} | \Phi_0 \rangle + 2C_0 C_1 \langle \Phi_1 | \vec{L} | \Phi_0 \rangle + C_1^2 \langle \Phi_1 | \vec{L} | \Phi_1 \rangle$$

After the action of the angular momentum operator on the kets

$$\vec{L} |\Phi_i\rangle = \varepsilon_i |\Phi'_i\rangle [\hbar]$$

one gets

$$L_{ij} = [C_0^2 \varepsilon_0 \langle \Phi_0 | \Phi'_0 \rangle + 2C_0 C_1 \varepsilon_0 \langle \Phi_1 | \Phi'_0 \rangle + C_1^2 \varepsilon_1 \langle \Phi_1 | \Phi'_1 \rangle] [\hbar]$$

For example, in tetrahedral complexes the following mixing of kets is possible

$$|XZ\rangle = C_0 |d_{xz}\rangle + C_1 |p_y\rangle$$

$$|YZ\rangle = C_0 |d_{yz}\rangle + C_1 |p_x\rangle$$

since the kets $|d_{xy}\rangle, |d_{xz}\rangle, |d_{yz}\rangle, |p_x\rangle, |p_y\rangle$ and $|p_z\rangle$ transform according to the representation T_2 of the T_d group. It follows that

$$\begin{aligned}\langle XZ|\hat{L}_z|YZ\rangle &= C_0^2\langle d_{xz}|\hat{L}_z|d_{yz}\rangle + C_0C_1\langle d_{xz}|\hat{L}_z|p_x\rangle \\ &\quad + C_0C_1\langle p_y|\hat{L}_z|d_{yz}\rangle + C_1^2\langle p_y|\hat{L}_z|p_x\rangle \\ &= [C_0^2(-i) + C_0C_1(0) + C_0C_1(0) + C_1^2(i)][\hbar] \\ &= -i(C_0^2 - C_1^2)[\hbar] = -i\kappa[\hbar]\end{aligned}$$

Then the *CI reduction factor* becomes

$$\kappa = C_0^2 - C_1^2$$

and using the normalisation condition

$$\begin{aligned}\langle \Psi_i|\Psi_i\rangle &= C_0^2\langle \Phi_0|\Phi_0\rangle + 2C_0C_1\langle \Phi_0|\Phi_1\rangle + C_1^2\langle \Phi_1|\Phi_1\rangle \\ &= C_0^2 + C_1^2 = 1\end{aligned}$$

one gets the CI reduction factor in the form of

$$\kappa = 1 - 2C_1^2 \leq 1$$

For a single determinantal wave function $\kappa = 1$ holds true (no reduction).

8.5.8 *T-P isomorphism*

The angular momentum operators acting on the set of complex (p_1, p_0, p_{-1}) functions yield

$$\hat{l}_x \begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} [\hbar]$$

$$\hat{l}_y \begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} = \frac{i}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} [\hbar]$$

$$\hat{l}_z \begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} [\hbar]$$

Except for the sign, equivalent results are obtained for the set of t_2 functions forming the basis of the T_2 term

$$\begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} = \begin{pmatrix} |2, -1\rangle \\ (1/\sqrt{2})(|2, 2\rangle - |2, -2\rangle) \\ -|2, 1\rangle \end{pmatrix}$$

Namely

$$\hat{l}_x \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} = -\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} [\hbar]$$

$$\hat{l}_y \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} = -\frac{i}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} [\hbar]$$

$$\hat{l}_z \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} = -\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} [\hbar]$$

Thus it is legitimate to claim that the transformation matrix of $\vec{l}$ within the t_2 representation of the d -functions is equal to the matrix of $(-\vec{l})$ for the p -functions (see Table 8.36).

As far as the spin-orbit coupling for a one-electron system is concerned, one can use an equivalence

$$\hat{H}^{\text{so}} = \xi_d \vec{l}_{t_2} \cdot \vec{s} [\hbar^{-2}] = -\xi_d \vec{l}_p \cdot \vec{s} [\hbar^{-2}]$$

TABLE 8.36
 T - P isomorphism

O_h group	T_d group
${}^2T_{2g}(d^1, t_2^1) \leftrightarrow {}^2P(p^5)$	${}^2T_2(d^9, [t_2^1]) \leftrightarrow {}^2P(p^5)$
${}^3T_{1g}(d^2, t_2^2) \leftrightarrow {}^3P(p^4)$	${}^3T_1(d^8, [t_2^2]) \leftrightarrow {}^3P(p^4)$
${}^3T_{1g}(d^4, t_2^4) \leftrightarrow {}^3P(p^2)$	
${}^2T_{2g}(d^5, t_2^5) \leftrightarrow {}^2P(p^1)$	
${}^5T_{2g}(d^6, t_2^4 e_g^2) \leftrightarrow {}^5P(p^2)^a$	${}^5T_2(d^4, e^2 t_2^2) \leftrightarrow {}^5P(p^4)^{a,b}$
${}^4T_{1g}(d^7, t_2^5 e_g^2) \leftrightarrow {}^4P(p^1)^a$	${}^4T_1(d^3, e^2 t_2^1) \leftrightarrow {}^4P(p^5)^{a,b}$

^aHypothetical terms with required spin multiplicity.

^b $[t_2^i]$ are holes in the filled d^{10} shell.

and the spin Hamiltonian is of the form

$$\hat{H}^S = \nu_\xi \vec{l}_p \cdot \vec{s} [\hbar^{-2}] + \mu_B \vec{B} \cdot (\gamma \vec{l}_p + g_e \vec{s}) [\hbar^{-1}]$$

with the *equivalence coefficients*

$$\gamma = -1$$

and

$$\nu_\xi = -\xi_d$$

For a many-electron problem the spin-Hamiltonian is written as follows

$$\hat{H}^S = \nu_\xi \vec{L}_p \cdot \vec{S} [\hbar^{-2}] + \mu_B \vec{B} \cdot (\gamma \vec{L}_p + g_e \vec{S}) [\hbar^{-1}]$$

A proper determination of the equivalence coefficients depends upon which set of the crystal field functions is actually used [5, 6, 12]:

- (a) strong-field functions (for low-spin complexes), $\gamma = -1$;
- (b) weak-field functions (for high-spin complexes), $\gamma = -3/2$;
- (c) intermediate-field functions, $-3/2 < \gamma < -1$.

In the strong-field limit one can include a mixing of terms arising from different electron configurations as follows

$$\begin{aligned} |\Psi'(^3T_1)\rangle &= C_0 |\Psi(^3T_1; t_2^2)\rangle + C_1 |\Psi(^3T_1; t_2^1 e^1)\rangle \\ &= \cos \alpha |\Psi(^3T_1; t_2^2)\rangle + \sin \alpha |\Psi(^3T_1; t_2^1 e^1)\rangle \end{aligned}$$

and thus

$$\begin{aligned} \left\langle \Psi'(^3T_1) \left| \sum_i \hat{l}_{iz} \right| \Psi'(^3T_1) \right\rangle &= \cos^2 \alpha \left\langle \Psi(^3T_1; t_2^2) \left| \sum_i \hat{l}_{iz} \right| \Psi(^3T_1; t_2^2) \right\rangle \\ &\quad + \sin^2 \alpha \left\langle \Psi(^3T_1; t_2^1 e^1) \left| \sum_i \hat{l}_{iz} \right| \Psi(^3T_1; t_2^1 e^1) \right\rangle \\ &\quad + 2 \cos \alpha \sin \alpha \\ &\quad \times \left\langle \Psi(^3T_1; t_2^2) \left| \sum_i \hat{l}_{iz} \right| \Psi(^3T_1; t_2^1 e^1) \right\rangle \end{aligned}$$

Knowing the exact form of the strong-field kets $|\Psi(^3T_1; t_2^2, S, M_S)\rangle$ we arrive at the result [12]

$$\left\langle \Psi'(^3T_1) \left| \sum_i \hat{l}_{iz} \right| \Psi'(^3T_1) \right\rangle = [\cos^2 \alpha \cdot (-1) + \sin^2 \alpha \cdot (1/2) + 2 \cos \alpha \sin \alpha \cdot (+1)] [\hbar]$$

On the other hand, the T - P isomorphism says that the following correspondence of the functions $|JM\rangle = |2, 2\rangle$ of the P -term and $|\Psi'(^3T_1)\rangle$ exists

$$\left\langle \Psi'(^3T_1) \left| \vec{L} \right| \Psi'(^3T_1) \right\rangle = \langle 2, 2 | \gamma \vec{L} | 2, 2 \rangle = \gamma \cdot (+1) [\hbar]$$

yielding the equivalence coefficient

$$\gamma = -\cos^2 \alpha + \frac{1}{2} \sin^2 \alpha + 2 \cos \alpha \sin \alpha$$

For a very strong field (when the $10Dq$ parameter is very large) the sine component vanishes, $\cos \alpha = 1$, and then $\gamma = -1$.

Analogously, we can write the second equivalence equation

$$\left\langle \Psi'(^3T_1) \left| \xi_d \sum_i \vec{l}_i \cdot \vec{s}_i \right| \Psi'(^3T_1) \right\rangle = \langle 2, 2 | v_\xi \vec{L} \cdot \vec{S} | 2, 2 \rangle = v_\xi \cdot (+1) [\hbar^2]$$

and since it holds true that

$$\left\langle \Psi'(^3T_1) \left| \sum_i \vec{l}_i \cdot \vec{s}_i \right| \Psi'(^3T_1) \right\rangle = \frac{\gamma}{2} [\hbar^2]$$

(this result follows from the exact form of the strong-field kets) we get

$$v_\xi = \frac{\gamma}{2} \xi_d$$

For the very strong field it is

$$v_\xi = -\frac{1}{2} \xi_d$$

An analogous procedure done for the known form of the weak-field kets $|\Psi(^3T_1; ^3F, S, M_S)\rangle$ brings the result $\gamma = -3/2$ and $v_\xi = -(3/4)\xi_d$.

The relevant equivalence coefficients for T_1 and T_2 terms of the d^n configurations are collected in Table 8.37.

TABLE 8.37

Coefficients of the susceptibility formula for octahedral d^n complexes [6, 12]

d^n	Term	γ	ν_ξ	J	g_J^γ	A_J	B_J
d^1	${}^2T_2(t_2^1)$	-1	$-\xi_d$	1/2	-2	3	-8
				3/2	0	0	4
d^2	${}^3T_1(t_2^2)$	-1	$-(1/2)\xi_d$	0	5	0	-72
				1	1/2	1/2	9
				2	1/2	3/2	9
d^2	${}^3T_1({}^3F)^a$	-3/2	$-(3/4)\xi_d$	0	11/2	0	-196/3
				1	1/4	1/8	49/6
				2	1/4	3/8	49/6
d^4	${}^3T_1(t_2^4)$	-1	$(1/2)\xi_d$	0	5	0	72
				1	1/2	1/2	-9
				2	1/2	3/2	-9
d^5	${}^2T_2(t_2^5)$	-1	ξ_d	1/2	-2	3	8
				3/2	0	0	-4
d^6	${}^5T_2(t_2^4e^2)$	-1	$(1/4)\xi_d$	1	7/2	49/2	54
				2	3/2	27/2	-10
				3	1	12	-16
d^7	${}^4T_1(t_2^5e^2)$	-1	$(1/3)\xi_d$	1/2	4	12	60
				3/2	6/5	27/5	-264/25
				5/2	4/5	28/5	-324/25
d^7	${}^4T_1({}^4F)^a$	-3/2	$(1/2)\xi_d$	1/2	13/3	169/12	490/9
				3/2	16/15	64/15	-2156/225
				5/2	3/5	63/20	-294/25

^aWeak-field reference; otherwise strong-field reference.

8.5.9 Multiplets with magnetic angular momentum

The zero-order energy accounting for the equivalence coefficients adopts the form of

$$\begin{aligned}
 E_0(J) &= \langle JM | v_\xi \vec{L} \cdot \vec{S} | JM \rangle [\hbar^{-2}] = v_\xi \frac{1}{2} \langle JM | \hat{J}^2 - \hat{L}^2 - \hat{S}^2 | JM \rangle [\hbar^{-2}] \\
 &= v_\xi \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)]
 \end{aligned}$$

It leads to the following zero-order van Vleck coefficient

$$E_J^{(0)} = v_\xi \frac{1}{2} J(J+1)$$

The first-order perturbation correction to the energy is given by the electronic Zeeman term as follows

$$\begin{aligned} E_1(J, M) &= \langle JM | \hat{H}^Z | JM \rangle = \mu_B \vec{B} \cdot \langle JM | \gamma \vec{L} + g_e \vec{S} | JM \rangle [\hbar^{-1}] \\ &= \mu_B \vec{B} \cdot \langle JM | g_e \vec{J} + (\gamma - g_e) \vec{L} | JM \rangle [\hbar^{-1}] \\ &\approx \mu_B \vec{B} \cdot \langle JM | 2\vec{J} + (\gamma - 2) \vec{L} | JM \rangle [\hbar^{-1}] \end{aligned}$$

and for the z-component of the magnetic field it is

$$\begin{aligned} E_1(J, M) &= \mu_B B_z \langle JM | 2\hat{J}_z + (\gamma - 2)\hat{L}_z | JM \rangle [\hbar^{-1}] \\ &= \mu_B B_z \left[2 + (\gamma - 2) \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} \right] M \end{aligned}$$

Then the comparison with

$$E_1(J, M) = \mu_B B_z g_J^\gamma \langle JM | \hat{J}_z | JM \rangle [\hbar^{-1}] = \mu_B B_z g_J^\gamma M$$

yields the Landé factor modified to the form

$$g_J^\gamma = \gamma + (2 - \gamma) \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

Consequently the first-order van Vleck coefficients become

$$E_{J,M}^{(1)} = \mu_B g_J^\gamma M_J$$

In the derivation of the second-order energy the perturbation operator is

$$\begin{aligned} \langle J'M | \hat{H}^Z | JM \rangle &= \langle J'M | \hat{H}_z^Z | JM \rangle \\ &= 2\mu_B B_z \langle J'M | \hat{J}_z | JM \rangle [\hbar^{-1}] \\ &\quad + (\gamma - 2)\mu_B B_z \langle J'M | \hat{L}_z | JM \rangle [\hbar^{-1}] \end{aligned}$$

where the first term vanishes. This yields the result

$$E_2(J, M) = -(\gamma - 2)^2 (\mu_B B_z)^2 \sum_{J'=J\pm 1} \frac{\langle J'M | \hat{L}_z | JM \rangle^2}{E_0(J') - E_0(J)} [\hbar^{-2}]$$

and thus the second-order van Vleck coefficients

$$E_{J,M}^{(2)} = -(\gamma - 2)^2 \mu_B^2 \left\{ \frac{[f(SL, J+1)]^2 [(J+1)^2 - M^2]}{v_\xi(J+1)} - \frac{[f(SLJ)]^2 [J^2 - M^2]}{v_\xi J} \right\}$$

are summed up as follows

$$\sum_{M=-J}^{+J} E_{J,M}^{(2)} = -(\gamma - 2)^2 \mu_B^2 \sum_{M=-J}^{+J} \left\{ \frac{[f(SL, J+1)]^2 [(J+1)^2 - M^2]}{v_\xi(J+1)} - \frac{[f(SLJ)]^2 [J^2 - M^2]}{v_\xi J} \right\}$$

yielding

$$\sum_{M=-J}^{+J} E_{J,M}^{(2)} = -\frac{(\gamma - 2)^2 \mu_B^2}{3v_\xi} (2J+1) \{ [f(SL, J+1)]^2 (2J+3) - [f(SLJ)]^2 (2J-1) \}$$

Finally, using

$$\begin{aligned} & (2 - \gamma)^2 \{ [f(SL, J+1)]^2 (2J+3) - [f(SLJ)]^2 (2J-1) \} \\ &= (2 - \gamma)^2 \frac{[(S+L+1)(S-L)]^2 - [J(J+1)]^2}{[2J(J+1)]^2} \\ &= (g_J^\gamma - \gamma)(g_J^\gamma - 2) \end{aligned}$$

we arrive at the simple expression

$$\sum_{M=-J}^{+J} E_{J,M}^{(2)} = -\frac{\mu_B^2}{3v_\xi} (2J+1)(g_J^\gamma - \gamma)(g_J^\gamma - 2)$$

yielding the particular susceptibility function for a given multiplet

$$\begin{aligned} \chi_J &= \frac{N_A \mu_0 \mu_B^2}{3} \left[\frac{(g_J^\gamma)^2}{kT} J(J+1) + \frac{2}{v_\xi} (g_J^\gamma - \gamma)(g_J^\gamma - 2) \right] \\ &= \frac{N_A \mu_0 \mu_B^2}{3kT} \left[A_J + \frac{B_J}{x} \right] \end{aligned}$$

with the coefficients

$$A_J = (g_J^\gamma)^2 J(J+1)$$

$$B_J = \frac{2}{(v_\xi/\xi_d)} (g_J^\gamma - \gamma)(g_J^\gamma - 2)$$

and

$$x = \xi_d/kT$$

Then the molar magnetic susceptibility is

$$\bar{\chi}_{\text{mol}} = \frac{\sum_{J=|L-S|}^{L+S} (2J+1) \chi_J \exp[-v_\xi J(J+1)/2kT]}{\sum_{J=|L-S|}^{L+S} (2J+1) \exp[-v_\xi J(J+1)/2kT]}$$

In the above formulae, we have to use $L = 1$ as a consequence of the T - P isomorphism. Hence

$$g_0^\gamma = 4 - \gamma$$

$$g_J^\gamma = \gamma + (2 - \gamma) \frac{J(J+1) - 2 + S(S+1)}{2J(J+1)}$$

The corresponding coefficients for the susceptibility formula are collected in Table 8.37 and the product functions $\chi_{\text{mol}} T$ versus x^{-1} are displayed in Fig. 8.20.

8.5.10 Inclusion of term interaction

According to Figgis [5] one can consider a limited configuration interaction starting from the weak-field kets

$$\begin{aligned} |\Psi(^3T_1)\rangle &= C_0 |\Psi(^3T_1; ^3F)\rangle + C_1 |\Psi(^3T_1; ^3P)\rangle \\ &= \frac{1}{\sqrt{1+C^2}} [|\Psi(^3T_1; ^3F)\rangle + C |\Psi(^3T_1; ^3P)\rangle] \end{aligned}$$

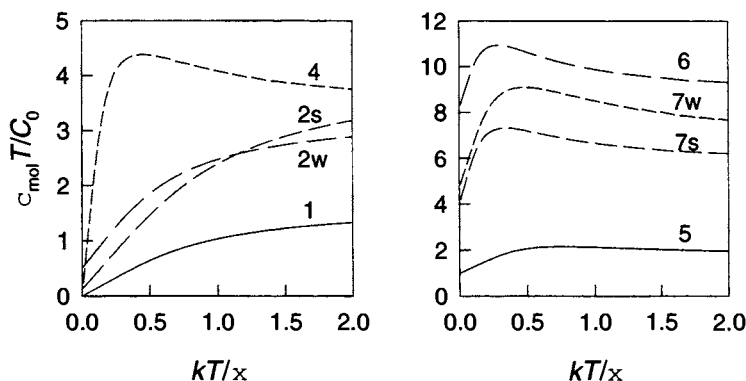


Fig. 8.20. The product function $\chi_{\text{mol}}T$ versus x^{-1} for T_1 and T_2 terms of octahedral d^n complexes: s—strong-field reference, w—weak-field reference.

The corresponding secular equation is

$$\det \begin{pmatrix} \langle \Psi(^3T_1; ^3F) | \hat{V}^{\text{cf}} | \Psi(^3T_1; ^3F) \rangle - \varepsilon & \langle \Psi(^3T_1; ^3F) | \hat{V}^{\text{cf}} | \Psi(^3T_1; ^3P) \rangle \\ \langle \Psi(^3T_1; ^3P) | \hat{V}^{\text{cf}} | \Psi(^3T_1; ^3F) \rangle & \langle \Psi(^3T_1; ^3P) | \hat{V}^{\text{cf}} | \Psi(^3T_1; ^3P) \rangle - \varepsilon \end{pmatrix} = 0$$

which, after evaluation of matrix elements, relaxes to

$$\det \begin{pmatrix} -6Dq - \varepsilon & 4Dq \\ 4Dq & 15B - \varepsilon \end{pmatrix} = 0$$

where $10Dq$ is the crystal-field splitting and B the Racah parameter. Then the secular equation

$$\varepsilon^2 + (6Dq - 15B)\varepsilon - 16(Dq)^2 - 90(Dq)B = 0$$

has two eigenvalues ε . The lower one is used to determine the CI expansion coefficient as

$$C = \frac{6Dq + \varepsilon}{4Dq} = \frac{3}{2} - \frac{15}{2} \left(\frac{B}{Dq} \right) - \sqrt{25 + 45 \left(\frac{B}{Dq} \right) + \frac{225}{4} \left(\frac{B}{Dq} \right)^2}$$

In the weak-field limit with $\varepsilon = -6Dq$ one gets $C = 0$. On the contrary, the strong-field limit with $\varepsilon = -8Dq$ yields $C = 1/2$ (Fig. 8.21).

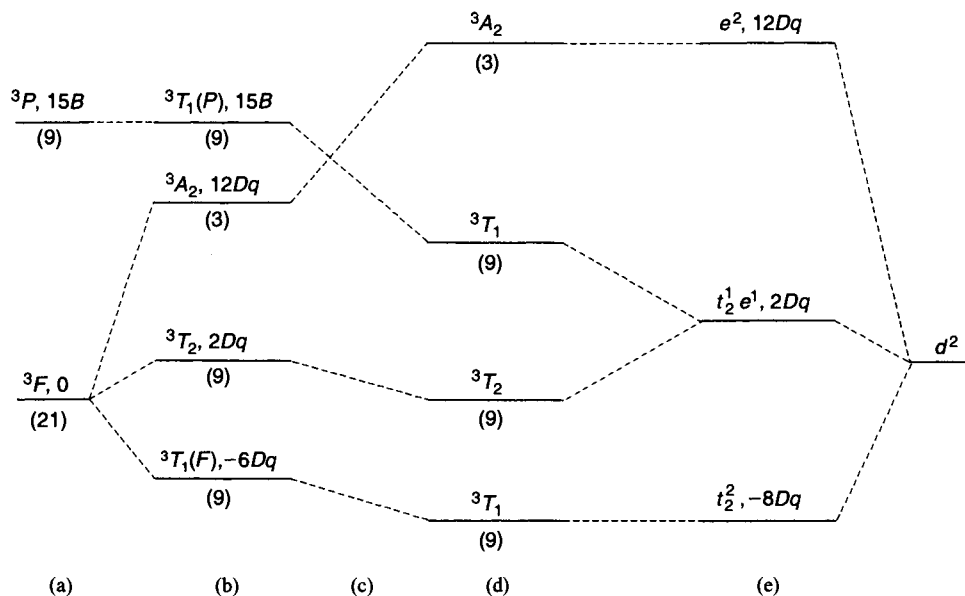


Fig. 8.21. Correlation diagram for the triplet terms of d^2 configuration in the octahedral crystal field: (a) free ion terms ($\hat{H}^0$ includes $\hat{V}^{ee}$); (b) weak field limit ($\hat{H}' = \hat{V}^{cf}$); (c) intermediate field ($\hat{H}' = \hat{V}^{ee} + \hat{V}^{cf}$); (d) strong field limit ($\hat{H}' = \hat{V}^{ee}$); (e) strong field configurations ($\hat{H}^0$ includes $\hat{V}^{cf}$).

TABLE 8.38

Terms of the susceptibility formula for the intermediate crystal field

d^n	Term	J	g_J^A	$E_J^{(0)}$	$F_{J,J+1}$
d^2	${}^3T_{1g}$	0	0	$3A\lambda$	$(2/3)(2+A)^2/A\lambda$
		1	$1 - (1/2)A$	$2A\lambda$	$(5/12)(2+A)^2/A\lambda$
		2	$1 - (1/2)A$	0	
d^3	${}^4T_{1g}$	1/2	$(10 + 2A)/3$	$4A\lambda$	$(20/27)(2+A)^2/A\lambda$
		3/2	$(22 - 4A)/15$	$(5/2)A\lambda$	$(12/25)(2+A)^2/A\lambda$
		5/2	$(6 - 2A)/5$	0	

In the case of the intermediate field Figgis [5] derived the magnetic susceptibility formula in the form (Table 8.38)

$$\bar{\chi}_{\text{mol}} = N_A \mu_0 \mu_B^2 \times \frac{\sum_{J=|L-S|}^{L+S} \left[\frac{(g_J^A)^2 J(J+1)(2J+1)}{3kT} - 2F_{J,J+1} + 2F_{J-1,J} \right] \exp(-E_J^{(0)}/kT)}{\sum_{J=|L-S|}^{L+S} (2J+1) \exp(-E_J^{(0)}/kT)}$$

with

$$g_J^A = 1 - \frac{A}{2} + (2 + A) \frac{S(S+1) - 2}{2J(J+1)}$$

and the second-order factors for the adjacent terms

$$F_{J,J+1} = \frac{(2+A)^2}{A} F_{J,J+1}^{[\text{free ion } P \text{ term}]} = \frac{(2+A)^2}{A} \times \frac{(J+L+S+2)(-J+L+S)(J-L+S+1)(J+L-S+1)}{12(J+1)^2 \lambda}$$

with $L = 1$. This yields the final formula in the form

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{3kT} \mu_{\text{eff}}^2 = \frac{N_A \mu_0 \mu_B^2}{3kT} \frac{N}{D} = \frac{C_0}{3T} \frac{N}{D}$$

where the numerators and denominators are:

(a) for the $^3T_1$ terms

$$N = 3 \left\{ \frac{5(A-2)^2}{2} + \frac{5(A+2)^2}{6Ax} + \left[\frac{(A-2)^2}{2} + \frac{(A+2)^2}{2Ax} \right] \exp(-2Ax) - \frac{4(A+2)^2}{3Ax} \exp(-3Ax) \right\}$$

$$D = 5 + 3 \exp(-2Ax) + \exp(-3Ax)$$

(b) for the $^4T_1$ terms

$$N = 3 \left\{ \frac{7(3-A)^2}{5} + \frac{12(A+2)^2}{25Ax} + \left[\frac{2(11-2A)^2}{45} + \frac{176(A+2)^2}{675Ax} \right] \exp[-(5/2)Ax] + \left[\frac{(A+5)^2}{9} - \frac{20(A+2)^2}{27Ax} \right] \exp(-4Ax) \right\}$$

$$D = 3 + 2 \exp[-(5/2)Ax] + \exp(-4Ax)$$

with the parameters

$$x = \lambda/kT$$

$$A = \left\langle \Psi'(^3T_1) \left| \hat{L}_z \right| \Psi'(^3T_1) \right\rangle [\hbar^{-1}] = \frac{(3/2) - C^2}{1 + C^2}$$

and

$$C = \frac{6Dq + \varepsilon}{4Dq}$$

where ε is the lower root of the equation

$$\varepsilon^2 + (6Dq - 15B)\varepsilon - 16(Dq)^2 - 90(Dq)B = 0$$

Then

$$1 < A < 3/2$$

holds true between the strong-field and weak-field limits.

8.5.11 Symmetry lowering

It is unlikely that the ground states of really existing metal complexes are degenerate (T or E terms), for three reasons:

1. The actual crystal packing may require lower than cubic symmetry.
2. The relativistic double group approach allows only doubly degenerate levels and in the case of cubic symmetry the maximum degeneracy of Γ_8 is four; consequently no orbital triplets are allowed, only spin-orbital quadruplets.
3. The Jahn–Teller effect excludes the ground state being orbitally degenerate: there exists an internal disposition of the complex for a geometrical distortion that removes the orbital degeneracy. Among cubic systems the distortion applies either along the $e_{(g)}$ mode, which results in axial (or rhombic) symmetry, or along the $t_{2(g)}$ mode which leads to trigonal symmetry (Table 8.39).

Consequently the complex has a lower than cubic symmetry, which is equivalent to the addition of a low-symmetry crystal field potential to the spin Hamiltonian

$$\hat{V}^{\text{cf}} = \begin{cases} \hat{V}^{\text{axial}}(\mathbf{D}_{4h}) = \hat{V}(\mathbf{O}_h) + B_{2D}^0 \hat{O}_2^2 + B_{4D}^0 \hat{O}_4^0 \\ \hat{V}^{\text{trigonal}}(\mathbf{D}_{3d}) = \hat{V}(\mathbf{O}_h) + B_{2D}^0 \hat{O}_2^2 + B_{4D}^0 \hat{O}_4^0 \end{cases}$$

TABLE 8.39
Symmetry lowering owing to the Jahn–Teller effect

Term in O_h	Distortion mode	Terms in lower symmetry
${}^2T_{2g}$	$e_g \rightarrow D_{4h}$	${}^2B_{2g}, {}^2E_g$
	$t_{2g} \rightarrow D_{3d}$	${}^2A_{1g}, {}^2E_g$
${}^3T_{1g}$	$e_g \rightarrow D_{4h}$	${}^3A_{2g}, {}^3E_g$
	$t_{2g} \rightarrow D_{3d}$	${}^3A_{2g}, {}^3E_g$
${}^4T_{1g}$	$e_g \rightarrow D_{4h}$	${}^4A_{2g}, {}^4E_g$
	$t_{2g} \rightarrow D_{3d}$	${}^4A_{2g}, {}^4E_g$
${}^5T_{2g}$	$e_g \rightarrow D_{4h}$	${}^5B_{2g}, {}^5E_g$
	$t_{2g} \rightarrow D_{3d}$	${}^5A_{1g}, {}^5E_g$
${}^2E_g$	$e_g \rightarrow D_{4h}$	${}^2A_{1g}, {}^2B_{1g}$
${}^5E_g$	$e_g \rightarrow D_{4h}$	${}^5A_{1g}, {}^5B_{1g}$

The most common axial distortion can be described by the operator equivalent

$$\hat{V}^{\text{dis}} = \Delta\{\hat{L}_z^2[\hbar^{-2}] - L(L+1)/3\}$$

The basis set consists of all combinations of the orbital kets $|L, M_L\rangle$ and the spin kets $|S, M_S\rangle$, yielding the number $N = (2L+1)(2S+1)$. The perturbation operator includes the crystal field distortion, $\hat{V}^{\text{dis}}$, and the spin–orbit coupling, $\hat{H}^{\text{so}}$, terms

$$\hat{H}' = \hat{V}^{\text{dis}} + \hat{H}^{\text{so}}$$

Then the interaction matrix of the perturbation operator

$$H'_{ij} = \langle M_L M_S | \hat{H}' | M_L M_S \rangle$$

for a given value of L and S has the dimension of $N \times N$.

The matrix associated with $\hat{V}^{\text{dis}}$ is diagonal in the $|M_L M_S\rangle$ basis set, viz.

$$\langle M_L M_S | \hat{V}^{\text{dis}} | M_L M_S \rangle = \Delta(M_L^2 - 2/3)$$

where we apply $L = 1$.

The operator of the spin–orbit interaction can be manipulated using the escalator operators as follows

$$\vec{L} \cdot \vec{S} = \hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z = (1/2)(\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+) + \hat{L}_z \hat{S}_z$$

Then the non-zero matrix elements are

$$\begin{aligned}\langle M_L M_S | \lambda \vec{L} \cdot \vec{S} | M_L M_S \rangle &= \lambda M_L M_S [\hbar^2] \\ \langle M_L M_S | \lambda \vec{L} \cdot \vec{S} | M_L + 1, M_S - 1 \rangle &= \langle M_L + 1, M_S - 1 | \lambda \vec{L} \cdot \vec{S} | M_L M_S \rangle \\ &= (\lambda/2)[(L - M_L)(L + M_L + 1)]^{1/2} \\ &\quad \times [(S + M_S)(S - M_S + 1)]^{1/2} [\hbar^2]\end{aligned}$$

and

$$\begin{aligned}\langle M_L M_S | \lambda \vec{L} \cdot \vec{S} | M_L - 1, M_S + 1 \rangle &= \langle M_L - 1, M_S + 1 | \lambda \vec{L} \cdot \vec{S} | M_L M_S \rangle \\ &= (\lambda/2)[(L + M_L)(L - M_L + 1)]^{1/2} \\ &\quad \times [(S - M_S)(S + M_S + 1)]^{1/2} [\hbar^2]\end{aligned}$$

Owing to the T - P isomorphism, we have to substitute $L = 1$ when dealing with T -term kets.

There are two possible routes to determining the magnetic susceptibility:

1. The interaction matrix

$$H'_{ij} = \langle \Psi_i | \hat{V}^{\text{dis}} + \hat{H}^{\text{so}} | \Psi_j \rangle$$

is diagonalised, yielding the set of zero-field eigenvalues

$$\varepsilon_i = \langle \Psi'_i | \hat{V}^{\text{dis}} + \hat{H}^{\text{so}} | \Psi'_j \rangle \delta_{ij}$$

and eigenvectors $|\Psi'_i\rangle$. Using these eigenvectors as a new basis set (of coupled angular momenta kets) the matrix elements of the Zeeman operator $\hat{H}^Z$ are evaluated, for B parallel and perpendicular to the z (distortion) axis

$$H''_{ij} = \varepsilon_i \delta_{ij} + \langle \Psi'_i | \hat{H}^Z | \Psi'_j \rangle$$

(Notice that in the transformed basis set the z -component of the Zeeman operator is no longer diagonal: there are off-diagonal matrix elements of the type $\langle \Psi'_i | \hat{H}^Z_z | \Psi'_j \rangle$.) The full spin Hamiltonian matrix H''_{ij} is then diagonalised. The obtained eigenvalues $\varepsilon_i(B)$ are expanded in powers of B , yielding the van Vleck coefficients.

2. Alternatively, the matrix elements of the Zeeman operator are included in the spin Hamiltonian on the original basis set (of uncoupled angular momenta kets)

$$H'_{ij} = \langle M_L M_S | \hat{V}^{\text{dis}} + \hat{H}^{\text{so}} + \hat{H}^Z | M_L M_S \rangle$$

and this matrix is diagonalised.

Normally a numerical treatment on computers becomes ultimate.

In order to explain this procedure in more detail let us give an example of the ${}^2T_{2g}$ term with no axial distortion ($\hat{V}^{\text{dis}} = 0$). The orbital kets can be identified as follows

$$|\Psi({}^2T_2)\rangle = \begin{cases} |A\rangle = d_{-1} \\ |B\rangle = (1/\sqrt{2})(d_{+2} - d_{-2}) = |0\rangle \\ |C\rangle = d_{+1} \end{cases}$$

A different phase choice can be applied for the kets but the eigenvalues should remain invariant. Using the following order of the kets $|m_l\rangle|m_s\rangle$

$$\begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \\ \Psi_6 \end{pmatrix} = \begin{pmatrix} |A\rangle|-1/2\rangle \\ |A\rangle|+1/2\rangle \\ |B\rangle|-1/2\rangle \\ |B\rangle|+1/2\rangle \\ |C\rangle|-1/2\rangle \\ |C\rangle|+1/2\rangle \end{pmatrix}$$

the matrix elements of the spin-orbit operator, according to the rules listed above, are evaluated as follows

$$\begin{aligned} & \langle \Psi_i | \vec{L} \cdot \vec{S} | \Psi_j \rangle [\hbar^{-2}] \\ &= \begin{pmatrix} (-1) \cdot (-\frac{1}{2}) & 0 & 0 & 0 & 0 & 0 \\ 0 & (-1) \cdot (+\frac{1}{2}) & \frac{1}{2}\sqrt{2} \cdot 1 & 0 & 0 & 0 \\ 0 & \frac{1}{2}\sqrt{2} \cdot 1 & 0 \cdot (-\frac{1}{2}) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \cdot (+\frac{1}{2}) & \frac{1}{2}\sqrt{2} \cdot 1 & 0 \\ 0 & 0 & 0 & \frac{1}{2}\sqrt{2} \cdot 1 & (+1) \cdot (-\frac{1}{2}) & 0 \\ 0 & 0 & 0 & 0 & 0 & (+1) \cdot (+\frac{1}{2}) \end{pmatrix} \end{aligned}$$

Now, applying an equivalence coefficient that properly accounts for the T - P isomorphism

$$\hat{H}^{\text{so}} = v_{\xi} \vec{L} \cdot \vec{S} [\hbar^{-2}]$$

we get

$$H_{ij}^{\text{so}} = v_{\xi} \begin{pmatrix} +1/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1/2 & +1/\sqrt{2} & 0 & 0 & 0 \\ 0 & +1/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & +1/\sqrt{2} & 0 \\ 0 & 0 & 0 & +1/\sqrt{2} & +1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & +1/2 \end{pmatrix}$$

Since the secular equation naturally splits into four secular equations of dimensions 1, 2, 2 and 1, the eigenvalues can be evaluated in an analytic form

$$\varepsilon_1 = \frac{1}{2} v_{\xi}$$

$$\varepsilon_{2,3} = -\frac{1 \pm 3}{4} v_{\xi}$$

$$\varepsilon_{4,5} = -\frac{1 \pm 3}{4} v_{\xi}$$

$$\varepsilon_6 = \frac{1}{2} v_{\xi}$$

The corresponding transformation matrix, which makes the spin-orbit interaction operator diagonal, is

$$\begin{pmatrix} \Psi'_1 \\ \Psi'_2 \\ \Psi'_3 \\ \Psi'_4 \\ \Psi'_5 \\ \Psi'_6 \end{pmatrix} = \begin{pmatrix} |1/2, -1/2\rangle \\ |1/2, +1/2\rangle \\ |3/2, -3/2\rangle \\ |3/2, -1/2\rangle \\ |3/2, +1/2\rangle \\ |3/2, +3/2\rangle \end{pmatrix} = \begin{pmatrix} 0 & -\sqrt{2/3} & +\sqrt{1/3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{1/3} & +\sqrt{2/3} & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & +\sqrt{1/3} & +\sqrt{2/3} & 0 & 0 & 0 \\ 0 & 0 & 0 & +\sqrt{2/3} & +\sqrt{1/3} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \\ \Psi_6 \end{pmatrix}$$

or

$$\{|JM\rangle\} = C\{|m_l\rangle|m_s\rangle\}$$

Here we have applied a special ordering of $|JM\rangle$ kets, in an ascending order of the quantum numbers J and M , and thus the eigenvalues need a reordering to be consistent with the required (orthogonal) transformation to a diagonal form

$$\mathbf{eI} = \mathbf{CH}^{\text{so}}\mathbf{C}^T$$

Hence,

$$e_{1,2} = -v_\xi$$

$$e_{3,4,5,6} = \frac{1}{2}v_\xi$$

The matrix elements of the z -component of the Zeeman operator

$$\hat{H}_z^Z = \mu_B B(\gamma \hat{L}_z + 2\hat{S}_z)[\hbar^{-1}]$$

in the original basis set $|m_l\rangle|m_s\rangle$ were diagonal, i.e.

$$\mathbf{H}_z^Z = \mu_B B \begin{pmatrix} -\gamma - 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\gamma + 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 & 0 & 0 \\ 0 & 0 & 0 & 0 & +\gamma - 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & +\gamma + 1 \end{pmatrix}$$

and they transform into the basis set of $|JM\rangle$ kets as follows

$$\mathbf{H}_z'^Z = \mathbf{CH}_z^Z\mathbf{C}^T$$

yielding

$$\mathbf{H}_z'^Z = \mu_B B \begin{pmatrix} -(2\gamma - 1)/3 & 0 & 0 & \sqrt{2}(\gamma - 2)/3 & 0 & 0 \\ 0 & (2\gamma - 1)/3 & 0 & 0 & \sqrt{2}(\gamma - 2)/3 & 0 \\ 0 & 0 & -\gamma - 1 & 0 & 0 & 0 \\ \sqrt{2}(\gamma - 2)/3 & 0 & 0 & -(\gamma + 1)/3 & 0 & 0 \\ 0 & \sqrt{2}(\gamma - 2)/3 & 0 & 0 & (\gamma + 1)/3 & 0 \\ 0 & 0 & 0 & 0 & 0 & \gamma + 1 \end{pmatrix}$$

One has to use the equivalence coefficients $v_{\xi} = -1\xi_d = -\lambda$ and $\gamma = -1$ for the ${}^2T_{2g}$ term kets. Then the matrix elements of the total perturbation operator in the basis set of $|JM\rangle$ kets become

$$\mathbf{H}'_z = \mathbf{eI} + \mathbf{H}'_z{}^Z = \xi_d \begin{pmatrix} 1+G & 0 & 0 & -\sqrt{2}G & 0 & 0 \\ 0 & 1-G & 0 & 0 & -\sqrt{2}G & 0 \\ 0 & 0 & -(1/2) & 0 & 0 & 0 \\ -\sqrt{2}G & 0 & 0 & -(1/2) & 0 & 0 \\ 0 & -\sqrt{2}G & 0 & 0 & -(1/2) & 0 \\ 0 & 0 & 0 & 0 & 0 & -(1/2) \end{pmatrix}$$

where we introduce a dimensionless parameter

$$G = \frac{\mu_B B}{\xi_d}$$

The evaluation of the energy levels in the presence of the magnetic field, as eigenvalues of the above matrix, is straightforward, i.e.

$$\varepsilon_{3,6} = -\frac{1}{2}\xi_d$$

$$\varepsilon_{1,4} = \frac{1}{4}\xi_d \left[1 + 2G \pm 3\sqrt{1 + (4/3)G + 4G^2} \right]$$

$$\varepsilon_{2,5} = \frac{1}{4}\xi_d \left[1 - 2G \pm 3\sqrt{1 - (4/3)G + 4G^2} \right]$$

The expansion of the square roots according to the formula

$$\sqrt{1+x} = 1 + \frac{x}{2} - \frac{x^2}{8} + \dots$$

($x \ll 1$) with the omission of the remainders $O(G^3)$ yields

$$\varepsilon_1 = \xi_d \left[1 + G + \frac{4}{3}G^2 \right]$$

$$\varepsilon_4 = -\xi_d \left[\frac{1}{2} + \frac{4}{3}G^2 \right]$$

$$\varepsilon_2 = \xi_d \left[1 - G + \frac{4}{3} G^2 \right]$$

$$\varepsilon_5 = -\xi_d \left[\frac{1}{2} + \frac{4}{3} G^2 \right]$$

whence the van Vleck coefficients are obvious, i.e.

Level $ JM\rangle$	$E_i^{(0)}$	$E_i^{(1)}/\mu_B$	$E_i^{(2)}/\mu_B^2$
1, $\Gamma_7, 1/2, -1/2\rangle$	$+\xi_d$	+1	$+(4/3)/\xi_d$
2, $\Gamma_7, 1/2, -1/2\rangle$	$+\xi_d$	-1	$+(4/3)/\xi_d$
3, $\Gamma_8, 3/2, -3/2\rangle$	$-(1/2)\xi_d$	0	0
4, $\Gamma_8, 3/2, -1/2\rangle$	$-(1/2)\xi_d$	0	$-(4/3)/\xi_d$
5, $\Gamma_8, 3/2, +1/2\rangle$	$-(1/2)\xi_d$	0	$-(4/3)/\xi_d$
6, $\Gamma_8, 3/2, +3/2\rangle$	$-(1/2)\xi_d$	0	0

The application of a parallel (x or y) component of the Zeeman operator (which is non-diagonal in the $|m_l\rangle|m_s\rangle$ basis set) should bring about the same result.

In an alternative approach, the total perturbation operator in the basis set of $|m_l\rangle|m_s\rangle$ kets has the following matrix elements

$$H'_{ij} = \nu_\xi \begin{pmatrix} +1/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1/2 & +1/\sqrt{2} & 0 & 0 & 0 \\ 0 & +1/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & +1/\sqrt{2} & 0 \\ 0 & 0 & 0 & +1/\sqrt{2} & +1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & +1/2 \end{pmatrix} \\ + \mu_B B \begin{pmatrix} -\gamma - 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\gamma + 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 & 0 & 0 \\ 0 & 0 & 0 & 0 & +\gamma - 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & +\gamma + 1 \end{pmatrix}$$

and, with the equivalence coefficients of $\nu_\xi = -1\xi_d$ and $\gamma = -1$ for the $^2T_{2g}$ term kets, we get

$$H'_{ij} = -\xi_d \begin{pmatrix} 1/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -(1/2) - 2G & 1/\sqrt{2} & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & G & 0 & 0 & 0 \\ 0 & 0 & 0 & -G & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & (1/2) + 2G & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2 \end{pmatrix}$$

Then the one-step diagonalisation yields exactly the same eigenvalues as above.

8.5.12 Magnetic angular momentum with lowered symmetry

In the case of the ${}^2T_{2(g)}$ term the orbital kets appropriate for $\hat{V}^{\text{dis}}(\mathbf{D}_{4h})$ can be redefined as follows

$$|\Psi({}^2T_2)\rangle = \begin{cases} |a\rangle = d_{+1} \\ |b\rangle = (1/\sqrt{2})(d_{+2} - d_{-2}) = |0\rangle \\ |c\rangle = d_{-1} = |-a\rangle \end{cases}$$

and those appropriate for $\hat{V}^{\text{dis}}(\mathbf{D}_{3d})$ can be

$$|\Psi({}^2T_2)\rangle = \begin{cases} |a\rangle = \sqrt{2/3}d_{-2} + \sqrt{1/3}d_{+1} \\ |b\rangle = d_0 \\ |c\rangle = \sqrt{2/3}d_{+2} + \sqrt{1/3}d_{-1} \end{cases}$$

The perturbation Hamiltonian, in the form that properly accounts for the $T-P$ isomorphism, is

$$\hat{H}' = \hat{V}^{\text{dis}} + v_\xi \vec{L} \cdot \vec{S}[\hbar^{-2}]$$

with the equivalence coefficient $v_\xi = -1\xi_d = -\lambda$. We use v_ξ for the equivalence coefficient—not to be confused with an axial splitting parameter v introduced as follows

$$v = \Delta/\lambda$$

The matrix elements in the basis set of ${}^2T_{2(g)}$ kets are

$$H'_{ij} = \lambda \begin{pmatrix} \frac{v}{3} + \frac{1}{2} & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{v}{3} - \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{2v}{3} & 0 & 0 & -\frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & 0 & 0 & -\frac{2v}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{v}{3} - \frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & \frac{v}{3} + \frac{1}{2} \end{pmatrix}$$

The corresponding 6×6 secular equation

$$\det\{H'_{ij} - \varepsilon \delta_{ij}\} = 0$$

can be factorized into a set of secular equations of lower dimensions, namely

$$\det \begin{Bmatrix} \lambda \left(\frac{v}{3} + \frac{1}{2} \right) - \varepsilon & \lambda \left(-\frac{1}{\sqrt{2}} \right) \\ \lambda \left(-\frac{1}{\sqrt{2}} \right) & \lambda \left(-\frac{2v}{3} \right) - \varepsilon \end{Bmatrix} = 0$$

$$\det \begin{Bmatrix} \lambda \left(-\frac{2v}{3} \right) - \varepsilon & \lambda \left(-\frac{1}{\sqrt{2}} \right) \\ \lambda \left(-\frac{1}{\sqrt{2}} \right) & \lambda \left(\frac{v}{3} + \frac{1}{2} \right) - \varepsilon \end{Bmatrix} = 0$$

$$\det \left\{ \lambda \left(\frac{v}{3} - \frac{1}{2} \right) - \varepsilon \right\} = 0, \quad [\text{twice}]$$

The resulting zero-field eigenvalues are listed in Table 8.40 and plotted in Fig. 8.22.

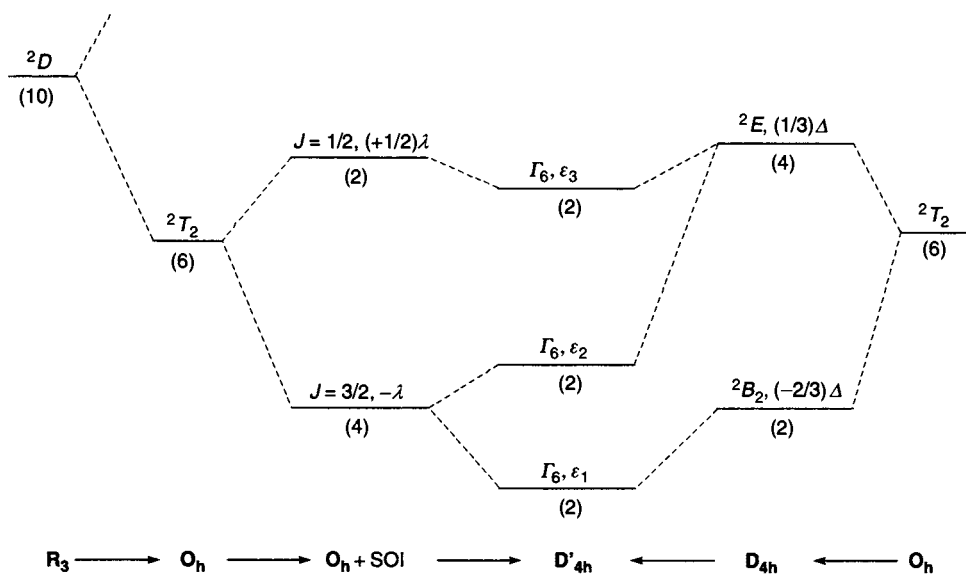
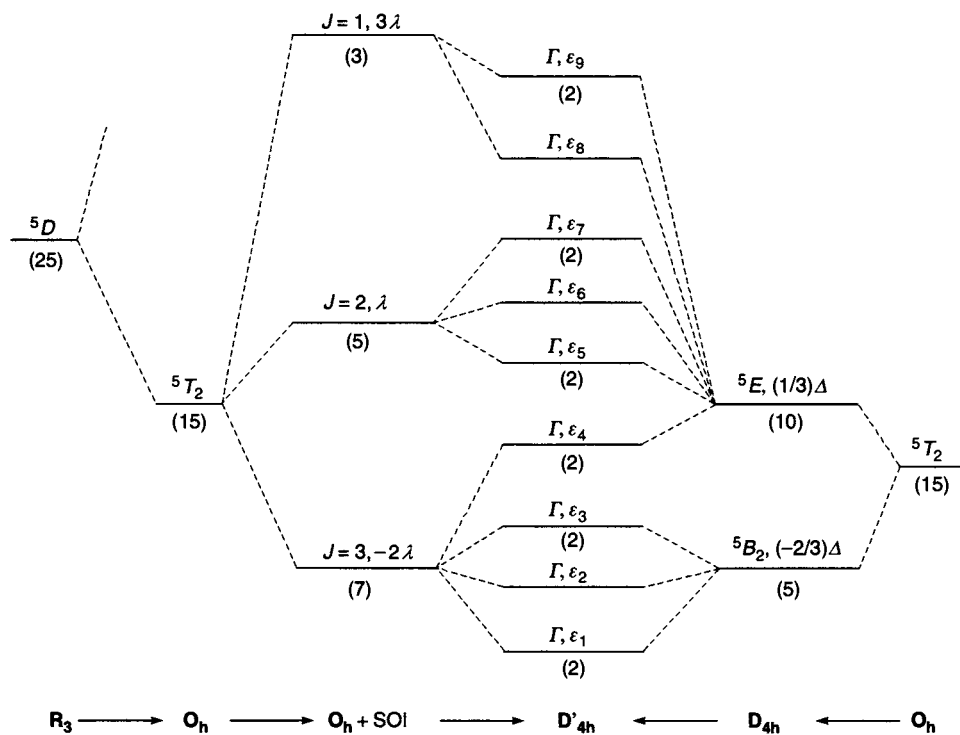
In the case of the ${}^5T_{2(g)}$ term the orbital kets are the same as for the ${}^2T_{2(g)}$ term. A higher spin multiplicity enlarges the dimension of the interaction matrix to $N = 3 \cdot 5 = 15$. The secular equation can be split into a set of secular equations of lower dimension (Table 8.40). The zero-field energy levels are shown in Fig. 8.23.

TABLE 8.40

Relationships for T -type terms under symmetry lowering

$^m T$	Kets $ M_L\rangle M_S\rangle$	Factorised interaction matrix	Zero-field eigenvalues ^a
$^2 T_2$	$ \pm a\rangle \mp 1/2\rangle$ $ 0\rangle \pm 1/2\rangle$ $ \pm a\rangle \pm 1/2\rangle$	$\lambda \begin{pmatrix} v/3 + 1/2 & -1/\sqrt{2} \\ -1/\sqrt{2} & -2v/3 \end{pmatrix}$ $\lambda(v/3 - 1/2)$	$\varepsilon_{1,3} = \lambda[-v/3 + 1/2 \pm (v^2 + v + 9/4)^{1/2}]/2$ $\varepsilon_2 = \lambda(v/3 - 1/2)$
$^5 T_2$	$ \pm a\rangle \pm 2\rangle$ $ 0\rangle \pm 1\rangle$ $ \mp a\rangle 0\rangle$ $ +a\rangle +1\rangle$ $ 0\rangle 0\rangle$ $ -a\rangle -1\rangle$ $ \pm a\rangle \mp 1\rangle$ $ 0\rangle \mp 2\rangle$ $ \pm a\rangle \mp 2\rangle$	$\lambda \begin{pmatrix} v/3 + 2 & \pm\sqrt{2} & 0 \\ \pm\sqrt{2} & -2v/3 & \mp\sqrt{3} \\ 0 & \mp\sqrt{3} & v/3 \end{pmatrix}$ $\lambda \begin{pmatrix} v/3 + 1 & +\sqrt{3} & 0 \\ +\sqrt{3} & -2v/3 & -\sqrt{3} \\ 0 & -\sqrt{3} & v/3 + 1 \end{pmatrix}$ $\lambda \begin{pmatrix} v/3 - 1 & \pm\sqrt{2} \\ \pm\sqrt{2} & -2v/3 \end{pmatrix}$ $\lambda(-v/3 - 2)$	$\varepsilon_{3,7,9} = \lambda[v/3 - \text{roots}_x\{x^3 + x^2(2 - v) + x(-5 - 2v) - 6 = 0\}]$ $\varepsilon_{8,2} = \lambda[-v/3 + 1 \pm (v^2 + 2v + 25)^{1/2}]/2$ $\varepsilon_6 = \lambda(v/3 + 1)$ $\varepsilon_{5,1} = \lambda[-v/3 - 1 \pm (v^2 - 2v + 9)^{1/2}]/2$ $\varepsilon_1 = \lambda(-v/3 - 2)$
$^3 T_1$	$ +A\rangle 1\rangle$ $ 0\rangle 0\rangle$ $ -A\rangle -1\rangle$ $ \pm A\rangle 0\rangle$ $ 0\rangle \mp 1\rangle$ $ \pm A\rangle \mp 1\rangle$	$\lambda \begin{pmatrix} v/3 + A & -A & 0 \\ -A & -2v/3 & -A \\ 0 & -A & v/3 + A \end{pmatrix}$ $\lambda \begin{pmatrix} v/3 & -A \\ -A & -2v/3 \end{pmatrix}$ $\lambda(v/3 - A)$	$\varepsilon_{6,2} = \lambda[-v/3 + A \pm (v^2 + 2Av + 9A^2)^{1/2}]/2$ $\varepsilon_5 = \lambda(v/3 + A)$ $\varepsilon_{4,1} = \lambda[-v/3 \pm (v^2 + 4A^2)^{1/2}]/2$ $\varepsilon_3 = \lambda(v/3 - A)$
$^4 T_1$	$ \pm A\rangle \pm 3/2\rangle$ $ 0\rangle \pm 1/2\rangle$ $ \mp A\rangle \mp 1/2\rangle$ $ \pm A\rangle \mp 1/2\rangle$ $ 0\rangle \mp 3/2\rangle$ $ \pm A\rangle \mp 3/2\rangle$	$\lambda \begin{pmatrix} v/3 + 3A/2 & \sqrt{3/2}A & 0 \\ \sqrt{3/2}A & -2v/3 & \sqrt{2}A \\ 0 & \sqrt{2}A & v/3 + A/2 \end{pmatrix}$ $\lambda \begin{pmatrix} v/3 - A/2 & \sqrt{3/2}A \\ \sqrt{3/2}A & -2v/3 \end{pmatrix}$ $\lambda(v/3 - 3A/2)$	$\varepsilon_{2,4,6} = \lambda[v/3 + 3A/2 - \text{roots}_x\{x^3 + x^2(-v - 5A/2) + x(Av - 2A^2) + 3A^3/2 = 0\}]$ $\varepsilon_{5,1} = \lambda[-v/3 - A/2 \pm (v^2 - vA + A^2 25/4)^{1/2}]/2$ $\varepsilon_3 = \lambda(v/3 - 3A/2)$

^a $\text{roots}_x\{x^3 + bx^2 + cx + d = 0\}$ are the three real roots of the cubic equation.

Fig. 8.22. Splitting pattern for the ${}^2T_{2(g)}$ term on symmetry lowering.Fig. 8.23. Splitting pattern for the ${}^5T_{2(g)}$ term on symmetry lowering.

In the case of the ${}^3T_{1(g)}$ term the non-interacting term functions are proper combinations of the determinantal functions $|L, M_L\rangle$, hence

$$|\Psi({}^3T_1, {}^3F)\rangle = \begin{cases} |a\rangle = \sqrt{15/24}|3, +3\rangle - \sqrt{9/24}|3, -1\rangle \\ |b\rangle = |3, 0\rangle \\ |c\rangle = \sqrt{15/24}|3, -3\rangle - \sqrt{9/24}|3, +1\rangle \end{cases}$$

and

$$|\Psi({}^3T_1, {}^3P)\rangle = \begin{cases} |1, +1\rangle \\ |1, 0\rangle \\ |1, -1\rangle \end{cases}$$

The perturbed kets accounting for the limited configuration interaction become

$$|\Psi'({}^3T_1)\rangle = \begin{cases} |+A\rangle = (1 + C^2)^{-1/2}(|a\rangle + C|1, +1\rangle) \\ |0\rangle = (1 + C^2)^{-1/2}(|b\rangle + C|1, 0\rangle) \\ |-A\rangle = (1 + C^2)^{-1/2}(|c\rangle + C|1, -1\rangle) \end{cases}$$

These functions produce an interaction matrix of the perturbation operator

$$\hat{H}' = \hat{V}^{\text{dis}} + A\hat{H}^{\text{so}}$$

whose dimension is 9×9 ; the mixing parameter is

$$A = \frac{(3/2) - C^2}{1 + C^2}$$

In evaluating the matrix elements the orbital kets obey the relationships

$$\langle \pm A | \hat{L}_z | \pm A \rangle = \pm A[\hbar]$$

$$\langle \pm A | \hat{L}_x | 0 \rangle = -(1/\sqrt{2})A[\hbar]$$

and

$$\langle \pm A | \hat{L}_y | 0 \rangle = -i(1/\sqrt{2})A[\hbar]$$

Fortunately the secular equation can be factorised into a set of secular equations of lower dimension having analytic solutions (Table 8.40). The zero-field energy levels are displayed in Fig. 8.24.

An analogous procedure can be applied for the ${}^4T_{1(g)}$ term on symmetry lowering. The orbital parts of the wave functions are identical to those for the ${}^3T_{1(g)}$ term and only the spin functions alter. The secular equation of the order of 12×12 is factorised into a set of lower-dimension problems again having analytic solutions (Table 8.40). The zero-field energy levels are shown in Fig. 8.25.

The addition of the Zeeman term makes the problem more complex since no factorisation of the secular equation may appear. However, the problem is tractable numerically, using computers. The complete spin Hamiltonian is of the form

$$\hat{H}^S = \Delta \{ \hat{L}_z^2 [\hbar^{-2}] - L(L+1)/3 \} + \kappa v_{\xi}^{[\text{strong field}]} A \vec{L} \cdot \vec{S} [\hbar^{-2}] \\ + \mu_B (\kappa \gamma^{[\text{strong field}]} A \vec{L} + g_e \vec{S}) \cdot \vec{B} [\hbar^{-1}]$$

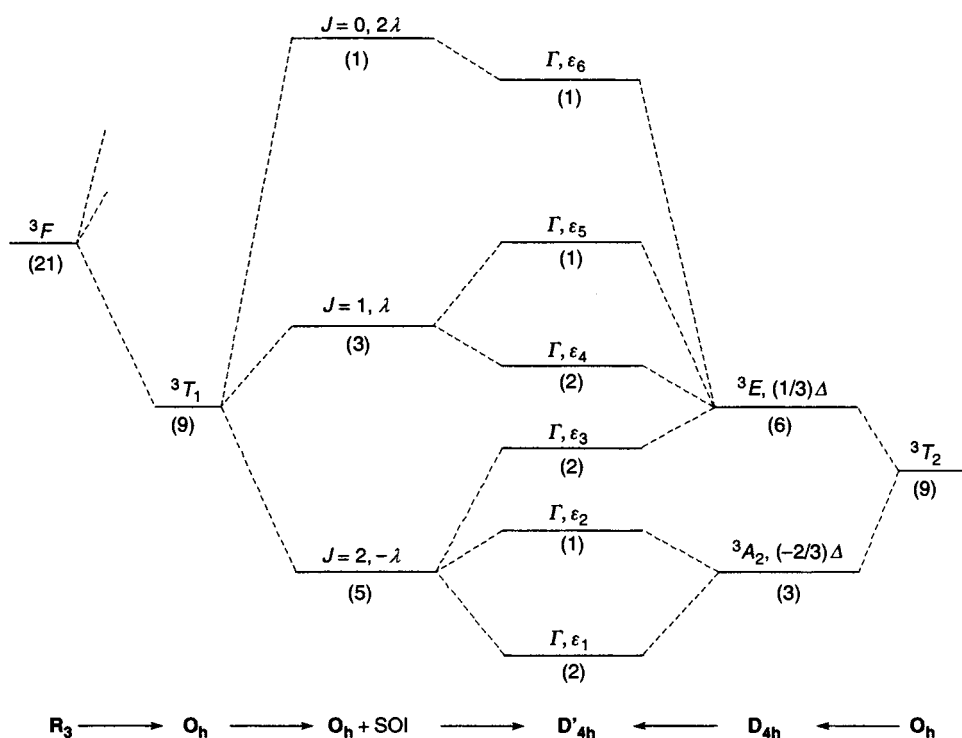


Fig. 8.24. Splitting pattern for the ${}^3T_{1(g)}$ term on symmetry lowering.

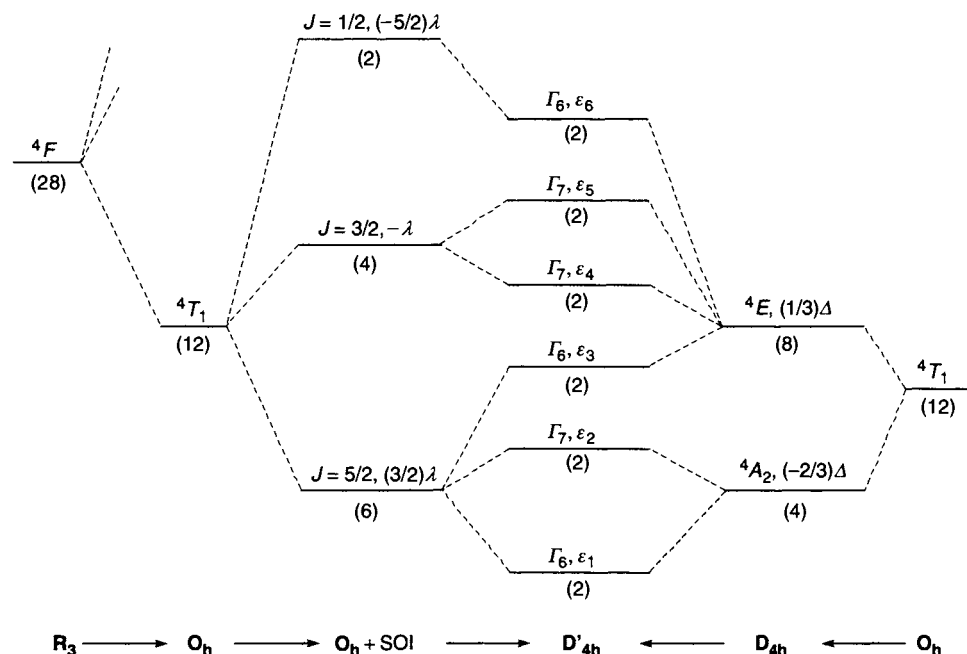


Fig. 8.25. Splitting pattern for the ${}^4T_{1(g)}$ term on symmetry lowering.

and the parameters entering the theoretical relationships cover the axial splitting parameter $v = \Delta/\lambda$, the orbital reduction factor κ and eventually the CI mixing parameter A , the last one originating in the CI form of the orbital kets. The effective magnetic moment becomes an implicit function of the reduced variable $x^{-1} = kT/\lambda$, hence

$$\mu_{\text{eff}}/\mu_B = f(v, \kappa, A; x^{-1})$$

for the fixed equivalence coefficients γ and ν_ξ associated with the particular term. An extensive tabulation of these functions was provided by Figgis et al. [36–39]. These are given in Figs. 8.26 and 8.27.

One trivial note should be added: in dealing with the reduced parameter $x^{-1} = kT/\lambda$ the value of the spin-orbit splitting parameter should be given in Kelvin units: λ/k has the dimension of [K]; the usual tabulation of the spin-orbit splitting parameter corresponds to the wave number λ/hc and has the dimension of $[\text{cm}^{-1}]$. Then the conversion is

$$\lambda \text{ (in the meaning of } \lambda/hc \text{) in } [\text{cm}^{-1}] = 1/1.438769 \text{ [K cm}^{-1}] \cdot (\lambda/k) \text{ in [K]}$$

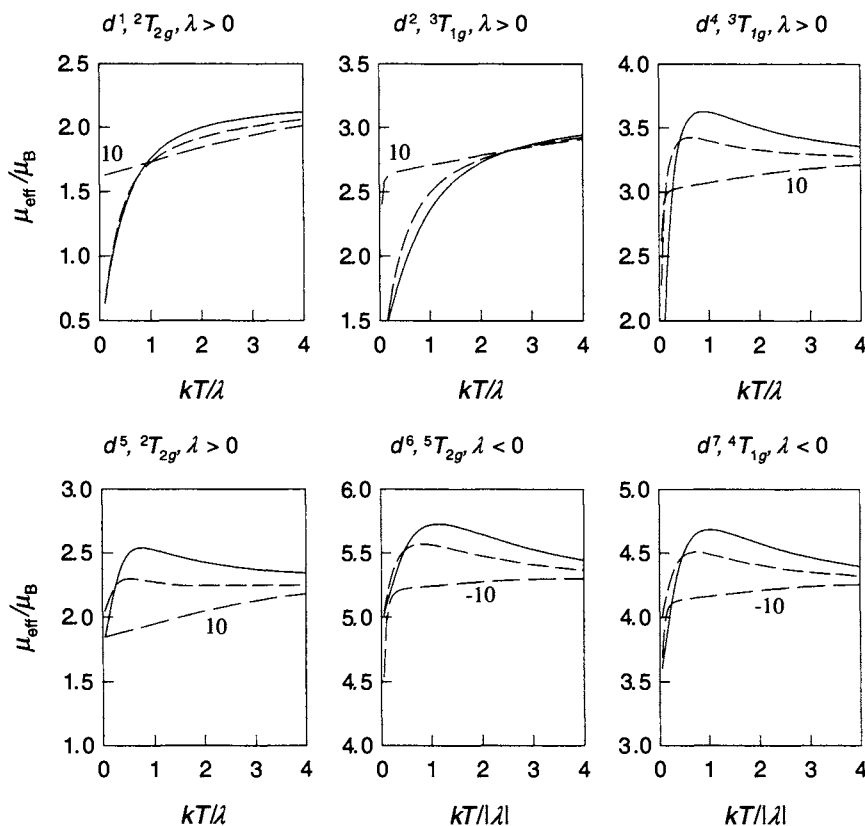


Fig. 8.26. Effective magnetic moment versus reduced temperature for octahedral complexes: full line— $v = 0$; dashed— $v = \pm 10$.

However, the reduced parameter alters the sign when passing from the less-than-half-filled shells to more-than-half-filled ones (since λ alters the sign); then, also, the axial splitting parameter $v = \Delta/\lambda$ alters the sign.

A more detailed inspection is given by Fig. 8.28 where the case of an octahedral d^7 complex, e.g. Co^{2+} , with $^4T_{1g}$ ground term is analysed. The spin-orbit splitting parameter entering the spin Hamiltonian was $v_{\xi}^{[\text{strong field}]}/hc = [(1/3)\xi_d]/hc = (540/3)\text{cm}^{-1} = 180\text{cm}^{-1}$

On the basis of these figures one can conclude:

- (1) the orbital reduction factor leads to lowering of the effective magnetic moment;
- (2) the CI mixing parameter A brings an increase of the effective magnetic moment when passing from the strong-field limit ($A = 1$) to the weak-field one ($A = 1.5$);
- (3) the axial splitting parameter reduces the effective magnetic moment, irrespective of its sign; the reduction, however, is different for positive and negative v ;

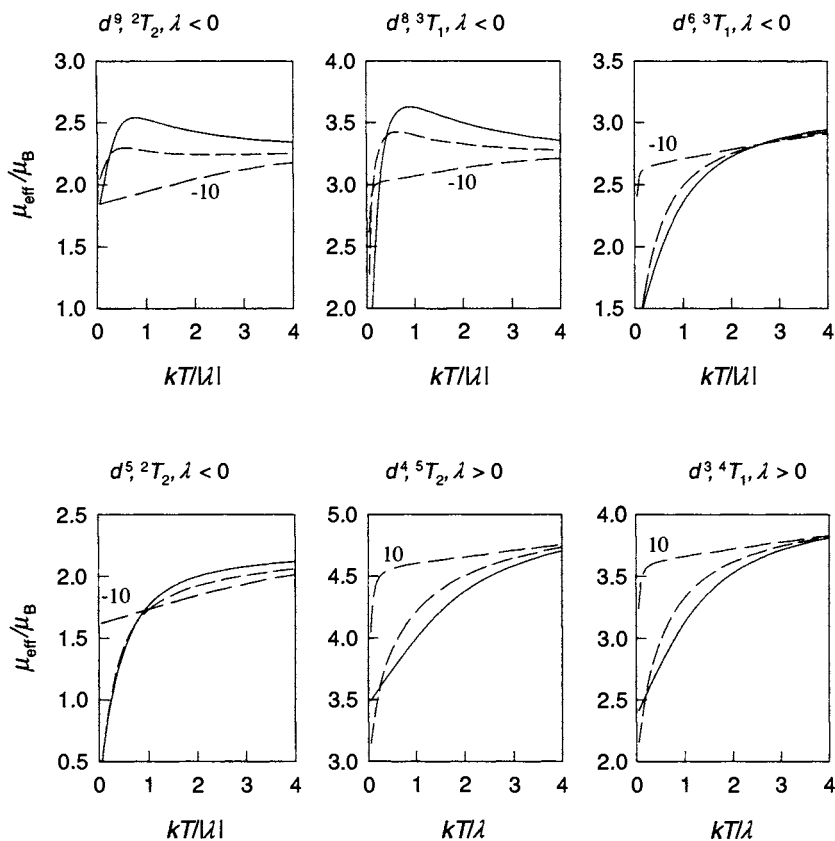


Fig. 8.27. Effective magnetic moment versus reduced temperature for tetrahedral complexes: full line— $v = 0$; dashed— $v = \pm 10$.

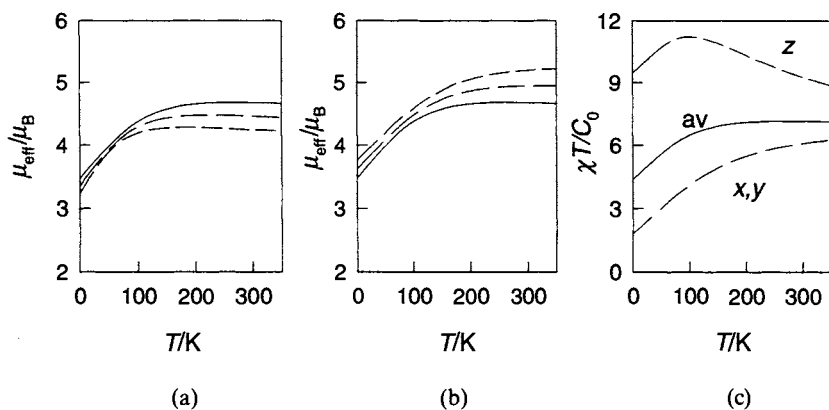


Fig. 8.28. Temperature variation of the magnetic functions for an octahedral complex with the ${}^4T_{1g}$ ground term: (a) $\kappa = 1.0$ (solid), 0.8 and 0.6 [for $A = 1.0$]; (b) $A = 1.0$ (solid), 1.25 and 1.5 [for $\kappa = 1$]; (c) $\Delta/hc = -500 \text{ cm}^{-1}$ [for $A = 1, \kappa = 1$].

(4) there is a pronounced magnetic anisotropy at relatively high temperatures.

An interesting point is that the spin Hamiltonian appropriate for the mononuclear complexes with the first-order angular momentum has an analogous form to the spin Hamiltonian that describes an isotropic binuclear exchange

$$\hat{H}^S = -J\vec{S}_1 \cdot \vec{S}_2[\hbar^{-2}] + \mu_B(g_1\vec{S}_1 + g_2\vec{S}_2) \cdot \vec{B}[\hbar^{-1}]$$

with the correspondences

$$\vec{L} \leftrightarrow \vec{S}_1$$

$$\vec{S} \leftrightarrow \vec{S}_2$$

$$-J \leftrightarrow \nu_\xi \kappa A$$

$$g_1 \leftrightarrow \gamma \kappa A$$

$$g_2 \leftrightarrow g_e$$

Therefore the transformation matrix **C** which diagonalises the spin-orbit coupling operator can be generated by the well-known techniques for coupling of two angular momenta, one of them having $S_1 = 1$.

It should be mentioned, however, that the procedure just described still suffers from several simplifications among which the following may be important:

- (1) a component of the symmetry lowering is not necessarily oriented along the C_4 and/or C_3 axis of the cubic group;
- (2) the orbital reduction factor κ appearing in $\hat{H}^{so}$ and $\hat{H}^Z$ can be anisotropic;
- (3) the spin-orbit splitting parameter λ can be anisotropic as well;
- (4) there is a mixing of the ground and excited terms through the spin-orbit operator since some matrix elements are in fact non-zero, e.g. $\langle {}^3T_1 | \hat{H}^{so} | {}^3T_2 \rangle \neq 0$.

In one particular case of the ${}^2T_{2(g)}$ term the eigenproblem of the spin Hamiltonian

$$\hat{H}^S = A\{\hat{L}_z^2[\hbar^{-2}] - 2/3\} - \kappa\lambda\vec{L} \cdot \vec{S}[\hbar^{-2}] + \mu_B(-\kappa\vec{L} + 2\vec{S}) \cdot \vec{B}[\hbar^{-1}]$$

was solved analytically. It led to the set of van Vleck coefficients listed in Table 8.41 where the following substitutions hold true

TABLE 8.41

Van Vleck coefficients for the ${}^2T_{2(g)}$ term on symmetry lowering [47]

Level	$E_i^{(1)}/\mu_B$	$E_i^{(2)}/\mu_B^2$
(a) Parallel direction:		
1, 2	$\pm(\kappa - 1)$	0
4, 6	$\pm \frac{\kappa + 1 - b^2}{1 + b^2}$	$-\frac{2}{\lambda} \frac{(\kappa + 1 - ab)^2}{(1 + a^2)(1 + b^2)c}$
3, 5	$\pm \frac{\kappa + 1 - a^2}{1 + a^2}$	$+\frac{2}{\lambda} \frac{(\kappa + 1 - ab)^2}{(1 + a^2)(1 + b^2)c}$
(b) Perpendicular direction:		
1, 2	0	$+\frac{4}{\lambda} \frac{(1 - \kappa a/\sqrt{2})^2}{(1 + a^2)(v - 3/2 - c)} + \frac{(1 - \kappa b/\sqrt{2})^2}{(1 + b^2)(v - 3/2 + c)}$
4, 6	$\pm \frac{\sqrt{2}\kappa b - b^2}{1 + b^2}$	$-\frac{4}{\lambda} \frac{(\kappa a/\sqrt{2} + \kappa b/\sqrt{2} - ab)^2}{2(1 + a^2)(1 + b^2)c} + \frac{(1 - \kappa b/\sqrt{2})^2}{(1 + b^2)(v - 3/2 + c)}$
3, 5	$\pm \frac{\sqrt{2}\kappa a - a^2}{1 + a^2}$	$+\frac{4}{\lambda} \frac{(\kappa a/\sqrt{2} + \kappa b/\sqrt{2} - ab)^2}{2(1 + a^2)(1 + b^2)c} - \frac{(1 - \kappa a/\sqrt{2})^2}{(1 + a^2)(v - 3/2 - c)}$

$$c = (v^2 + v + 9/4)^{1/2}$$

$$a = \frac{v + 1/2 - c}{\sqrt{2}}$$

$$b = \frac{v + 1/2 + c}{\sqrt{2}}$$

and the zero-field eigenvalues (coefficients) are

$$E_{1,2}^{(0)} = \lambda \left(\frac{v}{3} - \frac{\kappa}{2} \right)$$

$$E_{3,4}^{(0)} = \frac{\lambda}{2} \left[-\frac{v}{3} + \frac{\kappa}{2} \pm \left(v^2 + \kappa v + \frac{9}{4} \kappa^2 \right)^{1/2} \right]$$

$$E_{5,6}^{(0)} = \frac{\lambda}{2} \left[-\frac{v}{3} + \frac{\kappa}{2} \pm \left(v^2 + \kappa v + \frac{9}{4} \kappa^2 \right)^{1/2} \right]$$

which can be arbitrarily shifted to a new origin.

If the symmetry lowering is switched off ($v = 0$), then the effective magnetic moment for the ${}^2T_{2(g)}$ term becomes

$$\mu_{\text{eff}}^2/\mu_B^2 = \{[30(1 - \kappa)^2x + 8(2 + \kappa)^2] + [3(1 + 2\kappa)^2x - 8(2 + \kappa)^2] \exp(-3x/2)\} / \{9x[2 + \exp(-3x/2)]\}$$

with

$$x = (\kappa\lambda)/kT$$

When also the orbital reduction is switched off ($\kappa = 1$) then a simplification is obtained

$$\mu_{\text{eff}}^2/\mu_B^2 = \{8 + (3x - 8) \exp(-3x/2)\} / \{x[2 + \exp(-3x/2)]\}$$

8.5.13 Complete treatment for d^n configurations

The limitations of considering only the ground-state term within the basis set can be overcome by a quite general theory of multiplets in the presence of the crystal field [40]. The Hamiltonian involved is of the form

$$\hat{H} = \hat{H}^0 + \hat{V}^{\text{ee}} + \hat{V}^{\text{cf}} + \hat{H}^{\text{so}} + \hat{H}^Z$$

whose terms have their usual meaning. In order to define the basis set of kets we need to introduce two additional aspects which are important for systems with more than two identical electrons ($n \geq 3$):

- (a) the seniority number,
- (b) the coefficients of fractional parentage (CFP).

The *seniority number* interrelates two or more identical terms ${}^mL$ which arise from different electron configurations d^n and $d^{n'}$. The idea originates in the fact that some kets $|LS\rangle$ for the d^{n+2} electron system can be constructed with the help of the kets for the d^n system. In other words, the d^{n+2} configuration contains also those terms which were present in the configuration d^n . For example, among terms of the d^5 configuration the ${}^2D$ was already present in the configuration d^3 as well as in the configuration d^1 .

The *seniority number* (shortly “seniority”), v , is a number associated with each term, viz. ${}^m_vL$, and it behaves like a quantum number: there exists an operator (Racah seniority operator) whose eigenvalues are functions of v . The kets of many-electron atoms may be indexed as $|vLSJM\rangle$ and for d^n configurations they are evolved according to the scheme

n	v
5	5, 3, 1
4	4, 2, 0
3	3, 1
2	2, 0
1	1

We shall see later that some matrix elements of the operators involved in the Hamiltonian are diagonal in v so that their off-diagonal counterparts vanish.

The concept of fractional parentage originates in the fact that the kets of a d^n configuration can be built up from those of the d^{n-1} configuration, hence

$$|d^n \alpha JM\rangle = \sum_i a_i |d^{n-1}(\bar{\alpha}\bar{J})d^1; JM\rangle$$

Here the summation extends over all states $|d^{n-1}(\bar{\alpha}\bar{J})\rangle$ of the complete set for the d^{n-1} configuration; these states are orthonormal and fully antisymmetric with respect to d^{n-1} electrons and are referred to as *parents* of the state $|d^n \alpha JM\rangle$. The expansion coefficients are termed the *coefficients of the fractional parentage*

$$a_i \equiv \langle d^{n-1}(\bar{\alpha}\bar{J}), d^1 | \rangle d^n \alpha J \rangle$$

and an extensive tabulation of them exists in specialised monographs [1, 12, 41] (Table 8.42).

The coefficients of fractional parentage are particularly useful in evaluating some matrix elements. For example, let us assume a one-electron operator

$$\mathbf{T}^{(k)} = \sum_{i=1}^n \mathbf{t}_i^{(k)}$$

which, in fact, is a tensor of rank k . If we restrict ourselves to configurations of equivalent electrons then we arrive at the expression

$$\langle l^n \alpha LS | \mathbf{T}^{(k)} | l^n \alpha' L' S' \rangle = n \langle l^n \alpha LS | \mathbf{t}_1^{(k)} | l^n \alpha' L' S' \rangle$$

With the help of the formulae already met in Section 1.5, the reduced matrix element is given as follows

$$\begin{aligned} & \langle \alpha_1 l_1 l_2 L \| \mathbf{T}^{(k)} \| \alpha'_1 l'_1 l'_2 L' \rangle \\ &= \delta_{l_2, l'_2} (-1)^{l_1 + l_2 + L' + k} (2L + 1)^{1/2} (2L' + 1)^{1/2} \begin{Bmatrix} L & L' & k \\ l'_1 & l_1 & l_2 \end{Bmatrix} \langle \alpha_1 l_1 \| \mathbf{T}^{(k)} \| \alpha'_1 l'_1 \rangle \end{aligned}$$

TABLE 8.42

Coefficients of fractional parentage for d^n configurations $\{d^{n-1}\overline{SL}\}\{d^n SL\}$

Term $\{d^n SL\}$	Norm	Parents ^a $\{d^{n-1}\overline{SL}\}$							
d^5		^5D	^3H	^3G	$^3F_1$	$^3F_2$	^3D	$^3P_1$	$^3P_2$
^6S	1	1	0	0	0	0	0	0	0
^4G	$\sqrt{420}$	$-\sqrt{105}$	$\sqrt{154}$	$-\sqrt{66}$	0	$-\sqrt{70}$	5	0	0
^4F	$\sqrt{700}$	$-\sqrt{175}$	$-\sqrt{110}$	$-\sqrt{90}$	$\sqrt{224}$	$\sqrt{14}$	$-\sqrt{15}$	$-\sqrt{56}$	-4
^4D	$\sqrt{700}$	$-\sqrt{175}$	0	$\sqrt{180}$	0	$-\sqrt{84}$	$-\sqrt{135}$	0	$\sqrt{126}$
^4P	$\sqrt{300}$	$-\sqrt{75}$	0	0	$-\sqrt{56}$	$\sqrt{56}$	$\sqrt{35}$	-8	$\sqrt{14}$
^2I	$\sqrt{550}$	0	$\sqrt{231}$	$\sqrt{99}$	0	0	0	0	0
^2H	$\sqrt{1100}$	0	$\sqrt{286}$	$-\sqrt{99}$	$-\sqrt{220}$	$\sqrt{55}$	0	0	0
$^2G_1$	$\sqrt{8400}$	0	$\sqrt{924}$	$\sqrt{891}$	$\sqrt{1680}$	$\sqrt{945}$	$\sqrt{600}$	0	0
$^2G_2$	$\sqrt{18480}$	0	$-\sqrt{308}$	$-\sqrt{5577}$	0	$\sqrt{4235}$	$\sqrt{968}$	0	0
$^2F_1$	$\sqrt{2800}$	0	$\sqrt{220}$	$-\sqrt{405}$	$\sqrt{112}$	$-\sqrt{175}$	$\sqrt{120}$	$\sqrt{448}$	$-\sqrt{200}$
$^2F_2$	$\sqrt{2800}$	0	$-\sqrt{396}$	-3	0	$-\sqrt{315}$	$\sqrt{600}$	0	$\sqrt{360}$
$^2D_1$	$\sqrt{50}$	0	0	0	$-\sqrt{21}$	0	0	-3	0
$^2D_2$	$\sqrt{350}$	0	0	$\sqrt{45}$	$\sqrt{21}$	$-\sqrt{21}$	$\sqrt{60}$	-7	$-\sqrt{14}$
$^2D_3$	$\sqrt{700}$	0	0	$\sqrt{45}$	0	$\sqrt{189}$	$\sqrt{60}$	0	$\sqrt{126}$
^2P	$\sqrt{150}$	0	0	0	-4	-5	$\sqrt{10}$	$\sqrt{14}$	5
^2S	$\sqrt{5}$	0	0	0	0	0	$\sqrt{3}$	0	0
d^5		^1I	$^1G_1$	$^1G_2$	^1F	$^1D_1$	$^1D_2$	$^1S_1$	$^1S_2$
^6S	1	0	0	0	0	0	0	0	0
^4G	$\sqrt{420}$	0	0	0	0	0	0	0	0
^4F	$\sqrt{700}$	0	0	0	0	0	0	0	0
^4D	$\sqrt{700}$	0	0	0	0	0	0	0	0
^4P	$\sqrt{300}$	0	0	0	0	0	0	0	0
^2I	$\sqrt{550}$	$-\sqrt{175}$	0	$-\sqrt{45}$	0	0	0	0	0
^2H	$\sqrt{1100}$	$\sqrt{182}$	$\sqrt{220}$	$-\sqrt{5}$	$\sqrt{33}$	0	0	0	0
$^2G_1$	$\sqrt{8400}$	$-\sqrt{728}$	$\sqrt{880}$	$\sqrt{845}$	$-\sqrt{7}$	$-\sqrt{800}$	-10	0	0
$^2G_2$	$\sqrt{18480}$	$-\sqrt{2184}$	0	$-\sqrt{1215}$	$-\sqrt{2541}$	0	$\sqrt{1452}$	0	0
$^2F_1$	$\sqrt{2800}$	0	-20	$\sqrt{275}$	$\sqrt{105}$	$-\sqrt{160}$	$\sqrt{180}$	0	0
$^2F_2$	$\sqrt{2800}$	0	0	$\sqrt{495}$	$-\sqrt{525}$	0	-10	0	0
$^2D_1$	$\sqrt{50}$	0	-3	0	0	$-\sqrt{5}$	0	$\sqrt{6}$	0
$^2D_2$	$\sqrt{350}$	0	-5	$-\sqrt{11}$	$\sqrt{35}$	$\sqrt{45}$	$-\sqrt{10}$	0	$-\sqrt{14}$
$^2D_3$	$\sqrt{700}$	0	0	$\sqrt{99}$	$\sqrt{35}$	0	$\sqrt{90}$	0	$-\sqrt{56}$
^2P	$\sqrt{150}$	0	0	0	$-\sqrt{15}$	$\sqrt{30}$	$\sqrt{15}$	0	0
^2S	$\sqrt{5}$	0	0	0	0	0	$-\sqrt{2}$	0	0
d^4		^4F	^4P	^2H	^2G	^2F	$^2D_1$	$^2D_2$	^2P
^5D	$\sqrt{10}$	$\sqrt{7}$	$\sqrt{3}$	0	0	0	0	0	0
^3H	$\sqrt{60}$	$\sqrt{20}$	0	$\sqrt{26}$	-3	$\sqrt{5}$	0	0	0
^3G	$\sqrt{1680}$	$-\sqrt{560}$	0	$\sqrt{308}$	$\sqrt{297}$	$\sqrt{315}$	0	$\sqrt{200}$	0
$^3F_1$	$\sqrt{840}$	$\sqrt{224}$	$-\sqrt{56}$	$\sqrt{110}$	$\sqrt{90}$	$-\sqrt{14}$	$\sqrt{315}$	$\sqrt{15}$	4
$^3F_2$	$\sqrt{1680}$	$-\sqrt{112}$	$-\sqrt{448}$	$\sqrt{220}$	$-\sqrt{405}$	$-\sqrt{175}$	0	$\sqrt{120}$	$-\sqrt{200}$
^3D	$\sqrt{210}$	$-\sqrt{21}$	7	0	$\sqrt{45}$	$-\sqrt{21}$	0	$\sqrt{60}$	$-\sqrt{14}$
$^3P_1$	$\sqrt{360}$	$-\sqrt{56}$	-8	0	0	$-\sqrt{56}$	$\sqrt{135}$	$-\sqrt{35}$	$-\sqrt{14}$

TABLE 8.42

Coefficients of fractions parentage for d^n configurations $\{d^{n-1}\overline{SL}\}d^n SL$ (contd.)

Term $ d^n SL\rangle$	Norm	Parents ^a $ d^{n-1}\overline{SL}\rangle$							
d^4		^4F	^4P	^2H	^2G	^2F	$^2D_1$	$^2D_2$	^2P
$^3P_2$	$\sqrt{90}$	4	$-\sqrt{14}$	0	0	-5	0	$\sqrt{10}$	5
^1I	$\sqrt{10}$	0	0	$\sqrt{7}$	$\sqrt{3}$	0	0	0	0
$^1G_1$	$\sqrt{504}$	0	0	$-\sqrt{154}$	$\sqrt{66}$	$\sqrt{70}$	$\sqrt{189}$	-5	0
$^1G_2$	$\sqrt{1008}$	0	0	$-\sqrt{28}$	$-\sqrt{507}$	$\sqrt{385}$	0	$\sqrt{88}$	0
^1F	$\sqrt{560}$	0	0	$-\sqrt{132}$	$-\sqrt{3}$	$-\sqrt{105}$	0	$\sqrt{200}$	$\sqrt{120}$
$^1D_1$	$\sqrt{280}$	0	0	0	$-\sqrt{60}$	$\sqrt{28}$	$\sqrt{105}$	$\sqrt{45}$	$-\sqrt{42}$
$^1D_2$	$\sqrt{140}$	0	0	0	$\sqrt{15}$	$\sqrt{63}$	0	$\sqrt{20}$	$\sqrt{42}$
$^1S_1$	1	0	0	0	0	0	1	0	0
$^1S_2$	1	0	0	0	0	0	0	1	0
d^3		^3F	^3P	^1G	^1D	^1S			
^4F	$\sqrt{5}$	2	-1	0	0	0			
^4P	$\sqrt{15}$	$-\sqrt{7}$	$-\sqrt{8}$	0	0	0			
^2H	$\sqrt{2}$	-1	0	1	0	0			
^2G	$\sqrt{42}$	$\sqrt{21}$	0	$\sqrt{11}$	$-\sqrt{10}$	0			
^2F	$\sqrt{70}$	$\sqrt{7}$	$\sqrt{28}$	-5	$-\sqrt{10}$	0			
$^2D_1$	$\sqrt{60}$	$-\sqrt{21}$	-3	-3	$-\sqrt{5}$	4			
$^2D_2$	$\sqrt{140}$	$\sqrt{21}$	-7	-5	$\sqrt{45}$	0			
^2P	$\sqrt{30}$	$-\sqrt{8}$	$\sqrt{7}$	0	$\sqrt{15}$	0			

^aEach parent's coefficient should be *divided* by the corresponding norm.

Now, using the concept of fractional parentage

$$|d^n \alpha JM\rangle = \sum_{\bar{\alpha}} \sum_{\bar{j}} \langle d^{n-1}(\bar{\alpha}\bar{j}), d^1 | \rangle d^n \alpha J \cdot |d^{n-1}(\bar{\alpha}\bar{j})d^1; JM\rangle$$

we get a decomposition

$$\begin{aligned}
\langle d^n vL \| \mathbf{T}^{(k)} \| d^n v'L' \rangle &= n(2L+1)^{1/2}(2L'+1)^{1/2} \langle l \| \mathbf{t}_1^{(k)} \| l \rangle \\
&\times \sum_{\bar{v}} \sum_{\bar{L}} \langle d^n vL \{ |d^{n-1} \bar{v}\bar{L}, d \rangle \\
&\times \langle d^{n-1} \bar{v}\bar{L}, d | \rangle d^n v'L' \rangle (-1)^{\bar{L}+L+l+k} \left\{ \begin{matrix} L & L' & k \\ l & l & \bar{L} \end{matrix} \right\}
\end{aligned}$$

If the operator refers to the orbital angular momentum ($k=1$), then

$$\langle l \| \mathbf{t}_1^{(k)} \| l \rangle = \langle l \| \mathbf{t}_1^{(1)} \| l \rangle = [l(l+1)(2l+1)]^{1/2} [\hbar]$$

and, in the case of the spin, one has

$$\langle s \| \mathbf{t}_1^{(k)} \| s \rangle = \langle s \| \mathbf{s}_1^{(1)} \| s \rangle = [s(s+1)(2s+1)]^{1/2} [\hbar] = \sqrt{3/2} [\hbar]$$

In order to build up an appropriate basis set of kets let us start from the weak-field coupling scheme. At the beginning we have defined the kets for free-atom multiplets $|vSLJM\rangle$. Notice that $|L-S| \leq J \leq L+S$ and $-J \leq M \leq J$. The effect of the crystal field then consists in splitting the free-atom levels into crystal field states. The symmetry group $\mathbf{G}$ appropriate to the system is a subgroup of the rotation group $\mathbf{R}_3$. Then the representation $D^{(J)}(\mathbf{R}_3)$ subduces a representation $D^{(J)}(\mathbf{G})$ which is, in general, reducible according to

$$D^{(J)}(\mathbf{G}) = \Gamma_{\text{red}} = \sum_i a_i^{(J)} \Gamma_i$$

The branching multiplicity index is normally $a_i^{(J)} > 1$ since Γ_i occurs more than once: the equivalent states need to be distinguished by the index a . (Only in the special case of the d^2 configuration and cubic symmetry does $a_i^{(J)} = 1$.) The appropriate basis set kets transforming according to irreducible representation Γ , component γ , of group $\mathbf{G}$ are then given by a unitary transformation

$$|vSLJ\Gamma\gamma a\rangle = \sum_M C_M |vSLJM\rangle$$

where the expanding (symmetry adaptation) coefficients

$$C_M \equiv \langle JM | J\Gamma\gamma a \rangle$$

may be found by applying the projection technique (Section 1.6). Actually [42]

$$|J\Gamma\gamma a\rangle = \frac{g(\Gamma)}{g(\mathbf{G})} \sum_R \langle \Gamma\gamma | \hat{R} | \Gamma\gamma \rangle^* \hat{R} |JM\rangle$$

and the coefficients employ a system of equations

$$\sum_a \langle JM' | J\Gamma\gamma' a \rangle \cdot \langle J\Gamma\gamma a | JM \rangle = \frac{g(\Gamma)}{g(\mathbf{G})} \sum_R \langle \Gamma\gamma' | \hat{R} | \Gamma\gamma \rangle^* \cdot \langle JM' | \hat{R} | JM \rangle$$

The resulting crystal field states are classified in Table 8.43.

TABLE 8.43

Representations of weak-field kets in crystal fields of different symmetry

Config.	O _h	$g(\Gamma)$	D ₄	$g(\Gamma)$	D ₃	$g(\Gamma)$
d^2, d^8	${}^3A_2$	1	${}^3A_2$	2	${}^3A_1$	1
	${}^3T_1$	2	${}^3B_1$	1	${}^3A_2$	3
	${}^3T_2$	1	${}^3B_2$	1	${}^3E$	3
			${}^3E$	3		
	${}^1A_1$	2	${}^1A_1$	4	${}^1A_1$	4
	${}^1E$	2	${}^1A_2$	1	${}^1A_2$	1
	${}^1T_1$	1	${}^1B_1$	2	${}^1E$	5
	${}^1T_2$	2	${}^1B_2$	2		
d^3, d^7			${}^1E$	3		
	${}^4A_2$	1	${}^4A_2$	2	${}^4A_1$	1
	${}^4T_1$	2	${}^4B_1$	1	${}^4A_2$	3
	${}^4T_2$	1	${}^4B_2$	1	${}^4E$	3
			${}^4E$	3		
	${}^2A_1$	1	${}^2A_1$	5	${}^2A_1$	6
	${}^2A_2$	1	${}^2A_2$	5	${}^2A_2$	6
	${}^2E$	4	${}^2B_1$	5	${}^2E$	14
	${}^2T_1$	5	${}^2B_2$	5		
	${}^2T_2$	5	${}^2E$	10		
	${}^5E$	1	${}^5A_1$	1	${}^5A_1$	1
	${}^5T_2$	1	${}^5B_1$	1	${}^5E$	2
d^4, d^6			${}^5B_2$	1		
			${}^5E$	1		
	${}^3A_1$	1	${}^3A_1$	4	${}^3A_1$	6
	${}^3A_2$	2	${}^3A_2$	7	${}^3A_2$	9
	${}^3E$	3	${}^3B_1$	5	${}^3E$	15
	${}^3T_1$	7	${}^3B_2$	5		
	${}^3T_2$	5	${}^3E$	12		
	${}^1A_1$	5	${}^1A_1$	10	${}^1A_1$	12
	${}^1A_2$	2	${}^1A_2$	4	${}^1A_2$	6
	${}^1E$	5	${}^1B_1$	7	${}^1E$	16
	${}^1T_1$	4	${}^1B_2$	7		
	${}^1T_2$	7	${}^1E$	11		
	${}^6A_1$	1	${}^6A_1$	1	${}^6A_1$	1
	${}^4A_1$	1	${}^4A_1$	3	${}^4A_1$	4
	${}^4A_2$	1	${}^4A_2$	3	${}^4A_2$	4
	${}^4E$	2	${}^4B_1$	3	${}^4E$	8
	${}^4T_1$	3	${}^4B_2$	3		
	${}^4T_2$	3	${}^4E$	6		
d^5	${}^2A_1$	4	${}^2A_1$	11	${}^2A_1$	14
	${}^2A_2$	3	${}^2A_2$	8	${}^2A_2$	11
	${}^2E$	7	${}^2B_1$	10	${}^2E$	25
	${}^2T_1$	8	${}^2B_2$	10		
	${}^2T_2$	10	${}^2E$	18		

With the basis set of appropriate weak-field kets determined, the evaluation of matrix elements can proceed. We need

(1) the crystal field interaction

$$\left\langle vSLJ\Gamma\gamma a \left| \sum_{i=1}^n \hat{V}_i^{\text{cf}}(r_i, \vartheta_i, \varphi_i) \right| v'S'L'J'\Gamma'\gamma'a' \right\rangle$$

(2) the spin-orbit coupling

$$\left\langle vSLJ\Gamma\gamma a \left| \sum_{i=1}^n \kappa \xi(r_i) \vec{s}_i \cdot \vec{l}_i \right| v'S'L'J'\Gamma'\gamma'a' \right\rangle$$

(3) the Zeeman interaction

$$\left\langle vSLJ\Gamma\gamma a \left| \sum_{i=1}^n (\kappa \vec{l}_i + g_e \vec{s}_i) \cdot \vec{B} \right| v'S'L'J'\Gamma'\gamma'a' \right\rangle$$

The evaluation of the crystal field interaction is listed below for the three most common situations [40]:

(a) cubic symmetry ($\mathbf{O}_h$, $\mathbf{T}_d$)

$$\begin{aligned} & \left\langle vSLJ\Gamma\gamma a \left| \hat{V}^{\text{cf}}(\mathbf{O}_h) \right| v'S'L'J'\Gamma'\gamma'a' \right\rangle \\ &= \delta_{\Gamma, \Gamma'} \delta_{\gamma, \gamma'} \delta_{S, S'} (-1)^{S+L'} [(2J+1)(2J'+1)]^{1/2} \\ & \times 3\sqrt{70} \left\{ \begin{matrix} J & J' & 4 \\ L' & L & S \end{matrix} \right\} \left\langle vSL \left\| \mathbf{U}^{(4)} \right\| v'S'L' \right\rangle (Dq) \\ & \times \sum_M \sum_{M'} (-1)^M \langle J\Gamma\gamma a | JM \rangle \langle J'M' | J'\Gamma'\gamma'a' \rangle \\ & \times \left\{ \begin{pmatrix} J & 4 & J' \\ -M & 0 & M' \end{pmatrix} + \left(\frac{5}{14}\right)^{1/2} \begin{pmatrix} J & 4 & J' \\ -M & 4 & M' \end{pmatrix} \right. \\ & \left. + \left(\frac{5}{14}\right)^{1/2} \begin{pmatrix} J & 4 & J' \\ -M & -4 & M' \end{pmatrix} \right\} \end{aligned}$$

(b) tetragonal symmetry ($\mathbf{D}_{4h}$, $\mathbf{D}_4$, $\mathbf{C}_{4v}$)

$$\begin{aligned}
& \left\langle vSLJ\Gamma\gamma a \left| \hat{V}^{\text{cf}}(\mathbf{D}_4) \right| v'S'L'J'\Gamma'\gamma'a' \right\rangle \\
&= \delta_{\Gamma,\Gamma'} \delta_{\gamma,\gamma'} \delta_{S,S'} (-1)^{S+L'} [(2J+1)(2J'+1)]^{1/2} \\
&\quad \times \left\{ \sqrt{70} \begin{Bmatrix} J & J' & 2 \\ L' & L & S \end{Bmatrix} \left\langle vSL \left\| \mathbf{U}^{(2)} \right\| v'S'L' \right\rangle \right. \\
&\quad \times (Ds) \sum_M (-1)^M \langle J\Gamma\gamma a | JM \rangle \begin{pmatrix} J & 2 & J' \\ -M & 0 & M \end{pmatrix} \langle J'M | J'\Gamma'\gamma'a' \rangle \\
&\quad + 3\sqrt{70} \begin{Bmatrix} J & J' & 4 \\ L' & L & S \end{Bmatrix} \left\langle vSL \left\| \mathbf{U}^{(4)} \right\| v'S'L' \right\rangle \\
&\quad \times \left[(Dq - Dt) \sum_M (-1)^M \langle J\Gamma\gamma a | JM \rangle \begin{pmatrix} J & 4 & J' \\ -M & 0 & M \end{pmatrix} \langle J'M | J'\Gamma'\gamma'a' \rangle \right. \\
&\quad + (Dq) \left(\frac{5}{14} \right)^{1/2} \sum_M \sum_{M'} (-1)^M \langle J\Gamma\gamma a | JM \rangle \left\{ \begin{pmatrix} J & 4 & J' \\ -M & 4 & M' \end{pmatrix} \right. \\
&\quad \left. \left. + \begin{pmatrix} J & 4 & J' \\ -M & -4 & M' \end{pmatrix} \right\} \langle J'M | J'\Gamma'\gamma'a' \rangle \right] \left. \right\}
\end{aligned}$$

(c) trigonal symmetry ($\mathbf{D}_{3d}$, $\mathbf{D}_3$, $\mathbf{C}_{3v}$)

$$\begin{aligned}
& \left\langle vSLJ\Gamma\gamma a \left| \hat{V}^{\text{cf}}(\mathbf{D}_3) \right| v'S'L'J'\Gamma'\gamma'a' \right\rangle \\
&= \delta_{\Gamma,\Gamma'} \delta_{\gamma,\gamma'} \delta_{S,S'} (-1)^{S+L'} [(2J+1)(2J'+1)]^{1/2} \\
&\quad \times \left\{ \sqrt{70} \begin{Bmatrix} J & J' & 2 \\ L' & L & S \end{Bmatrix} \left\langle vSL \left\| \mathbf{U}^{(2)} \right\| v'S'L' \right\rangle \right. \\
&\quad \times (D\sigma) \sum_M (-1)^M \langle J\Gamma\gamma a | JM \rangle \begin{pmatrix} J & 2 & J' \\ -M & 0 & M \end{pmatrix} \langle J'M | J'\Gamma'\gamma'a' \rangle \\
&\quad + 2\sqrt{70} \begin{Bmatrix} J & J' & 4 \\ L' & L & S \end{Bmatrix} \left\langle vSL \left\| \mathbf{U}^{(4)} \right\| v'S'L' \right\rangle \\
&\quad \times \left[\left(-Dq - \frac{3}{2} D\tau \right) \sum_M (-1)^M \langle J\Gamma\gamma a | JM \rangle \begin{pmatrix} J & 4 & J' \\ -M & 0 & M \end{pmatrix} \right. \\
&\quad \times \langle J'M | J'\Gamma'\gamma'a' \rangle - (Dq) \left(\frac{10}{7} \right)^{1/2} \sum_M \sum_{M'} (-1)^M \langle J\Gamma\gamma a | JM \rangle \\
&\quad \times \left\{ \begin{pmatrix} J & 4 & J' \\ -M & 3 & M' \end{pmatrix} + \begin{pmatrix} J & 4 & J' \\ -M & -3 & M' \end{pmatrix} \right\} \langle J'M | J'\Gamma'\gamma'a' \rangle \left. \right] \left. \right\}
\end{aligned}$$

In these formulae the symmetry adaptation coefficients, $3j$ - and $6j$ -symbols occur along with the set of crystal field parameters Dq , Ds , Dt , $D\sigma$ and $D\tau$. In addition, there are the reduced matrix elements of the n -electron unit tensor operators, evaluable with the help of the coefficients of fractional parentage $\langle d^{n-1} \bar{v} \bar{S} \bar{L} | \{ d^n v SL \rangle$ as follows

$$\begin{aligned} \langle vSL \| \mathbf{U}^{(k)} \| v'S'L' \rangle &= n(2L+1)^{1/2}(2L'+1)^{1/2} \\ &\times \sum_{\bar{v}} \sum_{\bar{S}} \sum_{\bar{L}} \langle vSL \{ | \bar{v} \bar{S} \bar{L} \rangle \cdot \langle \bar{v} \bar{S} \bar{L} | \} v'S'L' \rangle \\ &\times (-1)^{\bar{L}+L+l+k} \begin{Bmatrix} L & L' & k \\ l & l & \bar{L} \end{Bmatrix} \end{aligned}$$

The spin-orbit coupling needs an expression

$$\begin{aligned} &\left\langle vSLJ\Gamma\gamma a \left| \sum_{i=1}^n \kappa \xi(r_i) \vec{s}_i \cdot \vec{l}_i \right| v'S'L'J'\Gamma'\gamma' a' \right\rangle \\ &= \delta_{\Gamma, \Gamma'} \delta_{\gamma, \gamma'} \delta_{a, a'} (-1)^{J+L+S'} [l(l+1)(2l+1)]^{1/2} \xi_{nl} \begin{Bmatrix} L & L' & 1 \\ S' & S & J \end{Bmatrix} \\ &\times \langle vSL \| \mathbf{V}^{(11)} \| v'S'L' \rangle \end{aligned}$$

Here the reduced matrix element of the double tensor operator $\langle vSL \| \mathbf{V}^{(11)} \| v'S'L' \rangle$ occurs; it becomes expressed as follows ($k=1$)

$$\begin{aligned} \langle vSL \| \mathbf{V}^{(1k)} \| v'S'L' \rangle &= n[s(s+1)(2s+1)(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2} \\ &\times \sum_{\bar{v}} \sum_{\bar{S}} \sum_{\bar{L}} \langle vSL \{ | \bar{v} \bar{S} \bar{L} \rangle \cdot \langle \bar{v} \bar{S} \bar{L} | \} v'S'L' \rangle \\ &\times (-1)^{\bar{S}+\bar{L}+S+L+s+l+k+1} \begin{Bmatrix} S & S' & 1 \\ s & s & \bar{S} \end{Bmatrix} \begin{Bmatrix} L & L' & k \\ l & l & \bar{L} \end{Bmatrix} [\hbar^2] \end{aligned}$$

The spin-orbit coupling constant ξ_{nl} used to be reduced in magnitude by the amount κ as compared to the free-ion value ξ_{nl}^0 .

The Zeeman operator can be expressed with the help of the relationship

$$B_{\pm} = B_x \pm iB_y$$

and by introducing the irreducible tensor operators

$$\mathbf{T}_0^{(1)} = \hat{T}_z$$

$$\mathbf{T}_{\pm 1}^{(1)} = \mp \frac{1}{\sqrt{2}} \hat{T}_{\pm}$$

as follows

$$\begin{aligned} \sum_{i=1}^n (\kappa \vec{l}_i + g_e \vec{s}_i) \cdot \vec{B} &= \sum_{i=1}^n \left[(\kappa_{\parallel} \hat{l}_{zi} + g_e \hat{s}_{zi}) B_z + \frac{1}{2} (\kappa_{\perp} \hat{l}_{+i} + g_e \hat{s}_{+i}) B_- \right. \\ &\quad \left. + \frac{1}{2} (\kappa_{\perp} \hat{l}_{-i} + g_e \hat{s}_{-i}) B_+ \right] \\ &= \sum_{i=1}^n \left[(\kappa_{\parallel} \mathbf{l}_{0,i}^{(1)} + g_e \mathbf{s}_{0,i}^{(1)}) \mathbf{B}_0^{(1)} - (\kappa_{\perp} \mathbf{l}_{1,i}^{(1)} + g_e \mathbf{s}_{1,i}^{(1)}) \mathbf{B}_{-1}^{(1)} \right. \\ &\quad \left. - (\kappa_{\perp} \mathbf{l}_{-1,i}^{(1)} + g_e \mathbf{s}_{-1,i}^{(1)}) \mathbf{B}_1^{(1)} \right] \end{aligned}$$

where we have introduced an anisotropic orbital reduction factor. Then each spherical component ($q = 0, \pm 1$) is evaluated according to the reduction

$$\begin{aligned} &\left\langle vSLJ\Gamma\gamma a \left| \sum_{i=1}^n [(\kappa_q \mathbf{l}_{q,i}^{(1)} + g_e \mathbf{s}_{q,i}^{(1)}) \mathbf{B}_{-q}^{(1)}] \right| v'S'L'J'\Gamma'\gamma'a' \right\rangle \\ &= B_{-q} (-1)^{L+S} [(2J+1)(2J'+1)]^{1/2} \sum_M \sum_{M'} (-1)^M \langle J\Gamma\gamma a | JM \rangle \\ &\quad \times \begin{pmatrix} J' & 1 & J \\ M' & q & -M \end{pmatrix} \langle J'M' | J'\Gamma'\gamma'a' \rangle \\ &\quad \times \left[\kappa_q (-1)^{J'-J} [L(L+1)(2L+1)]^{1/2} \begin{Bmatrix} L & L & 1 \\ J & J' & S \end{Bmatrix} \right. \\ &\quad \left. + g_e [S(S+1)(2S+1)]^{1/2} \begin{Bmatrix} S & S & 1 \\ J & J' & L \end{Bmatrix} \right] \end{aligned}$$

In the case of the parallel (z) direction a simplification is obtained

$$\begin{aligned}
& \left\langle vSLJ\Gamma\gamma a \left| \sum_{i=1}^n \left[(\kappa_{||} \mathbf{l}_{0,i}^{(1)} + g_e \mathbf{s}_{0,i}^{(1)}) \mathbf{B}_0^{(1)} \right] \right| v'S'L'J'\Gamma'\gamma'a' \right\rangle = \delta_{v,v'} \delta_{S,S'} \delta_{L,L'} \\
& \times B_z (-1)^{L+S} [(2J+1)(2J'+1)]^{1/2} \sum_M (-1)^M \langle J\Gamma\gamma a | JM \rangle \\
& \times \begin{pmatrix} J' & 1 & J \\ M & 0 & -M \end{pmatrix} \langle J'M | J'\Gamma'\gamma'a' \rangle \\
& \times \left[\kappa_{||} (-1)^{J'-J} [L(L+1)(2L+1)]^{1/2} \begin{Bmatrix} L & L & 1 \\ J & J' & S \end{Bmatrix} \right. \\
& \left. + g_e [S(S+1)(2S+1)]^{1/2} \begin{Bmatrix} S & S & 1 \\ J & J' & L \end{Bmatrix} \right]
\end{aligned}$$

The complete interaction matrices have the dimension of

d^n	$\begin{pmatrix} 10 \\ n \end{pmatrix}$
1, 9	10
2, 8	45
3, 7	120
4, 6	210
5	252

To be consistent within the irreducible tensor approach, the expressions for the matrix elements of the electron repulsion operator (which gives rise to terms) are presented

$$\begin{aligned}
& \left\langle d^n vSLJ\Gamma\gamma a \left| \sum_{i=1}^n \sum_{j<i}^n \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right| d^n v'S'L'J'\Gamma'\gamma'a' \right\rangle \\
& = \delta_{J,J'} \delta_{\Gamma,\Gamma'} \delta_{\gamma,\gamma'} \delta_{a,a'} \left\langle d^n vSL \left| \sum_{i=1}^n \sum_{j<i}^n \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right| d^n v'S'L' \right\rangle \\
& = \delta_{J,J'} \delta_{\Gamma,\Gamma'} \delta_{\gamma,\gamma'} \delta_{a,a'} \frac{e^2}{4\pi\epsilon_0} \sum_{k=0}^4 (-1)^L F_{nl,nl}^k \left[\langle l \| \mathbf{C}^{(k)} \| l \rangle \right]^2 \begin{Bmatrix} l & l & k \\ l & l & L \end{Bmatrix}
\end{aligned}$$

with the reduced matrix element of the Racah operator (rationalised spherical harmonics) as follows

$$\langle l \| \mathbf{C}^{(k)} \| l' \rangle = (-1)^l [(2l+1)(2l'+1)]^{1/2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}$$

Owing to the equivalence of d -electrons only the Slater–Condon parameters of the type F_{dd}^0 , F_{dd}^2 and F_{dd}^4 (direct integrals) occur.

A programming of these formulae has been provided by König and Kremer [43–46]. Also the intermediate-field and strong-field references have been applied; the results, however, should remain invariant.

Since the term labels of electron configurations are fixed, the evaluation of the reduced matrix elements $\langle LS \| \mathbf{V}^{(11)} \| LS \rangle$ is helpful (Table 8.44). This is of great utility since now one can readily see which terms are connected (interact) through the one-electron spin–orbit operator. However, the matrix elements between the J -components need the evaluation of one $6j$ -symbol.

One can see, for instance, that within the d^5 electron configuration the ${}^6S$ term can interact only with the ${}^4P$ one. The non-zero matrix element results from the settings

Term 1	Term 2	Configuration	Parents
$ {}^6S\rangle$	$ {}^4P\rangle$	d^5	$ {}^5D\rangle$
$L = 0$	$L' = 1$	$l = 2$	$\bar{L} = 2$
$S = 5/2$	$S' = 3/2$	$s = 1/2$	$\bar{S} = 2$
$J = 5/2$	$J' = 5/2$	$n = 5$	$\bar{n} = 4$

There is only a single parent term $|d^4, {}^5D\rangle$ that interconnects the children terms $|d^5, {}^6S\rangle$ and $|d^5, {}^4P\rangle$; then the relevant coefficients of fractional parentage, according to Table 8.42, are

$$\langle d^4, {}^5D \| d^5, {}^6S \rangle = 1$$

$$\langle d^4, {}^5D \| d^5, {}^4P \rangle = -\frac{\sqrt{75}}{\sqrt{300}} = -\frac{1}{2}$$

Consequently the reduced matrix element becomes

$$\begin{aligned}
 \langle SL \| \mathbf{V}^{(11)} \| S' L' \rangle &= n[s(s+1)(2s+1)(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2} \\
 &\times \sum_{\bar{v}} \sum_{\bar{S}} \sum_{\bar{L}} \langle vSL \| \bar{v}\bar{S}\bar{L} \rangle \cdot \langle \bar{v}\bar{S}\bar{L} \| v'S'L' \rangle (-1)^{\bar{S}+\bar{L}+S+L+s+l} \left\{ \begin{matrix} S & S' & 1 \\ s & s & \bar{S} \end{matrix} \right\} \\
 &\times \left\{ \begin{matrix} L & L' & 1 \\ l & l & \bar{L} \end{matrix} \right\} = 5 \cdot \left[\frac{1}{2} \cdot \frac{3}{2} \cdot 2 \cdot 6 \cdot 1 \cdot 4 \cdot 3 \right]^{1/2} \cdot (1) \cdot \left(-\frac{1}{2} \right) \\
 &\cdot (-1)^{2+4+5/2+0+1/2+2} \cdot \left\{ \begin{matrix} 5/2 & 3/2 & 1 \\ 1/2 & 1/2 & 2 \end{matrix} \right\} \cdot \left\{ \begin{matrix} 0 & 1 & 1 \\ 2 & 2 & 2 \end{matrix} \right\} \\
 &= 5 \cdot [108]^{1/2} \cdot \left(-\frac{1}{2} \right) \cdot (-1) \cdot \left(-\frac{1}{\sqrt{15}} \right) \cdot \left(-\frac{1}{\sqrt{15}} \right) = \sqrt{3}
 \end{aligned}$$

TABLE 8.44

Reduced matrix elements $\langle LS \| \mathbf{V}^{(11)} \| LS \rangle [\hbar^{-2}]$ by [1]

d^5	${}^6S$	${}^4G$	${}^4F$	${}^4D$	${}^4P$	${}^2I$	${}^2H$	${}^2G_1$
${}^6S$	0	0	0	0	$\sqrt{3}$	0	0	0
${}^4G$	0	0	$+\sqrt{2}$	0	0	0	$-\sqrt{110}/5$	$+\sqrt{15}/5$
${}^4F$	0	$-\sqrt{2}$	0	$+2\sqrt{6}/3$	0	0	0	0
${}^4D$	0	0	$-2\sqrt{6}/3$	0	$+\sqrt{21}/3$	0	0	0
${}^4P$	$\sqrt{3}$	0	0	$-\sqrt{21}/3$	0	0	0	0
${}^2I$	0	0	0	0	0	0	$+\sqrt{390}/10$	0
${}^2H$	0	$-\sqrt{110}/5$	0	0	0	$-\sqrt{390}/10$	0	0
${}^2G_1$	0	$-\sqrt{15}/5$	0	0	0	0	0	0
${}^2G_2$	0	0	$-\sqrt{55}/5$	0	0	0	$-2\sqrt{10}/5$	$-\sqrt{165}/10$
${}^2F_1$	0	$\sqrt{5}$	0	$4\sqrt{15}/15$	0	0	0	0
${}^2F_2$	0	0	$-\sqrt{21}/3$	0	0	0	0	$+3\sqrt{15}/10$
${}^2D_1$	0	0	$-2\sqrt{105}/15$	0	$-4\sqrt{30}/15$	0	0	0
${}^2D_2$	0	0	0	$-2\sqrt{6}/3$	0	0	0	0
${}^2D_3$	0	0	$-\sqrt{30}/15$	0	$-2\sqrt{105}/15$	0	0	0
${}^2P$	0	0	0	$2\sqrt{15}/15$	0	0	0	0
${}^2S$	0	0	0	0	$\sqrt{105}/15$	0	0	0
d^5	${}^2G_2$	${}^2F_1$	${}^2F_2$	${}^2D_1$	${}^2D_2$	${}^2D_3$	${}^2P$	${}^2S$
${}^6S$	0	0	0	0	0	0	0	0
${}^4G$	0	$\sqrt{5}$	0	0	0	0	0	0
${}^4F$	$-\sqrt{55}/5$	0	$+\sqrt{21}/3$	$-2\sqrt{105}/15$	0	$-\sqrt{30}/15$	0	0
${}^4D$	0	$4\sqrt{15}/15$	0	0	$+2\sqrt{6}/3$	0	$2\sqrt{15}/15$	0
${}^4P$	0	0	0	$-4\sqrt{30}/15$	0	$-2\sqrt{105}/15$	0	$\sqrt{105}/15$
${}^2I$	0	0	0	0	0	0	0	0
${}^2H$	$+2\sqrt{10}/5$	0	0	0	0	0	0	0
${}^2G_1$	$-\sqrt{165}/10$	0	$-3\sqrt{15}/10$	0	0	0	0	0
${}^2G_2$	0	$+\sqrt{55}/10$	0	0	0	0	0	0
${}^2F_1$	$-\sqrt{55}/10$	0	$-\sqrt{21}/6$	$-2\sqrt{105}/15$	0	$-4\sqrt{30}/15$	0	0

d^5	${}^2G_2$	${}^2F_1$	${}^2F_2$	${}^2D_1$	${}^2D_2$	${}^2D_3$	${}^2P$	${}^2S$
${}^2F_2$	0	$-\sqrt{21}/6$	0	0	$+2\sqrt{3}/3$	0	0	0
${}^2D_1$	0	$+2\sqrt{105}/15$	0	0	$-\sqrt{42}/6$	0	$+\sqrt{105}/15$	0
${}^2D_2$	0	0	$-2\sqrt{3}/3$	$-\sqrt{42}/6$	0	$\sqrt{3}/3$	0	0
${}^2D_3$	0	$+4\sqrt{30}/15$	0	0	$\sqrt{3}/3$	0	$-\sqrt{30}/30$	0
${}^2P$	0	0	0	$-\sqrt{105}/15$	0	$+\sqrt{30}/30$	0	$+2\sqrt{30}/15$
${}^2S$	0	0	0	0	0	0	$-2\sqrt{30}/15$	0
d^4	${}^5D$	${}^3H$	${}^3G$	${}^3F_1$	${}^3F_2$	${}^3D$	${}^3P_1$	${}^3P_2$
${}^5D$	$\sqrt{30}/4$	0	0	$-\sqrt{21}/3$	$\sqrt{21}/3$	$-\sqrt{210}/12$	$-2\sqrt{6}/3$	$\sqrt{21}/6$
${}^3H$	0	$\sqrt{66}/10$	$-\sqrt{66}/5$	0	0	0	0	0
${}^3G$	0	$+\sqrt{66}/5$	9/10	$-\sqrt{3}$	$+\sqrt{3}/2$	0	0	0
${}^3F_1$	$-\sqrt{21}/3$	0	$+\sqrt{3}$	$\sqrt{105}/15$	$-\sqrt{105}/15$	$-\sqrt{15}/3$	0	0
${}^3F_2$	$\sqrt{21}/3$	0	$-\sqrt{3}/2$	$-\sqrt{105}/15$	$-\sqrt{105}/30$	$-\sqrt{15}/15$	0	0
${}^3D$	$+\sqrt{210}/12$	0	0	$+\sqrt{15}/3$	$+\sqrt{15}/15$	$-\sqrt{6}/12$	0	$-3\sqrt{15}/10$
${}^3P_1$	$-2\sqrt{6}/3$	0	0	0	0	0	$\sqrt{30}/30$	$-2\sqrt{105}/15$
${}^3P_2$	$\sqrt{21}/6$	0	0	0	0	$+3\sqrt{15}/10$	$-2\sqrt{105}/15$	$\sqrt{30}/15$
${}^1I$	0	$-\sqrt{195}/10$	0	0	0	0	0	0
${}^1G_1$	0	$-\sqrt{55}/5$	$+\sqrt{30}/10$	$-\sqrt{10}/10$	$\sqrt{10}/2$	0	0	0
${}^1G_2$	0	$2\sqrt{5}/5$	$+\sqrt{330}/20$	$\sqrt{110}/10$	$-\sqrt{110}/20$	0	0	0
${}^1F$	0	0	$-3\sqrt{30}/20$	$+\sqrt{42}/6$	$-\sqrt{42}/12$	$-\sqrt{6}/3$	0	0
${}^1D_1$	0	0	0	$\sqrt{30}/15$	$2\sqrt{30}/15$	$+\sqrt{3}/3$	$-\sqrt{105}/30$	$\sqrt{30}/15$
${}^1D_2$	0	0	0	$\sqrt{15}/15$	$-4\sqrt{15}/15$	$-\sqrt{6}/6$	$\sqrt{210}/15$	$\sqrt{15}/30$
${}^1S_1$	0	0	0	0	0	0	$3\sqrt{10}/10$	0
${}^1S_2$	0	0	0	0	0	0	$-\sqrt{210}/30$	$2\sqrt{15}/15$
d^4	${}^1I$	${}^1G_1$	${}^1G_2$	${}^1F$	${}^1D_1$	${}^1D_2$	${}^1S_1$	${}^1S_2$
${}^5D$	0	0	0	0	0	0	0	0
${}^3H$	$-\sqrt{195}/10$	$-\sqrt{55}/5$	$2\sqrt{5}/5$	0	0	0	0	0
${}^3G$	0	$-\sqrt{30}/10$	$-\sqrt{330}/20$	$-3\sqrt{30}/20$	0	0	0	0
${}^3F_1$	0	$-\sqrt{10}/10$	$\sqrt{110}/10$	$-\sqrt{42}/6$	$\sqrt{30}/15$	$\sqrt{15}/15$	0	0

(contd.)

TABLE 8.44

Reduced matrix elements $\langle LS \| \mathbf{V}^{(11)} \| LS \rangle [\hbar^{-2}]$ by [1] (contd.)

d^4	^1I	$^1G_1$	$^1G_2$	^1F	$^1D_1$	$^1D_2$	$^1S_1$	$^1S_2$
$^3F_2$	0	$\sqrt{10}/2$	$-\sqrt{110}/20$	$-\sqrt{42}/12$	$2\sqrt{30}/15$	$-4\sqrt{15}/15$	0	0
^3D	0	0	0	$-\sqrt{6}/3$	$-2\sqrt{3}/3$	$+\sqrt{6}/6$	0	0
$^3P_1$	0	0	0	0	$-\sqrt{105}/30$	$\sqrt{210}/15$	$3\sqrt{10}/10$	$-\sqrt{210}/30$
$^3P_2$	0	0	0	0	$\sqrt{30}/15$	$\sqrt{15}/30$	0	$2\sqrt{15}/15$
^1I	0	0	0	0	0	0	0	0
$^1G_1$	0	0	0	0	0	0	0	0
$^1G_2$	0	0	0	0	0	0	0	0
^1F	0	0	0	0	0	0	0	0
$^1D_1$	0	0	0	0	0	0	0	0
$^1D_2$	0	0	0	0	0	0	0	0
$^1S_1$	0	0	0	0	0	0	0	0
$^1S_2$	0	0	0	0	0	0	0	0
d^3	^4F	^4P	^2H	^2G	^2F	$^2D_1$	$^2D_2$	^2P
^4F	$\sqrt{42}/3$	0	0	$-\sqrt{3}$	$+\sqrt{105}/15$	$-\sqrt{35}/5$	$\sqrt{15}/3$	0
^4P	0	$\sqrt{3}/3$	0	0	0	$-2\sqrt{10}/5$	0	$+2\sqrt{105}/15$
^2H	0	0	$\sqrt{66}/10$	$-\sqrt{66}/5$	0	0	0	0
^2G	$-\sqrt{3}$	0	$+\sqrt{66}/5$	$9/10$	$+\sqrt{3}/2$	0	0	0
^2F	$-\sqrt{105}/15$	0	0	$-\sqrt{3}/2$	$-\sqrt{105}/30$	$-\sqrt{35}/5$	$-\sqrt{15}/15$	0
$^2D_1$	$-\sqrt{35}/5$	$-2\sqrt{10}/5$	0	0	$+\sqrt{35}/5$	$\sqrt{6}/4$	$-\sqrt{14}/4$	$+\sqrt{35}/10$
$^2D_2$	$\sqrt{15}/3$	0	0	0	$+\sqrt{15}/15$	$-\sqrt{14}/4$	$-\sqrt{6}/12$	$-3\sqrt{15}/10$
^2P	0	$-2\sqrt{105}/15$	0	0	0	$-\sqrt{35}/10$	$+3\sqrt{15}/10$	$\sqrt{30}/15$
d^2	^3F	^3P	^1G	^1D	^1S			
^3F	$\sqrt{105}/5$	0	$-3\sqrt{10}/10$	$\sqrt{30}/5$	0			
^3P	0	$\sqrt{30}/10$	0	$-\sqrt{105}/10$	$\sqrt{15}/5$			
^1G	$-3\sqrt{10}/10$	0	0	0	0			
^1D	$\sqrt{30}/5$	$-\sqrt{105}/10$	0	0	0			
^1S	0	$\sqrt{15}/5$	0	0	0			

where we have checked a result of Table 8.44. We proceed in the evaluation with $J = 5/2$ as follows

$$\begin{aligned}
 \left\langle SLJ \left| \sum_{i=1}^n \vec{s}_i \cdot \vec{l}_i \right| S' L' J \right\rangle &= (-1)^{J+L+S'} [l(l+1)(2l+1)]^{1/2} \begin{Bmatrix} L & L' & 1 \\ S' & S & J \end{Bmatrix} \\
 &\times \left\langle SL \parallel \mathbf{V}^{(11)} \parallel S' L' \right\rangle \\
 &= (-1)^{5/2+0+3/2} \cdot [2 \cdot 3 \cdot 5]^{1/2} \\
 &\quad \cdot \begin{Bmatrix} 0 & 1 & 1 \\ 3/2 & 5/2 & 5/2 \end{Bmatrix} \cdot \sqrt{3} \\
 &= \sqrt{30} \cdot \left(-\frac{1}{\sqrt{18}} \right) \cdot \sqrt{3} = -\sqrt{5}
 \end{aligned}$$

Finally, it is found that

$$\left\langle d^5, {}^6S_{5/2} \left| \hat{H}^{\text{so}} \right| d^5, {}^4P_{5/2} \right\rangle = -\sqrt{5}\xi_{3d}$$

A direct consequence is that in a free atom some terms are interconnected (interacting) via the spin-orbit coupling, e.g.

$$\left\langle d^5, {}^6S_{5/2} \left| \hat{H}^{\text{so}} \right| d^5, {}^4P_{5/2} \right\rangle = -\sqrt{5}\xi_{3d}$$

This means that the ground state $|{}^6S_{5/2}\rangle$ contains an admixture of the excited term $|{}^4P_{5/2}\rangle$ which, using second-order perturbation theory, becomes

$$|{}^6S_{5/2}\rangle' = |{}^6S_{5/2}\rangle + \left(\frac{(-\sqrt{5}\xi_{3d})}{E({}^6S_{5/2}) - E({}^4P_{5/2})} \right) |{}^4P_{5/2}\rangle$$

8.5.14 A magneto-theoretical hierarchy

We have seen that mononuclear complexes, with or without the first-order angular momentum, can be theoretically treated in different degrees of complexity. Thus we can speak of some magneto-theoretical hierarchy (Table 8.45). Depending on the basic postulate about the extent of the active space (a space of kets involved in the zero-order Hamiltonian), various levels of the theory can be distinguished.

TABLE 8.45
Magneto-theoretical hierarchy

Level	Description	Active space	Free parameters	Magnetic parameters
7		All terms of $f^k d^n s^m p^l$	$\xi_d, \xi_f, \dots$	
6	König and Kremer [43–46]	All terms of d^n	ξ_d, Dq (or $D_s, D_t, \dots$)	$\overline{\overline{\Delta g}} = 0$ $\overline{\overline{\kappa}}^{\text{para}} = 0$ $\overline{\overline{D}} = 0$
5	Figgis et al. [36–39]	Limited CI, kets of lowered symmetry	$\lambda, A, \kappa, \Delta$ (or v)	$\overline{\overline{\Delta g}} = 0$ $\overline{\overline{\kappa}}^{\text{para}} \neq 0$
4	Figgis [5]	Limited CI	λ, A, κ	$\overline{\overline{\Delta g}} = 0$ $\overline{\overline{\kappa}}^{\text{para}} \neq 0$
3	Kotani [47]	Ground term ^{2S+1}T , kets $ L, M_L, S, M_S\rangle$ or $ J, M\rangle$	λ, κ	$\overline{\overline{\Delta g}} = 0$ $\overline{\overline{\kappa}}^{\text{para}} \neq 0$
2	Zero-field splitting	Ground term ^mS , kets $ S, M_S\rangle$	$g_{aa}, D, E, (a, F),$ χ^{TIP} (or A_{aa})	$\overline{\overline{\Delta g}} \neq 0$ $\overline{\overline{\kappa}}^{\text{para}} \neq 0$ $\overline{\overline{D}} \neq 0$
1	Effective spin	Lowest Kramers doublet $ \tilde{S}, \pm 1/2\rangle$	g_{aa}^{eff}	$\overline{\overline{\Delta g}} \neq 0$ $\overline{\overline{\kappa}}^{\text{para}} \neq 0$

The second-order “energy” correction arising from the excited states (out of the active space) is given by the standard formula of perturbation theory

$$\begin{aligned}
 \hat{H}^{(2)} &= - \sum_{K \neq 0} \frac{\langle 0 | \hat{H}' | K \rangle \langle K | \hat{H}' | 0 \rangle}{E_K - E_0} \\
 &= - \sum_{K \neq 0} \frac{[(\mu_B \vec{B} + \lambda \vec{S}[\hbar^{-1}]) \cdot \langle 0 | \vec{L} | K \rangle][(\mu_B \vec{B} + \lambda \vec{S}[\hbar^{-1}]) \cdot \langle K | \vec{L} | 0 \rangle]}{E_K - E_0} \\
 &\quad \times [\hbar^{-2}]
 \end{aligned}$$

With the help of the A -tensor

$$A_{ab} = - \sum_{K \neq 0} \frac{\langle 0 | \hat{L}_a | K \rangle \langle K | \hat{L}_b | 0 \rangle}{E_K - E_0} [\hbar^{-2}]$$

we can write the spin Hamiltonian in the form

$$\hat{H}^S = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} [\hbar^{-1}] - \frac{1}{2} \vec{S} \cdot \vec{D} \cdot \vec{S} [\hbar^{-2}] - \frac{1}{2} \vec{B} \cdot \vec{\kappa} \cdot \vec{B}$$

where the magnetic parameters (tensors) appear

$$g_{ab} = g_e \delta_{ab} + 2\lambda A_{ab}, \quad [\text{dimensionless}]$$

$$-\frac{1}{2} D_{ab} = \lambda^2 A_{ab}, \quad [\text{energy}]$$

$$-\frac{1}{2} \kappa_{ab}^{\text{para}} = \mu_B^2 A_{ab}, \quad [\text{energy} \cdot \text{induction}^{-2}]$$

In the most complete treatment (like the theory of König and Kremer [43–46]) there is almost nothing to be included by perturbation theory, except the Zeeman term. Therefore the differential g -tensor, the temperature-independent paramagnetic tensor and the spin–spin interaction tensor are blank: $\overline{\Delta g} = 0$, $\overline{\kappa}^{\text{para}} = 0$, $\overline{D} = 0$. Only higher excited kets can bring some contribution which is, however, assumed negligible since the energy denominator is then large

$$A_{ab} \approx (E_n - E_0)^{-1} \approx 0$$

In contrast, when the active space is restricted to the spin-only kets, the influence of all attainable excited states manifests itself in filling the magnetic parameters (tensors). In such a case the g -tensor deviates considerably from the free-electron value, the temperature-independent paramagnetism appears substantial and the spin–spin interaction tensor transforms to high values of the zero-field splitting parameters (D and E).

A direct comparison of the “magneto-chemical” g -values with the spectral ESR readings may make a little sense. This can work only when the effective spin approach is of use, or for systems where a Kramers doublet is the only relevant active space (like Cu^{2+} and V^{4+} complexes).

8.5.15 Magnetic field influence

According to König and Kremer [44], the magnitude of the magnetic field has an influence on the magnetic susceptibility and consequently on the effective magnetic moment at low temperature. This applies for A -terms, such as ${}^6A_{1g}$ for Mn(II) complexes, as well as for T -terms, such as ${}^4T_{1g}$ for Co(II) complexes.

Fig. 8.29 shows that the effective magnetic moment for the ${}^4T_{1g}$ term tends to decrease rapidly on cooling with the ramping field. At an intermediate field of $B = 5$ T the onset of the decrease appears at ca $T = 20$ K; thus the effect is well pronounced. The data in this figure have been generated on the basis of the mean magnetic susceptibility which is simply the ratio $\bar{\chi} = \mu_0 M/B$; the mean susceptibility has been obtained by a “polynomial fit formula” for eigenvalues (Chapter 6) with the subsequent application of the van Vleck formula. This, in fact, is equivalent to the original “finite difference formula” of König and Kremer [44].

It should be noted that the interpretation of the decrease of the effective magnetic moment at low temperature as an “intermolecular antiferromagnetic interaction”, giving rise to the negative Weiss constant Θ within the Curie–Weiss law, can be an artefact of mistaken ignorance of the non-linear magnetic behaviour.

The field dependence of the magnetisation is better described by applying the “polynomial magnetisation formula”: the M versus B function is fitted to a quadratic equation

$$M(B) = d^{(0)} + d^{(1)}B + d^{(2)}B^2$$

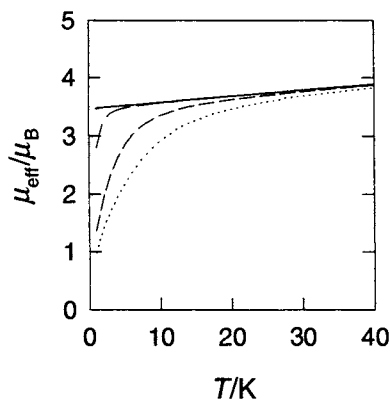


Fig. 8.29. Effective magnetic moment based on mean magnetic susceptibility versus temperature for the ${}^4T_{1g}$ term at different magnetic fields: $B = 0.001$ T (solid), $B = 1$ T (long dashed), $B = 5$ T (medium dashed), $B = 10$ T (dotted).

from which the expansion coefficients $d^{(0)}$, $d^{(1)}$ and $d^{(2)}$ result. These are displayed in Fig. 8.30. The important findings follow:

- (1) the magnitude of the magnetisation increases with the magnetic field;
- (2) its first derivative, which is proportional to the differential susceptibility

$$\tilde{\chi} = \mu_0 \frac{\partial M}{\partial B} = \mu_0 d^{(1)}$$

starts from zero, passes through a maximum and then escapes continuously; the higher the applied field, the lower the differential susceptibility; its maximum is shifted to higher temperature with the increasing field.

Evidently, the differential susceptibility deviates considerably from the Curie law at low temperature and a higher field.

The mean and differential magnetic susceptibilities are compared in Fig. 8.31. Their difference becomes dramatic at low temperature: the differential susceptibility approaches zero whereas the mean susceptibility retains a non-zero value. It is worth noting that at $T = 4.2$ K the difference may already be substantial.

Even more surprising is the difference between the effective magnetic moments when generated from the mean and/or differential magnetic susceptibilities (Fig. 8.32). This implies a conclusion that dealing with the mean magnetic susceptibilities at low temperature is, in principle, incorrect. The mean magnetic susceptibility is apparently a wrong approximation to the differential magnetic susceptibility; the latter represents a true thermodynamic quantity and, when taken at constant temperature, it becomes the isothermal magnetic susceptibility

$$\tilde{\chi} = \mu_0 \left(\frac{\partial M}{\partial B} \right)_T = \chi_T$$

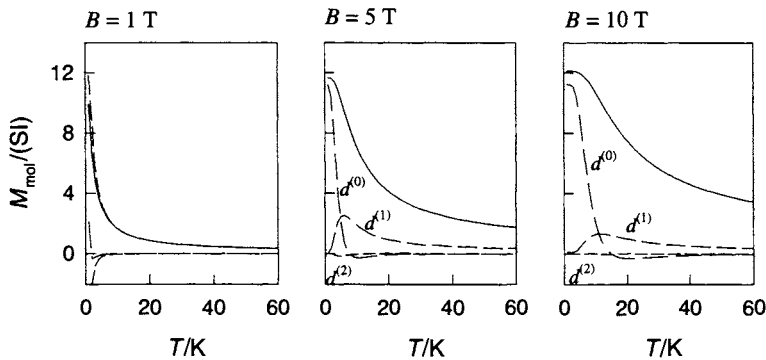


Fig. 8.30. Temperature dependence of magnetisation and its expansion coefficients for the ${}^4T_{1g}$ term at different magnetic fields.

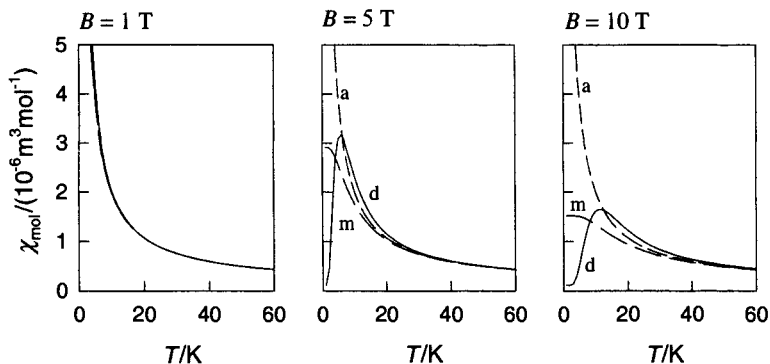


Fig. 8.31. Temperature dependence of magnetic susceptibilities for the ${}^4T_{1g}$ term at different applied fields: m—mean magnetic susceptibility; d—differential magnetic susceptibility (solid); a—approximate magnetic susceptibility based on the van Vleck equation.

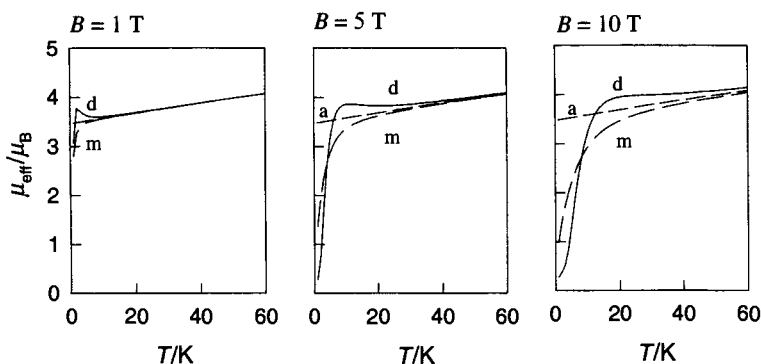


Fig. 8.32. Temperature dependence of effective magnetic moments for the ${}^4T_{1g}$ term at different applied fields: m—based on the mean magnetic susceptibility; d—based on the differential magnetic susceptibility (solid); a—based on the approximate magnetic susceptibility via the van Vleck equation.

8.6 OTHER INTERACTIONS IN MONONUCLEAR SYSTEMS

8.6.1 Spin-admixed states

In Section 8.5.13 we have seen that the matrix elements of the spin-orbit coupling can interconnect certain atomic terms. In real metal complexes, however, the matrix elements of the spin-orbit coupling operator have to be evaluated between the strong-field kets. In the crystal field of cubic (O_h) symmetry the following reduction applies

$$|3d^5, {}^6S\rangle \xrightarrow{R_3 \rightarrow O_h} |t_2^3 e^2, {}^6A_1\rangle \xrightarrow{O_h \rightarrow D_4} |b_2^1 e^2 a_1^1 b_1^1, {}^6A_1\rangle$$

$$|3d^5, {}^4P\rangle \xrightarrow{R_3 \rightarrow O_h} |t_2^4 e^1, {}^4T_1\rangle \xrightarrow{O_h \rightarrow D_4} |b_2^2 e^2 a_1^1 b_1^0, {}^4A_2\rangle$$

and it continues when the octahedron is axially distorted.

For the subsequent expression we need to introduce:

- (1) coupling coefficients within the (non-spherical) point group;
- (2) coefficients of fractional parentage;
- (3) reduced matrix elements of the tensor (double-tensor) operators.

The *coupling coefficients* $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma \rangle$ are introduced as members of the unitary matrix that transforms the uncoupled kets $|\Gamma_1 \gamma_1\rangle$ and $|\Gamma_2 \gamma_2\rangle$, belonging to the γ_i th component of the irreducible representation Γ_i , to the kets $|\Gamma \gamma\rangle$; hence

$$|\Gamma \gamma\rangle = \sum_{\gamma_1} \sum_{\gamma_2} \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma \rangle \cdot |\Gamma_1 \gamma_1\rangle |\Gamma_2 \gamma_2\rangle$$

or

$$|(\Gamma_1 \Gamma_2) \Gamma \gamma b\rangle = \sum_{\gamma_1} \sum_{\gamma_2} \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b \rangle \cdot |\Gamma_1 \gamma_1\rangle |\Gamma_2 \gamma_2\rangle$$

In this sense the coupling coefficients are the analogues of the Clebsch-Gordan coefficients (applicable to coupling of the angular momenta functions in free atoms belonging to the symmetry group $\mathbf{R}_3$). The index b is required only if the resulting representation Γ occurs more than once in the direct product

$$\Gamma_1 \otimes \Gamma_2 = \sum_i n_i \Gamma_i = \Gamma + \dots$$

The last condition is necessary for the non-vanishing coupling coefficient, i.e. Γ should be contained in the direct product of Γ_1 and Γ_2 .

The coupling coefficients are closely related to the *Griffith V-coefficients* [48]

$$V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix} = (d_{\Gamma_3})^{-1/2} \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma_3 \gamma_3 \rangle$$

with d_{Γ_3} representing the dimension of the irreducible representation Γ_3 . For the spin variable the $\bar{V}$ -coefficients are introduced via

$$\langle K k S' M' | S M \rangle = (-1)^{2S' - S - M} (2S + 1)^{1/2} \bar{V} \begin{pmatrix} K & S' & S \\ k & M' & -M \end{pmatrix}$$

They differ from the usual $3j$ -symbols by a phase factor, e.g.

$$\bar{V} \begin{pmatrix} S & S' & 1 \\ -M & M' & k \end{pmatrix} = (-1)^{S+S'+1} \begin{pmatrix} S & S' & 1 \\ -M & M' & k \end{pmatrix}$$

The V -coefficients and $\bar{V}$ -coefficients are constituents of more complex entities such as the W -coefficients, X -coefficients, $\bar{W}$ -coefficients and $\bar{X}$ -coefficients [48] which, in fact, are analogues of the $6j$ - and $9j$ -symbols. (Important note: one should deal with the coupling coefficients and the related symbols consistently from a single source since different phase choice and eventually different constant factor conventions exist.)

The basic expressions for the matrix elements of the spin-orbit coupling operator have been derived by Griffith [48]. A double tensor operator is $\hat{X}_{M\gamma}^{SF}$ where, for fixed γ and varying M , $\hat{X}_{M\gamma}^{SF}$ is an irreducible tensor operator with respect to spin variables. Similarly, for fixed S and varying γ , $\hat{X}_{M\gamma}^{SF}$ is an irreducible tensor operator with respect to space variables. A matrix element of a double tensor operator is now reduced as follows

$$\begin{aligned} \langle \Gamma \gamma S M | \hat{X}_{kg}^{KG} | \Gamma' \gamma' S' M' \rangle &= \langle \Gamma S || \hat{X}^{KG} || \Gamma' S' \rangle (-1)^{S-M} \\ &\times \bar{V} \begin{pmatrix} S & S' & K \\ -M & M' & k \end{pmatrix} \cdot V \begin{pmatrix} \Gamma & \Gamma' & G \\ \gamma & \gamma' & g \end{pmatrix} \end{aligned}$$

The coupling coefficients (V - and W -coefficients) of the double group $\mathbf{G}' = \mathbf{SU}(2) \otimes \mathbf{G}$ are simply products of $\bar{V}$ and $\bar{W}$ for the spinor group $\mathbf{SU}(2)$ with V and W for the point group $\mathbf{G}$. The matrix elements of the spin-orbit coupling operator become expressed as

$$\begin{aligned} \langle \Gamma \gamma S M | \hat{H}^{so} | \Gamma' \gamma' S' M' \rangle &= \left\langle \Gamma S \left\| \sum_{j=1}^n \vec{s}_j \cdot \vec{u}_j \right\| \Gamma' S' \right\rangle \\ &\times \sum_{k=-1}^{+1} [-1]^\Gamma [-1]^{\gamma'} (-1)^{k+1+S-M} \cdot \bar{V} \begin{pmatrix} S & S' & 1 \\ -M & M' & k \end{pmatrix} \cdot V \begin{pmatrix} \Gamma & \Gamma' & T_1 \\ -\gamma & \gamma' & -k \end{pmatrix} \end{aligned}$$

with the spatial variable

$$\vec{u}_j = \xi(r) \vec{l}_j$$

and the index k labels the components of the irreducible representation T_1 . There is a special symbol with the following meaning:

$$[-1]^{A_1} = [-1]^{A_2} = [-1]^E = +1$$

$$[-1]^{T_1} = [-1]^{T_2} = -1$$

$[-1]^\gamma = +1$, when γ is a component of A_1, A_2, E or T_2

$[-1]^\gamma = -1$, when γ is a component of T_1

The specific expressions for the reduced matrix elements depend on the electron configurations:

$$(a) \langle a^n \Gamma S \| \hat{H}^{so} \| a^n \Gamma' S' \rangle$$

$$(b) \langle a^n \Gamma S \| \hat{H}^{so} \| a^{n-1}(\Gamma_1 S_1) b \Gamma' S' \rangle$$

$$(c) \langle a^m(\Gamma_1 S_1) b^n(\Gamma_2 S_2) \Gamma S \| \hat{H}^{so} \| a^m(\Gamma'_1 S'_1) b^n(\Gamma'_2 S'_2) \Gamma' S' \rangle$$

$$(d) \langle a^m(\Gamma_1 S_1) b^{n-1}(\Gamma_2 S_2) \Gamma S \| \hat{H}^{so} \| a^{m-1}(\Gamma'_1 S'_1) b^n(\Gamma'_2 S'_2) \Gamma' S' \rangle$$

The individual formulae together with accompanying coefficients have been prepared by Griffith [48]; they were applied by Weissbluth [49] to Fe(III) systems in O_h symmetry. For instance

$$\begin{aligned} & \langle t_2^m(\Gamma_1 S_1) e^n(\Gamma_2 S_2) \Gamma S | \hat{H}^{so} | t_2^m(\Gamma'_1 S'_1) e^n(\Gamma'_2 S'_2) \Gamma' S' \rangle \\ &= (-1)^{S_1+S_2+\Gamma_1+\Gamma_2} (2S+1)^{1/2} (2S'+1)^{1/2} (d_r)^{1/2} (d_{r'})^{1/2} (-1)^{S'+\Gamma'} \\ & \quad \times \delta_{S_2, S'_2} \delta_{\Gamma_2, \Gamma'_2} \overline{W} \begin{pmatrix} S'_1 & S_1 & 1 \\ S & S' & S_2 \end{pmatrix} \cdot W \begin{pmatrix} \Gamma'_1 & \Gamma_1 & T_1 \\ \gamma & \gamma' & \gamma_2 \end{pmatrix} \\ & \quad \times G_n(S_1 \Gamma_1, S'_1 \Gamma') \cdot \langle 1/2, t_2 \| su \| 1/2, t_2 \rangle \end{aligned}$$

and

$$\begin{aligned} & \langle t_2^{m-1}(\Gamma_1 S_1) e^n(\Gamma_2 S_2) \Gamma S | \hat{H}^{so} | t_2^m(\Gamma'_1 S'_1) e^{n-1}(\Gamma'_2 S'_2) \Gamma' S' \rangle \\ &= (-1)^{S_1-S'_1-S_2+S'_2+\Gamma_1+\Gamma'_1+\Gamma_2+\Gamma'_2} \\ & \quad \times [mn(2S+1)(2S'+1)(2S'_1+1)(2S_2+1)(d_r)(d_{r'})(d_{r'_1})(d_{r'_2})]^{1/2} \\ & \quad \times \langle t_2^{m-1}(\Gamma_1 S_1), t_2 | \rangle \langle t_2^m \Gamma'_1 S'_1 \rangle \cdot \langle e^n(\Gamma_2 S_2) | \{e, e^{n-1}(\Gamma'_2 S'_2)\} \\ & \quad \times \overline{X} \begin{bmatrix} S_1 & S_2 & S \\ S'_1 & S'_2 & S' \\ 1/2 & 1/2 & 1 \end{bmatrix} \cdot X \begin{bmatrix} \Gamma_1 & \Gamma_2 & \Gamma \\ \Gamma'_1 & \Gamma'_2 & \Gamma' \\ t_2 & e & T_1 \end{bmatrix} \cdot \langle 1/2, e \| su \| 1/2, t_2 \rangle \end{aligned}$$

The matrix elements of the spin-orbit coupling within the manifold of states spanned by ${}^6A_1$ (six states) and ${}^4T_1$ (twelve states) fill an 18×18 matrix which can be rearranged into a block-diagonal form: there are two blocks 4×4 and two blocks 5×5 (Table 8.46).

TABLE 8.46

Matrix elements of the spin-orbit coupling among components of ${}^6A_1$ and ${}^4T_1$

Γ, M, γ	${}^6A_1, \pm 1/2, a_1$	${}^4T_1, \pm 1/2, 0$	${}^4T_1, \mp 1/2, \pm 1$	${}^4T_1, \pm 3/2, \mp 1$
${}^6A_1, \pm 1/2, a_1$	0	$-\sqrt{6/5}\xi$	$-\sqrt{3/5}\xi$	$-\sqrt{1/5}\xi$
${}^4T_1, \pm 1/2, 0$	$-\sqrt{6/5}\xi$	0	$-\sqrt{1/18}\xi$	$-\sqrt{1/24}\xi$
${}^4T_1, \mp 1/2, \pm 1$	$-\sqrt{3/5}\xi$	$-\sqrt{1/18}\xi$	$(1/12)\xi$	0
${}^4T_1, \pm 3/2, \mp 1$	$-\sqrt{1/5}\xi$	$-\sqrt{1/24}\xi$	0	$(1/4)\xi$

	${}^6A_1, \pm 5/2, a_1$	${}^6A_1, \mp 3/2, a_1$	${}^4T_1, \mp 3/2, 0$	${}^4T_1, \pm 3/2, \pm 1$	${}^4T_1, \mp 1/2, \mp 1$
${}^6A_1, \pm 5/2, a_1$	0	0	0	$-\sqrt{2}\xi$	0
${}^6A_1, \mp 3/2, a_1$	0	0	$-\sqrt{4/5}\xi$	0	$-\sqrt{6/5}\xi$
${}^4T_1, \mp 3/2, 0$	0	$-\sqrt{4/5}\xi$	0	0	$-\sqrt{1/24}\xi$
${}^4T_1, \pm 3/2, \pm 1$	$-\sqrt{2}\xi$	0	0	$-(1/4)\xi$	0
${}^4T_1, \mp 1/2, \mp 1$	0	$-\sqrt{6/5}\xi$	$-\sqrt{1/24}\xi$	0	$-(1/12)\xi$

After diagonalisation of the spin-orbit coupling matrices the set of the six lowest eigenvalues appears to be degenerate: the spin admixture of the excited ${}^4T_1$ term into the ground term ${}^6A_1$ uniformly shifts the energy levels and no removal of degeneracy is obtained. The application of second-order perturbation theory yields the same result, hence

$$E({}^6A_1, \pm 1/2, a_1) = -\frac{(6/5)\xi^2}{\Delta} - \frac{(3/5)\xi^2}{\Delta} - \frac{(1/5)\xi^2}{\Delta} = -\frac{2\xi^2}{\Delta}$$

$$E({}^6A_1, \pm 3/2, a_1) = -\frac{(4/5)\xi^2}{\Delta} - \frac{(6/5)\xi^2}{\Delta} = -\frac{2\xi^2}{\Delta}$$

$$E({}^6A_1, \pm 5/2, a_1) = -\frac{2\xi^2}{\Delta}$$

where the energy gap of the terms is

$$\Delta = E({}^4T_1) - E({}^6A_1)$$

When the cubic symmetry is reduced to tetragonal, the ${}^4T_1$ term is decomposed into ${}^4A_2$ and ${}^4E$; the components obey the following assignment

$$-i|{}^4T_1 0\rangle = |{}^4T_1 z\rangle \xrightarrow{\mathbf{O} \rightarrow \mathbf{D}_4} |{}^4A_2\rangle$$

Now, the application of second-order perturbation theory yields

$$E(^6A_1, \pm 1/2, a_1) = -\frac{(6/5)\xi^2}{\Delta} = -6D$$

$$E(^6A_1, \pm 3/2, a_1) = -\frac{(4/5)\xi^2}{\Delta} = -4D$$

$$E(^6A_1, \pm 5/2, a_1) = 0$$

where the energy gap

$$\Delta = E(^4T_1 0) - E(^6A_1) = E(^4A_2) - E(^6A_1)$$

is necessarily assumed to be large in absolute value. The result confirms the zero-field splitting with the axial splitting parameter $D = \xi^2/5\Delta$. For a small energy gap, however, perturbation theory is not applicable and one has to diagonalise the 10×10 zero-field matrix

$$\mathbf{H}^{\text{zf}} = \left(\begin{array}{ccccc|ccccc} 0 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ & 0 & \cdot & \cdot & \cdot & -\sqrt{4/5}\xi & \cdot & \cdot & \cdot & \cdot \\ & & 0 & \cdot & \cdot & \cdot & -\sqrt{6/5}\xi & \cdot & \cdot & \cdot \\ & & & 0 & \cdot & \cdot & \cdot & -\sqrt{6/5}\xi & \cdot & \cdot \\ & & & & 0 & \cdot & \cdot & \cdot & -\sqrt{4/5}\xi & \cdot \\ \hline & & & & & \Delta & \cdot & \cdot & \cdot & \cdot \\ & & & & & & \Delta & \cdot & \cdot & \cdot \\ & & & & & & & \Delta & \cdot & \cdot \\ & & & & & & & & \Delta & \cdot \\ & & & & & & & & & \Delta \end{array} \right)$$

This matrix is factorised

(a) for states $|\pm 1/2'\rangle = a|^6A_1, \pm 1/2\rangle + b|^4A_2, \pm 1/2\rangle$

$$\det \begin{pmatrix} -\varepsilon & -\sqrt{6/5}\xi \\ -\sqrt{6/5}\xi & \Delta - \varepsilon \end{pmatrix} = 0$$

(b) for states $|\pm 3/2'\rangle = a|^6A_1, \pm 3/2\rangle + b|^4A_2, \pm 3/2\rangle$

$$\det \begin{pmatrix} -\varepsilon & -\sqrt{4/5}\xi \\ -\sqrt{4/5}\xi & \Delta - \varepsilon \end{pmatrix} = 0$$

The resulting set of eigenvalues is

$$\begin{aligned}\varepsilon_{M=\pm 1/2} &= [\Delta \pm \sqrt{\Delta^2 + (24/5)\xi^2}]/2 \\ &= \xi[x \pm \sqrt{x^2 + (24/5)}]/2 \approx \Delta + 6D, \text{ or } -6D\end{aligned}$$

$$\begin{aligned}\varepsilon_{M=\pm 3/2} &= [\Delta \pm \sqrt{\Delta^2 + (16/5)\xi^2}]/2 \\ &= \xi[x \pm \sqrt{x^2 + (16/5)}]/2 \approx \Delta + 4D, \text{ or } -4D\end{aligned}$$

and

$$\varepsilon_{M=\pm 5/2} = 0$$

with

$$x = \Delta/\xi$$

These energy levels are plotted in Fig. 8.33. It can be seen that for sufficiently large argument $|x|$ the energy levels approach the zero-field splitting limit: the separation from the $|\pm 5/2\rangle$ state adopts values of either $4D$ or $6D$.

In the presence of the magnetic field the Zeeman matrices are added to the zero-field Hamiltonian matrix. As the z -component of the Zeeman interaction enters the diagonal, factorisation to the 2×2 secular equations is possible and from the analytical roots the identification of the van Vleck coefficients is possible

$$\varepsilon_{M=\pm 1/2} = \frac{1}{2} \left\{ [\Delta \pm (1/2)g_z\mu_B B] \pm \sqrt{[\Delta \pm (1/2)g_z\mu_B B]^2 + (24/5)\xi^2} \right\}$$

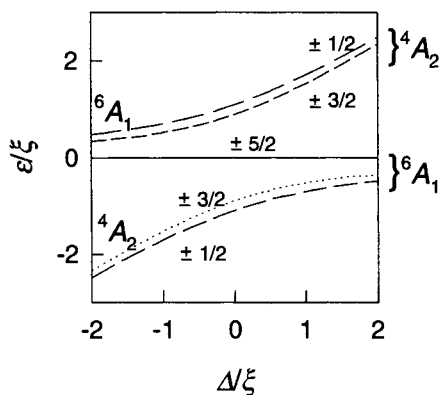


Fig. 8.33. Energy levels of a spin-admixed system ${}^6A_1 - {}^4A_2$ in the zero field.

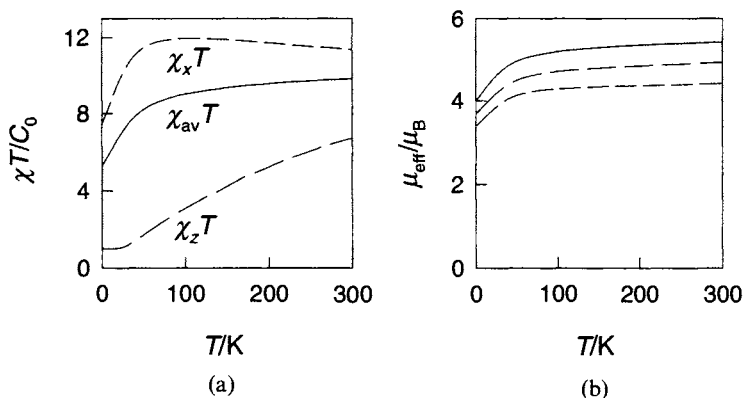


Fig. 8.34. Temperature variation of magnetic susceptibility functions (a) and effective magnetic moment (b) for the spin-admixed system ${}^6A_1 - {}^4A_2$, $\xi/hc = 460 \text{ cm}^{-1}$, $g_x = g_z = 2.0$: left—individual curves show magnetic anisotropy for $\Delta/hc = 500 \text{ cm}^{-1}$; right—different energy gap $\Delta/hc = +500 \text{ cm}^{-1}$ (solid), $\Delta/hc = 0$ (long dashed), $\Delta/hc = -500 \text{ cm}^{-1}$ (medium dashed).

$$\varepsilon_{M=\pm 3/2} = \frac{1}{2} \left\{ [\Delta \pm (3/2)g_z\mu_B B] \pm \sqrt{[\Delta \pm (3/2)g_z\mu_B B]^2 + (16/5)\xi^2} \right\}$$

and

$$\varepsilon_{M=\pm 5/2} = \pm (5/2)g_z\mu_B B$$

Consequently, the z-component of the magnetic susceptibility can be written in closed form. However, this is not the case of the parallel component where a numerical treatment is necessary; an application of the polynomial fit formula gave the data displayed in Fig. 8.34. It can be concluded that:

- a considerable magnetic anisotropy exists at high temperature;
- for the very positive energy gap the effective magnetic moment approaches the spin-only value of $\mu_{eff}/\mu_B = 5.92$ for five unpaired electrons; in such a case the ground term ${}^6A_1$ is little affected by an admixture from the excited ${}^4A_2$ term;
- for the negative energy gap the effective magnetic moment is reduced since then the ${}^4A_2$ state becomes the ground one; for the very negative energy gap the effective magnetic moment should approach the second limiting value of $\mu_{eff}/\mu_B = 3.87$ for three unpaired electrons.

8.6.2 Molecular field correction

The molecular field approximation assumes that the magnetoactive entity is under the influence of the external magnetic field as well as the internal

magnetic field characteristic for the substance. The internal (molecular) field acts against the external field and is given by the additional Hamiltonian term

$$\hat{H} = \hat{H}^Z - (zJ')\langle S_z \rangle \hat{S}_z [\hbar^{-1}]$$

where z is the number of nearest neighbours, J' is the intercentre coupling parameter. In the case of Curie paramagnets the energy levels become

$$\varepsilon(S, M_S) = M_S [\mu_B g B - (zJ')\langle S_z \rangle]$$

where the thermal (Boltzmann) average of the spin projection is

$$\begin{aligned} \langle S_z \rangle &= \frac{\sum_{M_S=-S}^S M_S \exp[-\varepsilon(S, M_S)/kT]}{\sum_{M_S=-S}^S \exp[-\varepsilon(S, M_S)/kT]} \\ &= \frac{\sum_{M_S=-S}^S M_S \exp\{-M_S [\mu_B g B - (zJ')\langle S_z \rangle]/kT\}}{\sum_{M_S=-S}^S \exp\{-M_S [\mu_B g B - (zJ')\langle S_z \rangle]/kT\}} \end{aligned}$$

Making use of the expansion of exponentials to the first order, well valid for small arguments, we get

$$\begin{aligned} \langle S_z \rangle &= \frac{\sum_{M_S=-S}^S M_S \{1 - M_S [\mu_B g B - (zJ')\langle S_z \rangle]/kT\}}{\sum_{M_S=-S}^S \{1 - M_S [\mu_B g B - (zJ')\langle S_z \rangle]/kT\}} \\ &= \frac{-[S(S+1)(2S+1)/3][\mu_B g B - (zJ')\langle S_z \rangle]/kT}{2S+1} \end{aligned}$$

After rearrangement

$$\langle S_z \rangle = -\frac{S(S+1)\mu_B g B}{3kT - (zJ')S(S+1)}$$

and the molar magnetisation becomes expressed as follows

$$M_{\text{mol}} = N_A \mu_B g \langle S_z \rangle = N_A \mu_B g \frac{S(S+1)\mu_B g B}{3kT - (zJ')S(S+1)}$$

Consequently the mean magnetic susceptibility is

$$\bar{\chi}_{\text{mol}} = \mu_0 \frac{M_{\text{mol}}}{B} = N_A \mu_0 \mu_B^2 g^2 \frac{S(S+1)}{3kT - (zJ')S(S+1)}$$

This formula can be rewritten in the form of the Curie–Weiss law

$$\bar{\chi}_{\text{mol}} = \frac{C}{T - \Theta}$$

with the Curie constant

$$C = \frac{N_A \mu_0 \mu_B^2 g^2 S(S+1)}{k} \frac{1}{3}$$

and the Weiss constant

$$\Theta = \frac{(zJ')S(S+1)}{3kT}$$

Usually (zJ') is considered as a single (molecular-field) parameter subjected to the fitting procedure.

SUMMARY

1. For Curie paramagnets non-linear behaviour is observed at low temperature and high fields, i.e. when the linear approximation to the Brillouin function is violated.
2. For systems with spin $S \geq 1$ the zero-field splitting of energy levels appears. These substances may exhibit a step increase of the magnetisation (the temperature should be low and the magnetic field high). Consequently the mean and differential magnetic susceptibilities differ substantially.
3. Transition metal centres with magnetic angular momentum, i.e. systems with ground T -terms, exhibit a complicated variance of magnetic susceptibility which is better visualised when the product function $(\chi_{\text{mol}}T)$ and/or the effective magnetic moment μ_{eff} is plotted versus the temperature. Its field dependence becomes pronounced with increasing magnetic field at low temperature.
4. A departure from cubic symmetry may generate a denser spacing of relevant, temperature-populated energy levels, and a non-linear magnetic response tends to be more pronounced.

5. Several levels of theory can be distinguished which more or less completely cover the active space of the state kets. When the active space is extended to all (relevant) terms of the given d^n electron configuration, then the magnetic parameters, i.e. the $\overline{\Delta g}$, $\overline{D}$ and $\overline{k}^{\text{para}}$ tensors, are blank. If the active space is more restricted, to only a few magnetic levels, the magnetic parameters become filled. Thus, in magnetochemistry no matching of g -factors with electron spin resonance readings is necessary: for a Co(II) system the magnetochemical g -values may be either close to the free-electron value of $g_e = 2.0023$ (when the active space is extended enough) or close to ESR values ($g_{\text{eff}} = 4 - 13$) when only a few magnetic levels are included in the active space.

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Spin Crossover Systems

9.1 IDENTIFICATION OF SPIN TRANSITION

9.1.1 General remarks

Several transition metal complexes, especially those with d^4 to d^7 metal ion configuration, can exist either in the low-spin (LS) or high-spin (HS) states. Exceptionally, they can exist also in an intermediate-spin (IS) state. When the high-spin state is the ground one, this is not altered by temperature variation. However, when the ground state is the low-spin, a spin transition to the high-spin state can occur. Whether the spin transition is observable within the accessible temperature interval depends upon the individual substance and its microscopic properties (electronic structure, vibration spectrum).

Substances in the low-spin and the high-spin states differ in a number of physical properties. Therefore the spin transition can be monitored by several techniques, as summarised in Table 9.1.

Spin crossover (SC) was observed for the first time by Cambi and Cagnasso [1]. This phenomenon was reviewed in a number of excellent reviews [2–7]. Because of its possible technological utilisation [8,9], spin crossover is widely studied at present. The usual induction of spin crossover is based on temperature variation but pressure and concentration variations may lead to the same effect. Recently, optical induction has been involved and such experiments were termed the LIESST (Light Induced Excited Spin State Trapping) and the reverse LIESST effects [7].

9.1.2 Determination of the high-spin mole fraction

A thermally induced spin transition is characterised by an $x_{\text{HS}} = f(T)$ curve with

$$x_{\text{HS}} = \frac{n_{\text{HS}}}{n_{\text{HS}} + n_{\text{LS}}}$$

representing the mole ratio of the HS molecules. Then $(1 - x_{\text{HS}}) = x_{\text{LS}}$ is the mole ratio of the LS molecules. The critical (transition) temperature T_c (or

TABLE 9.1

Experimental methods for monitoring the spin crossover

Experimental method	Monitored property	LS	HS
magnetic measurements	magnetic susceptibility, effective magnetic moment	low	high
calorimetric measurements	heat capacity	low	high
Mössbauer spectra	quadrupole splitting	low	high
X-ray diffraction	cell parameters, interatomic distances	low	high
nuclear magnetic resonance	paramagnetic shift, effective magnetic moment	low	high
volumetric measurements	partial molar volume	low	high
vibrational spectra	M–L stretching wavenumber	high	low
electron spin resonance	absorption, g-factor	no	yes
optical spectroscopy	excitation energy	low	high

$T_{1/2}$) is identified with a temperature at which $x_{\text{HS}} = x_{\text{LS}} = 1/2$. Various types of x_{HS} versus T curves have been observed in the solid state and can be classified as follows (Fig. 9.1):

- (1) abrupt transition occurring within a few K, or a gradual transition occurring within a large temperature interval;
- (2) complete transition at both a low ($x_{\text{HS}} = 0$) and a high temperature ($x_{\text{HS}} = 1$), or incomplete at a low temperature ($x_{\text{HS}} > 0$) or at a high temperature ($x_{\text{HS}} < 1$);
- (3) one-step or two-step transition;
- (4) transition without hysteresis or with the hysteresis effect (the critical temperature upon heating $T_c^\uparrow$ is higher than that upon cooling $T_c^\downarrow$).

Sometimes the transition curve depends upon the starting point of heating/cooling, rate of heating/cooling and the number of cycles of heating/cooling.

The construction of the x_{HS} versus T curve on the basis of magnetic susceptibility measurements is very simple. In the pure LS or HS state the product χT is a constant when the Curie law is obeyed (for pure LS Fe(II) systems this becomes zero if the corrections to underlying diamagnetism and temperature-independent paramagnetism were properly made). Thus the mole fraction of the HS state can be expressed as (Fig. 9.2)

$$x_{\text{HS}} = \frac{\chi T - (\chi T)_{\text{LS}}}{(\chi T)_{\text{HS}} - (\chi T)_{\text{LS}}}$$

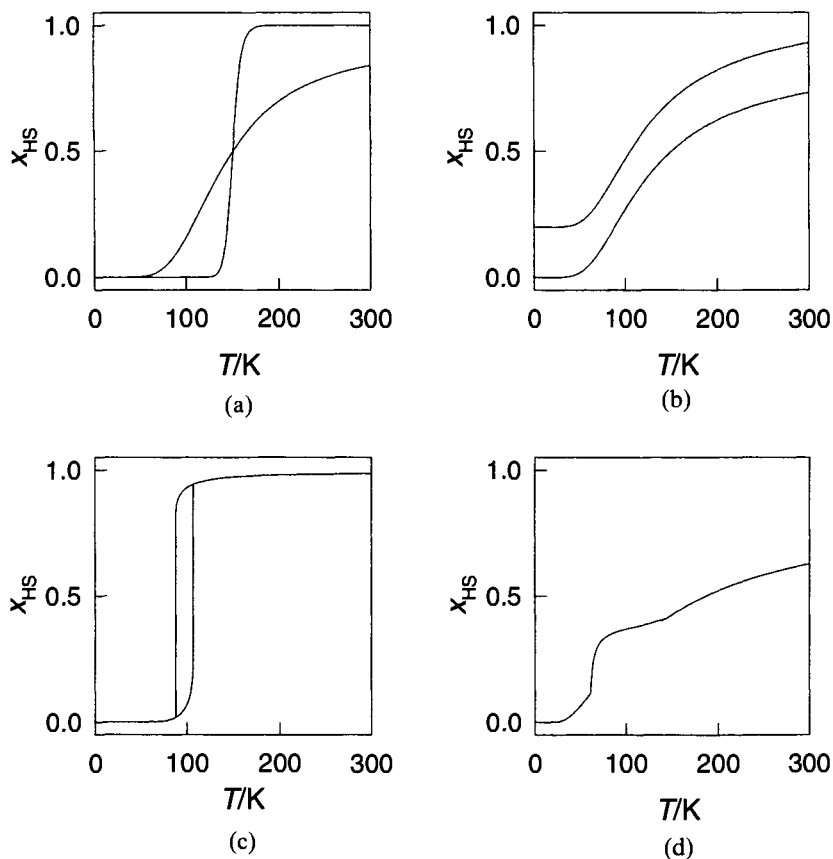


Fig. 9.1. Various types of spin transitions: (a) smooth or abrupt; (b) incomplete at low or high temperature; (c) with hysteresis on heating/cooling; (d) two-step spin transition.

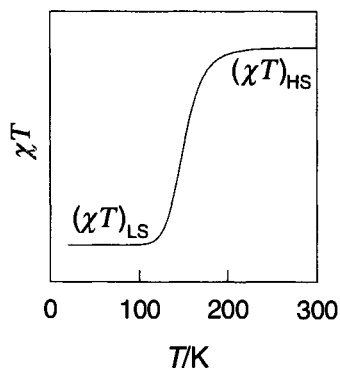


Fig. 9.2. Construction of the mole fraction x_{HS} on the basis of magnetic susceptibility data.

The Mössbauer spectra, particularly useful in the case of iron compounds, can be exploited for the construction of the x_{HS} versus T curve as well. They exhibit a characteristic quadrupole doublet for the HS state which is differently positioned (isomer shift) and possesses a different width (higher quadrupole splitting) when compared to the LS state (Fig. 9.3). Thus the area fraction of quadrupole splitting for the HS complex gives rise to

$$x_{\text{HS}} = \frac{A(\text{HS})}{A(\text{HS}) + A(\text{LS})}$$

A similar construction of the x_{HS} versus T curve is possible on the basis of infrared spectral data. The characteristic metal–ligand stretching wavenumbers appear at different regions (Fig. 9.4) and again the ratio of the area fraction yields x_{HS} .

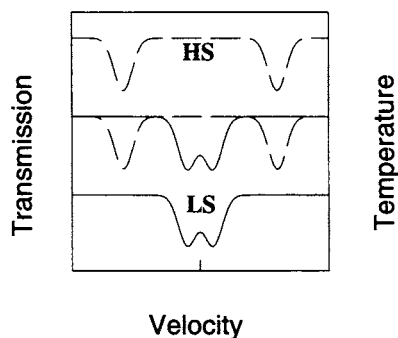


Fig. 9.3. Typical temperature evolution of Mössbauer spectra for a spin crossover system.

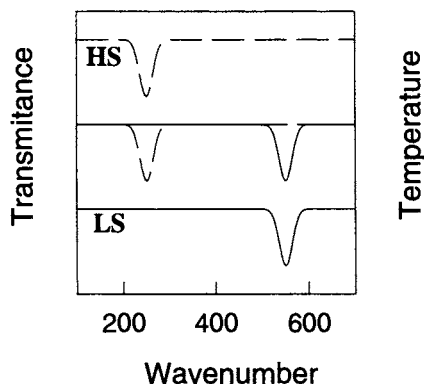


Fig. 9.4. Typical temperature evolution of infrared spectra for an SC system.

The electron spectroscopic transitions for the iron(II) LS state are $^1A_1 \rightarrow ^1T_1$ and $^1A_1 \rightarrow ^1T_2$, typically at 18 000 and 26 000 cm^{-1} , respectively. In contrast, the electron transition for the HS state is $^5T_2 \rightarrow ^5E$, typically at 12 000 cm^{-1} . Thus the area fractions of the absorption bands can be used in determining x_{HS} (Fig. 9.5).

In solutions, nuclear magnetic resonance is of use; from the ^1H paramagnetic shift ($\Delta\Delta\nu$) of a reference compound, corrected for the diamagnetic contribution of the ligands, the paramagnetic susceptibility is evaluable using the Evans method [10]

$$\chi_{\text{mol}} = 3K(\Delta\Delta\nu)/c$$

where c stands for the molar concentration of the paramagnetic ion. When the paramagnetic shift is given in ppm and the molar concentration through the molarity (mol dm^{-3}), then the conversion factor to SI units is $K = 10^{-9}$.

A temperature variation of the intensities of ESR signals can be exploited for the construction of the x_{HS} versus T curve, particularly for iron(III) and cobalt(II) compounds [11].

In the pure LS state of iron(II) the host lattice is diamagnetic and a suitable admixture, say Cu(II) centres, will possess a well-resolved ESR spectrum (with fine, hyperfine and eventually superhyperfine structures) [12]. When the system changes to the HS state, owing to the magnetic concentration of the host lattice, the ESR spectrum becomes poorly resolved. Such an effect can be used to identify the critical temperature.

One should take care of the fact that the iron(II) compounds are often accompanied by some impurity of iron(III) species and such an admixture can increase with sample handling and aging [13]. Therefore an “incompleteness” of the spin transition at low temperature may be a pure artefact originating in the admixture of the paramagnetic signal from the iron(III) centres.

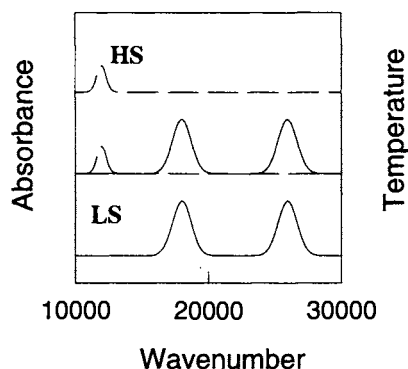


Fig. 9.5. Typical temperature evolution of electron spectra for an SC system.

9.1.3 Nature of the spin crossover

The total molecular energy of a system as a function of the nuclear coordinates (the adiabatic potential) exhibits different characteristics for the LS and HS states (Fig. 9.6).

The LS state is characterised by the adiabatic potential surface $E_{\text{LS}}(r)$ having a minimum $E_{0,\text{LS}}$ at a certain geometry (metal–ligand distances r_{LS}) with some definite curvature (the second derivative representing a force constant f_{LS}). Within this nearly parabolic function a set of vibration levels $e_{i,\text{LS}}$ occurs, the lowest one corresponding to the zero-point vibration, $e_{0,\text{LS}}$. The HS state differs in these characteristics in such a way that the relationships

$$E_{0,\text{LS}} < E_{0,\text{HS}}$$

$$r_{\text{LS}} < r_{\text{HS}}$$

$$f_{\text{LS}} > f_{\text{HS}}$$

are obeyed. Thus the enthalpy change for an LS to HS transition is

$$\Delta H_{\text{LH}}^0 = (E_{0,\text{HS}} + e_{0,\text{HS}}) - (E_{0,\text{LS}} + e_{0,\text{LS}}) > 0$$

The entropy change is expressed through the thermodynamic probability

$$\Delta S_{\text{LH}}^0 = k \ln g_{\text{HS}} - k \ln g_{\text{LS}} = k \ln \left(\frac{g_{\text{HS}}}{g_{\text{LS}}} \right) > 0$$

where the g_{HS} (g_{LS}) stands for the degeneracy of the HS (LS) state; thus ΔS_{LH}^0 is always positive. Then the Gibbs energy change

$$\Delta G_{\text{LH}} = \Delta H_{\text{LH}} - T \Delta S_{\text{LH}}$$

is positive below a certain temperature T_c and negative above it (Fig. 9.7).

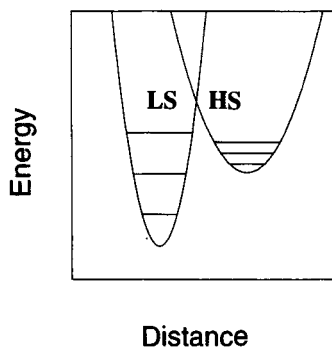


Fig. 9.6. Schematic drawing of the two adiabatic potential curves for LS and HS states

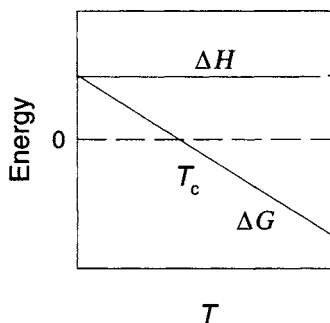


Fig. 9.7. Variation of the Gibbs energy and its increments with temperature for a spin crossover system.

Just at the transition temperature the following equation holds true

$$\Delta H_{\text{LH}} = T_c \Delta S_{\text{LH}}$$

The driving force for the LS to HS conversion is the drop of the Gibbs energy to a negative value above T_c . Whether the spin transition is observable or not depends upon the actual values of the enthalpy and entropy. Restricting ourselves to the spin-only value of the state degeneracy, we arrive at the expression

$$\Delta S_{\text{LH}}^0 = k \ln \left(\frac{2S_{\text{HS}} + 1}{2S_{\text{LS}} + 1} \right)$$

For the $S_{\text{LS}} = 0$ to $S_{\text{LS}} = 2$ transition, as an example, we get

$$\Delta S_{\text{LH}}^0/k = \ln 5 = 1.609$$

When also the orbital degeneracy is accounted for, then

$$\Delta S_{\text{LH}}^0 = k \ln \left[\frac{(2S_{\text{HS}} + 1)(2L_{\text{HS}} + 1)}{(2S_{\text{LS}} + 1)(2L_{\text{LS}} + 1)} \right]$$

and for the $^1A_{1g}$ to $^5T_{2g}$ transition this increases to

$$\Delta S_{\text{LH}}^0/k = \ln 15 = 2.708$$

The available experimental data for $\Delta S_{\text{LH}}^0/k$ range from 4.2 to 9.6 so that there are definitely some more contributions than pure electronic (spin and orbital) degeneracies. These may arise from the different vibration spectra of the respective LS and HS states. The adiabatic potential for the HS state is

flatter, the force constant higher, the vibration energies (wavenumbers) lower, which results in a higher vibration partition function Z for the HS state.

Having the entropy changes now roughly bracketed, we can estimate the required enthalpy changes to obtain the transition temperature in a physically accessible region (say, $4\text{ K} < T_c < 400\text{ K}$). A correspondence of the thermodynamic data is given in Table 9.2.

In terms of simple crystal field theory, the enthalpy change is predominantly due to a balance between the crystal field splitting energy Δ and the spin pairing energy E_p

$$\Delta H_{\text{LH}} \approx (\Delta - E_p)_{\text{HS}} - (\Delta - E_p)_{\text{LS}}$$

Although the crystal field splitting is available from spectroscopic series, the above relationship is not very useful because we have not at our disposal a straightforward way of estimating the spin pairing energy.

However, using good quality *ab initio* calculations (extended basis set, electron correlation included, some relativistic effects accounted for) appropriate partition functions can be generated; consequently, all the thermodynamic functions are evaluable (for an isolated pair of LS and HS molecules). Unfortunately, cooperativity effects in the solid (condensed) phase contribute to the thermodynamic functions and a proper estimation of such contributions is of extreme difficulty.

9.2 MODELS OF SPIN TRANSITION

9.2.1 *Non-interacting molecules*

In an assembly of N molecules there is a number $x_{\text{HS}}N$ of molecules in the HS state and the residual number $(1 - x_{\text{HS}})N$ of molecules in the LS state. The mixing entropy S_{mix} accounts for the fact that there are several ways of

TABLE 9.2
Interrelations of thermodynamic data for spin crossover

ΔS_{LH}	ΔH_{LH}	T_c
low	low	intermediate
low	high	high
high	low	low
high	high	intermediate

distributing the LS and HS molecules within the assembly of N molecules. Through statistical probability, this becomes

$$\begin{aligned} S_{\text{mix}} &= k \ln W = k \frac{N!}{(xN)![(1-x)N]!} \\ &= k\{N \ln N - xN \ln(xN) - (1-x)N \ln[(1-x)N]\} \\ &= -kN\{x \ln x + (1-x) \ln(1-x)\} \end{aligned}$$

where we apply the Stirling formula for the factorials and hereafter, for the sake of clarity, $x \equiv x_{\text{HS}}$. For one mole ($N = N_A$) of molecules the molar mixing entropy can be rewritten as

$$S_{\text{mix}} = -R\{x \ln x + (1-x) \ln(1-x)\}$$

($R = N_A k$ holds true, R is a perfect gas constant). The mixing entropy is maximum for $x = 0.5$ and zero in the limits of $x = 0$ and $x = 1$.

The molar Gibbs energy can be constructed from the following contributions

$$G = xG_{\text{HS}} + (1-x)G_{\text{LS}} - TS_{\text{mix}} + I$$

where the intermolecular interaction term I , in the first approximation, is neglected; G_{HS} and G_{LS} are the molar Gibbs energy for the HS and LS molecules. The condition for equilibrium demands

$$\left(\frac{\partial G}{\partial x}\right)_{T,p} = G_{\text{HS}} - G_{\text{LS}} + RT \ln\left(\frac{x}{1-x}\right) = 0$$

whence one gets

$$\ln\left(\frac{1-x}{x}\right) = \frac{\Delta G}{RT} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

The last equation can be rearranged in the form of

$$x = \frac{1}{1 + \exp[\Delta H/RT - \Delta S/R]} = \frac{1}{1 + \exp[(\Delta H/R)(1/T - \Delta S/\Delta H)]}$$

Since at $x = 0.5$ the Gibbs energy becomes zero, the transition temperature fulfils the relationship

$$T_c = \Delta H/\Delta S$$

so that another expression for the mole ratio of the HS molecules results

$$x = \frac{1}{1 + \exp[(\Delta H/R)(1/T - 1/T_c)]}$$

A representative plot of such a function is shown in Fig. 9.8.

The model predicts that at $T = 0$ all the molecules are in the LS state. On the other hand, the high temperature limit predicts an incomplete transition with $x < 1$. The transformation curve is fairly smooth through a broad temperature interval. Such a situation can be seen in solutions where the mechanism of spin conversion is mainly of the molecular character with loss of cooperativity.

9.2.2 Domain model

An attempt to include some cooperativity effects into the model of a spin transition was made with the domain model [14]. This model assumes that the HS and LS molecules form a number D of domains (units) of like spin. The number of molecules per domain is $n = N/D$ if the domains have a uniform size. Then the mixing entropy is

$$\begin{aligned} S_{\text{mix}} &= k \frac{D!}{(xD)![(1-x)D]!} \\ &= k\{D \ln D - xD \ln(xD) - (1-x)D \ln[(1-x)D]\} \\ &= -kD\{x \ln x + (1-x) \ln(1-x)\} \end{aligned}$$

and the molar mixing entropy becomes

$$S_{\text{mix}} = -(R/n)\{x \ln x + (1-x) \ln(1-x)\}$$

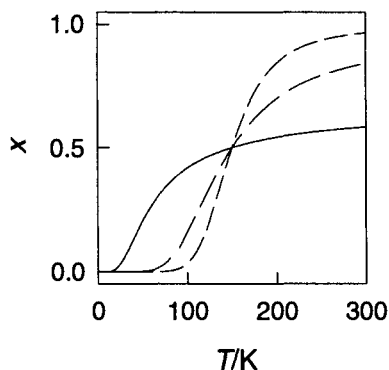


Fig. 9.8. High-spin mole fraction x versus T for non-interacting assembly of molecules; $T_c = 150$ K; $\Delta H/R = 100$ K (short dashed), 500 K (long dashed) and 1000 K (solid).

This expression, when substituted for $(\partial G/\partial x)_{T,p} = 0$, implies that

$$x = \frac{1}{1 + \exp[(n\Delta H/R)(1/T - 1/T_c)]}$$

The main goal of this model lies in the fact that the x versus T curve shows increasing abruptness with an increasing number of particles per domain n (Fig. 9.9). In the high temperature limit a complete transformation is predicted.

The spin transition can be viewed as a unimolecular reaction with the equilibrium constant

$$K_{\text{eq}} = \frac{x}{1-x} = \exp[-n\Delta H/RT + n\Delta S/R]$$

Then from the linear Arrhenius plot of $\ln K_{\text{eq}}$ versus $(1/T)$ the values of $(n\Delta H/R)$ and $(n\Delta S/R)$ are available. When the enthalpy of the transition is known from independent calorimetric measurements, then the average number of molecules per domain can be enumerated.

The domain model is partly successful also in the interpretation of calorimetric measurements: the C_p versus T curve, which is λ -shaped near T_c [9]. It is not capable of accounting for the hysteresis effect when the domains remain uniformly clustered. However, when the sizes of domains in the heating and cooling directions are different, then the hysteresis appears.

9.2.3 Regular solution model

The (regular) solution model assumes that the interaction energy responsible for the cooperative effects is given by the formula [15]

$$I(x) = \gamma x(1-x)$$

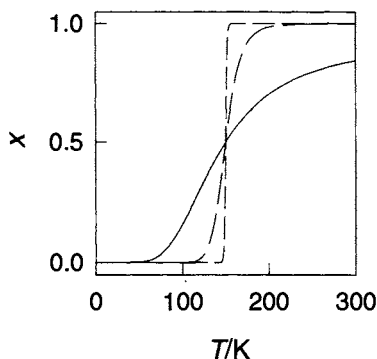


Fig. 9.9. Increasing abruptness of the spin transition with the number of particles per domain n ; $\Delta H/R = 500$ K, $T_c = 150$ K, $n = 1$ (solid), 5 (long dashed) and 50 (short dashed).

where γ is an interaction parameter (in units of energy) independent of temperature. An insertion into the molar Gibbs energy yields

$$\begin{aligned} G &= xG_{\text{HS}} + (1-x)G_{\text{LS}} - TS_{\text{mix}} + I \\ &= xG_{\text{HS}} + (1-x)G_{\text{LS}} + RT[x \ln x + (1-x) \ln(1-x)] + \gamma x(1-x) \end{aligned}$$

and from the condition of equilibrium $(\partial G/\partial x)_{T,p} = 0$ we get

$$\ln\left(\frac{1-x}{x}\right) = \frac{\Delta G}{RT} + \frac{\gamma(1-2x)}{RT} = \frac{\Delta H + \gamma(1-2x)}{RT} - \frac{\Delta S}{R}$$

For the given values of ΔH , ΔS and γ as parameters, $T = f(x)$ is a uniquely defined function

$$T = \frac{(\Delta H/R) + (\gamma/R)(1-2x)}{(\Delta S/R) + \ln\left(\frac{1-x}{x}\right)}$$

which can be analysed by considering three cases (Fig. 9.10) as follows:

- (1) $\gamma/2R < T_c$: T versus x is an increasing curve and its inverse function x versus T represents a gradual spin transition;
- (2) $\gamma/2R = T_c$: there is a vertical jump of x at T_c and the inverse plot x versus T represents an abrupt spin transition (this is not a function in a mathematical sense since one x is associated with a many-valued T);
- (3) $\gamma/2R > T_c$: the T versus x curve exhibits a maximum at $T > T_c$ and $x < 0.5$ and at this state the Gibbs energy adopts a (local) minimum value. For $T < T_c$ and $x > 0.5$ another minimum at the T versus x curve exists; the Gibbs energy adopts the second (local) minimum value (Fig. 9.11).

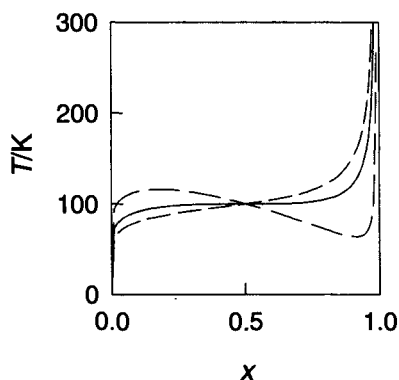


Fig. 9.10. Temperature versus high-spin mole fraction within the solution model; $\Delta H/R = 500$ K, $\Delta S/R = 5$, $\gamma/R = 100$ K (short dashed), 200 K (solid) and 400 K (long dashed).

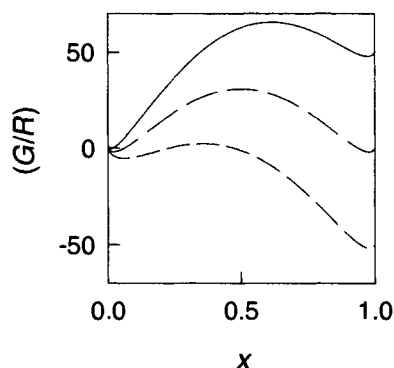


Fig. 9.11. Variation of the Gibbs energy G versus x within the solution model for $\gamma/2R > T_c$: $\Delta H/R = 500$ K, $\Delta S/R = 5$, $\gamma/R = 400$ K, $T = 90$ K (solid), 100 K (long dashed) and 110 K (short dashed).

The solution model is capable of describing the hysteresis effect (Fig. 9.12). In the heating direction the x versus T function increases smoothly up to the point $T_c^\uparrow$ where x jumps; then it increases smoothly again. In the cooling direction x decreases smoothly up to the point $T_c^\downarrow$, then drops abruptly and after that escapes continuously.

Although the construction of the T versus x function in the solution model is straightforward, the inverse function exists only in an implicit form

$$x = \frac{1}{1 + \exp[\Delta H/RT + \gamma(1 - 2x)/RT - \Delta S/R]}$$

This equation can be solved by an iterative procedure: by setting for $x = 0.5$ in the first approximation the left side yields the second approximation of x and the whole process is iterated until x adopts a stationary value.

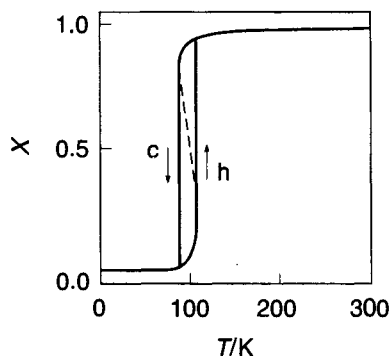


Fig. 9.12. High-spin mole fraction versus temperature curves in the solution model with hysteresis: **h**—heating direction; **c**—cooling direction; $\Delta H/R = 500$ K, $\Delta S/R = 5$, $\gamma/R = 300$ K.

An Arrhenius plot, i.e. the $(\ln K_{\text{eq}})$ versus $(1/T)$ function, brings information about the departure from an ideal solution behaviour (cooperativeness). A linear function is characteristic of the absence of cooperative effects (Fig. 9.13). The deviations from linearity increase with the value of the interaction parameter γ .

9.2.4 Other models

The above models have been developed on macroscopic (thermodynamic) arguments. It is possible, however, to make a more detailed inspection on the basis of microscopic arguments. For this purpose one can introduce the energy increments $I_{\text{LL}}, I_{\text{LH}}, I_{\text{HH}}$ referring to pair interactions between LS–LS, LS–HS and HS–HS pairs, respectively. The probability of having a pair of LS molecules is $(1-x)^2$, the probability of having a pair of HS molecules is x^2 , and finally the probability of having an LS–HS pair is $2(1-x)x$; the sum of these probabilities is equal to 1. Then the total interaction parameter can be written in the form

$$I(x) = I_{\text{LL}}(1-x)^2 + 2I_{\text{LH}}x(1-x) + I_{\text{HH}}x^2$$

This can be viewed as a quadratic form

$$I(x) = J_0 + J_1x + J_2x^2$$

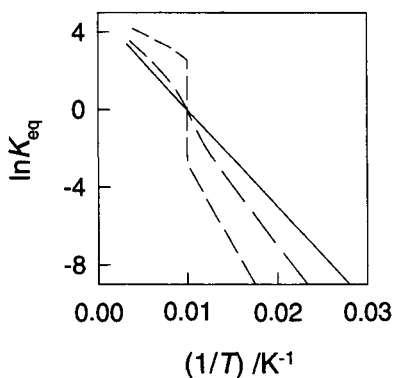


Fig. 9.13. Arrhenius plot in the solution model: $\Delta H/R = 500$ K, $\Delta S/R = 5$, $\gamma/R = 0$ (solid), 100 K (long dashed) and 300 K (short dashed).

with

$$J_0 = I_{LL}$$

$$J_1 = 2(I_{LH} - I_{LL})$$

$$J_2 = I_{LL} + I_{HH} - 2I_{LH}$$

Thus the assumption of the solution model

$$I(x) = \gamma x(1 - x)$$

corresponds to the interrelation

$$\gamma = J_1 = -J_2 = 2I_{LH} - I_{LL} - I_{HH}$$

This means an excess of the interaction energy between the molecules of different spin relative to the interaction energy of the molecules of like spin. It is a measure of the tendency for molecules of one type to interact effectively (to be surrounded) by molecules of like spin.

There are some more models for the description of spin crossover (Table 9.3). They can be classified into three groups:

- (1) thermodynamic models (Table 9.3) [14–22];
- (2) vibronic models based upon electron–phonon coupling [17, 23];
- (3) two-level (Ising-like) models [24, 25] extended to a two-step spin crossover [26], a two-step spin crossover in dinuclear compounds [27] and an improved model including molecular vibrations [28].

TABLE 9.3
Various models of spin transition

Model	Parameters	$x = f(T)$
Domain model: Sorai and Seki [14]	$J_1 = J_2 = 0$	$x = 1/\{1 + \exp(n\Delta G/RT)\}$
Solution model: Drickamer [15]	$J_1 = -J_2 = \gamma$	$x = 1/\{1 + \exp[(\Delta G + \gamma - 2\gamma x)/RT]\}$
McGarvey et al. [16]	$J_1 \neq 0, J_2 \neq 0$	$x = 1/\{1 + \exp[(\Delta G + J_1 + 2J_2 x)/RT]\}$
Zimmermann and König [17]	$J_1 = 0, J_2 = -J$	$x = 1/\{1 + \exp[(\Delta - RT \ln Z - 2Jx)/RT]\}$
Spiering et al. [18,19]	$J_1 = \Delta(c), J_2 = -\Gamma(c)$	$x = 1/\{1 + \exp[(\Delta G + \Delta(c) - 2\Gamma(c)x)/RT]\}$

9.2.5 Ising-like model

In order to model the solid-state properties, the coupled two-level systems can be characterised by a Hamiltonian of the form

$$\hat{H} = \sum_i \frac{\Delta_i}{2} \hat{\sigma}_i - \sum_i \sum_{j < i} J_{ij} \hat{\sigma}_i \cdot \hat{\sigma}_j$$

Here $\hat{\sigma}_i$ is a fictitious spin with the eigenvalues $\sigma = -1$ for the LS state and $\sigma = +1$ for the HS state. The postulated Hamiltonian formally describes an Ising-like system under the external field Δ_i . Unlike true magnetic systems, the degeneracies of the two levels are different; thus the suffix Ising-like. Within the mean field approach the single molecule can be characterised by the Hamiltonian

$$\hat{H} = \frac{\Delta_0}{2} \hat{\sigma} - J \langle \sigma \rangle \hat{\sigma}$$

with the corresponding eigenvalues

$$E_{(\sigma=+1)} = \frac{\Delta_0}{2} - J \langle \sigma \rangle$$

$$E_{(\sigma=-1)} = -\frac{\Delta_0}{2} + J \langle \sigma \rangle$$

The spin conversion is characterised by the mean value of

$$\langle \sigma \rangle = -x_{\text{LS}} + x_{\text{HS}} = 2x - 1$$

so that

$$x = \frac{1}{2}(1 + \langle \sigma \rangle)$$

The energy difference becomes

$$\Delta E = E_{(\sigma=+1)} - E_{(\sigma=-1)} = \Delta_0 - 2J \langle \sigma \rangle = \Delta_0 - 2J(2x - 1)$$

and thus the thermal population within the Boltzmann statistics yields

$$\begin{aligned} K_{\text{eq}} &= \frac{x_{\text{HS}}}{x_{\text{LS}}} = \frac{x}{1-x} = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \exp(-\Delta E/kT) \\ &= \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \exp\{-[\Delta_0 - 2J(2x - 1)]/kT\} \end{aligned}$$

which is equivalent to the expression

$$\frac{1 + \langle \sigma \rangle}{1 - \langle \sigma \rangle} = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \exp\{-[\Delta_0 - 2J\langle \sigma \rangle]/kT\}$$

This implies that the implicit equation

$$\langle \sigma \rangle = \frac{-1 + \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \exp\{-[\Delta_0 - 2J\langle \sigma \rangle]/kT\}}{1 + \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \exp\{-[\Delta_0 - 2J\langle \sigma \rangle]/kT\}}$$

should be satisfied.

Taking into account an analogy with the mass action law

$$K_{\text{eq}} = \exp(-\Delta H/RT + \Delta S/R)$$

we arrive at the result

$$\Delta S = R \ln \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e}$$

Since the transition temperature T_c is exactly at $x = 1/2$ then

$$K_{\text{eq}} = 1 = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \exp(-\Delta_0/kT_c)$$

and consequently

$$\Delta_0 = T_c \left(k \ln \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \right)$$

This yields a relationship between the molar enthalpy and molar entropy at T_c

$$\Delta H = N_A \Delta_0 = T_c \left(N_A k \ln \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \right) = T_c \Delta S$$

9.2.6 Ising-like model with molecular vibrations

The inclusion of *molecular vibrations* will effect the partition function which, in addition to the electronic contribution, will contain the vibration part [28]. Each molecule is assumed to behave as a set of $(3n - 6)$ independent harmonic oscillators with the fundamental frequencies ν_i so that the vibration partition functions are

$$\begin{aligned} z_{\text{LS}}^{\text{v}} &= \prod_{i=1}^{3n-6} \frac{\exp(-h\nu_{\text{LS},i}/2kT)}{1 - \exp(-h\nu_{\text{LS},i}/kT)} \\ &= \exp \left[- \sum_{i=1}^{3n-6} (h\nu_{\text{LS},i}/2kT) \right] \prod_{i=1}^{3n-6} \frac{1}{1 - \exp(-h\nu_{\text{LS},i}/kT)} \end{aligned}$$

and

$$\begin{aligned} z_{\text{HS}}^{\text{v}} &= \prod_{i=1}^{3n-6} \frac{\exp(-h\nu_{\text{HS},i}/2kT)}{1 - \exp(-h\nu_{\text{HS},i}/kT)} \\ &= \exp \left[- \sum_{i=1}^{3n-6} (h\nu_{\text{HS},i}/2kT) \right] \prod_{i=1}^{3n-6} \frac{1}{1 - \exp(-h\nu_{\text{HS},i}/kT)} \end{aligned}$$

Then the partition function associated with one molecule is constructed from the respective electronic and vibration increments as

$$z_{\text{LS}} = z_{\text{LS}}^{\text{e}} z_{\text{LS}}^{\text{v}} = g_{\text{LS}}^{\text{e}} \exp[-(E_{\text{LS}}^{\text{e}} - E_0)/kT] z_{\text{LS}}^{\text{v}}$$

and

$$z_{\text{HS}} = z_{\text{HS}}^{\text{e}} z_{\text{HS}}^{\text{v}} = g_{\text{HS}}^{\text{e}} \exp[-(E_{\text{HS}}^{\text{e}} - E_0)/kT] z_{\text{HS}}^{\text{v}}$$

Here the electronic energy of the LS state is taken as the energy origin: $E_0 = E_{\text{LS}}^{\text{e}}$.

For the system of equivalent but distinguishable particles (as in the solid state) the total partition function of a canonical system for one mole of particles becomes

$$Z_{\text{LS}} = (z_{\text{LS}})^{N_{\text{A}}^*}$$

and

$$Z_{\text{HS}} = (z_{\text{HS}})^{N_{\text{A}}^*}$$

where N_A^* stands for the number of particles per mole (the value of the Avogadro constant). Since our partition functions do not depend explicitly on the volume, the pressure is zero and consequently the molar Gibbs energy and molar Helmholtz free energy coincide

$$G = F = -\frac{kT}{1 \text{ mol}} \ln Z = -\frac{kT}{1 \text{ mol}} \ln(z)^{N_A^*} = -RT \ln z$$

The equilibrium constant for the unimolecular reaction



is expressed as

$$K_{\text{eq}} = \exp[-(G_{\text{HS}} - G_{\text{LS}})/RT] = \frac{z_{\text{HS}}}{z_{\text{LS}}}$$

The energy of *zero-point vibrations* can be summed up over all vibration modes of the system

$$\varepsilon_{\text{LS}}^{\text{v}} = \frac{1}{2} \sum_i^{3n-6} h\nu_{\text{LS},i}$$

and

$$\varepsilon_{\text{HS}}^{\text{v}} = \frac{1}{2} \sum_i^{3n-6} h\nu_{\text{HS},i}$$

Then we arrive at the expression

$$\begin{aligned} K_{\text{eq}} &= \frac{g_{\text{HS}}^{\text{e}}}{g_{\text{LS}}^{\text{e}}} \exp[-(E_{\text{HS}}^{\text{e}} + \varepsilon_{\text{HS}}^{\text{v}} - E_{\text{LS}}^{\text{e}} - \varepsilon_{\text{LS}}^{\text{v}})/kT] \frac{z_{\text{HS}}^{\text{v}}}{z_{\text{LS}}^{\text{v}}} \\ &= \frac{g_{\text{HS}}^{\text{e}}}{g_{\text{LS}}^{\text{e}}} \exp[-(E_{\text{HS}}^{\text{e}} + \varepsilon_{\text{HS}}^{\text{v}} - E_{\text{LS}}^{\text{e}} - \varepsilon_{\text{LS}}^{\text{v}})/kT] \frac{\prod_{i=1}^{3n-6} \frac{1}{1 - \exp(-h\nu_{\text{HS},i}/kT)}}{\prod_{i=1}^{3n-6} \frac{1}{1 - \exp(-h\nu_{\text{LS},i}/kT)}} \\ &= \frac{g_{\text{HS}}^{\text{e}}}{g_{\text{LS}}^{\text{e}}} \exp[-(E_{\text{HS}}^{\text{e}} + \varepsilon_{\text{HS}}^{\text{v}} - E_{\text{LS}}^{\text{e}} - \varepsilon_{\text{LS}}^{\text{v}})/kT] \prod_{i=1}^{3n-6} \frac{1 - \exp(-h\nu_{\text{LS},i}/kT)}{1 - \exp(-h\nu_{\text{HS},i}/kT)} \end{aligned}$$

or

$$\frac{x}{1-x} = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \prod_{i=1}^{3n-6} \frac{1 - \exp(-h\nu_{\text{LS},i}/kT)}{1 - \exp(-h\nu_{\text{HS},i}/kT)} \times \exp\{[-\Delta_0 + 2J(2x - 1) - (\varepsilon_{\text{HS}}^v - \varepsilon_{\text{LS}}^v)]/kT\}$$

This equation can be rewritten as follows

$$\frac{1 + \langle \sigma \rangle}{1 - \langle \sigma \rangle} = r_{\text{eff}} \exp[-(\Delta_{\text{eff}} - 2J\langle \sigma \rangle)/kT]$$

with the effective parameters

$$r_{\text{eff}} = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \prod_{i=1}^{3n-6} \frac{1 - \exp(-h\nu_{\text{LS},i}/kT)}{1 - \exp(-h\nu_{\text{HS},i}/kT)}$$

and

$$\Delta_{\text{eff}} = \Delta_0 + (\varepsilon_{\text{HS}}^v - \varepsilon_{\text{LS}}^v)$$

This implies that the implicit equation

$$\langle \sigma \rangle = \frac{-1 + r_{\text{eff}} \exp[-(\Delta_{\text{eff}} - 2J\langle \sigma \rangle)/kT]}{1 + r_{\text{eff}} \exp[-(\Delta_{\text{eff}} - 2J\langle \sigma \rangle)/kT]}$$

should be obeyed. The equation just derived is of identical form to that appearing in [26,28]. Now the effective parameters are taken as free parameters to be optimised by the fitting procedure to the experimental x versus T or $\langle \sigma \rangle$ versus T curves.

The microscopic parameters Δ_{eff} and r_{eff} are related to the macroscopic thermodynamic functions through

$$\Delta S = R \ln r_{\text{eff}}$$

and

$$\Delta H = N_{\text{A}} \Delta_{\text{eff}}$$

In the limit of *low vibration frequencies*, when $h\nu \ll kT$, the exponentials can be expanded into a Taylor series and the vibration partition function is simplified to

$$z^v \approx \prod_i^{3n-6} \frac{kT}{h\nu_i}$$

and consequently the equilibrium constant becomes

$$K_{\text{eq}} = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \prod_{i=1}^{3n-6} \frac{\nu_{\text{LS},i}}{\nu_{\text{HS},i}} \exp[-(\Delta_0 + \varepsilon_{\text{HS}}^v - \varepsilon_{\text{LS}}^v)/kT]$$

In a further approximation the average vibration frequencies $\bar{\nu}_{\text{HS}}$ and $\bar{\nu}_{\text{LS}}$ are introduced. Then the effective degeneracy ratio becomes a temperature-independent quantity

$$r_{\text{eff}} = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \left(\frac{\bar{\nu}_{\text{LS}}}{\bar{\nu}_{\text{HS}}} \right)^{3n-6}$$

On the basis of experimental data it is known that the average frequency ratio is of the order

$$\frac{\bar{\nu}_{\text{LS}}}{\bar{\nu}_{\text{HS}}} \approx 1.5$$

Thus for a hexacoordinate system, where 15 vibration models exist, one gets

$$r_{\text{eff}} = 5(1.5)^{15} = 2189$$

which yields the molar entropy

$$\Delta S/R = \ln r_{\text{eff}} = 7.7$$

This value spans the experimental data interval.

The effective degeneracy ratio is, in fact, a temperature-dependent quantity which may be approximated through the average vibration frequencies as

$$r_{\text{eff}} = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \left[\frac{1 - \exp(-h\bar{\nu}_{\text{LS}}/kT)}{1 - \exp(-h\bar{\nu}_{\text{HS}}/kT)} \right]^{3n-6}$$

Consequently the enthalpy and entropy depend upon temperature. In order to visualise such an effect different Arrhenius plots of $\ln K_{\text{eq}}$ versus $(1/T)$ were generated (Fig. 9.14) for $J = 0$ (no interaction) according to the formula

$$K_{\text{eq}} = \frac{g_{\text{HS}}^e}{g_{\text{LS}}^e} \left[\frac{1 - \exp(-h\bar{\nu}_{\text{LS}}/kT)}{1 - \exp(-h\bar{\nu}_{\text{HS}}/kT)} \right]^{3n-6} \times \exp \left\{ - \left[\Delta_0 + \frac{3n-6}{2} (h\bar{\nu}_{\text{HS}} - h\bar{\nu}_{\text{LS}}) \right] / kT \right\}$$

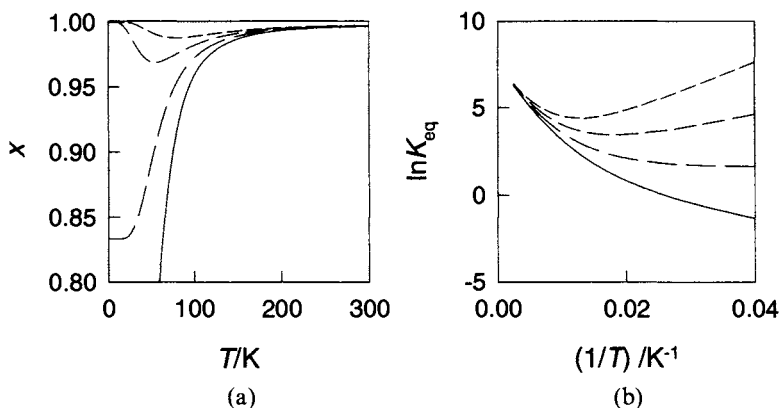


Fig. 9.14. High-spin mole fraction (a) and Arrhenius plot (b) in the absence of cooperativity ($J = 0$): $\bar{\nu}_{LS} = 1.5\bar{\nu}_{HS}$, $g_{HS}^e/g_{LS}^e = 5$, $(\Delta_0/k) = 600$ K, $(h\bar{\nu}_{HS}/k) = 140$ K (solid), 160 K (long dashed), 180 K (medium dashed) and 200 K (short dashed).

It is seen that there is a systematic deviation from linearity with increasing average frequencies. When the critical value of

$$\Delta_{crit} = \Delta_0 + \frac{15}{2} h(\bar{\nu}_{HS} - \bar{\nu}_{LS})$$

becomes negative the transition temperature is not reached and the system remains high-spin ($K_{eq} > 1$): this results from a high-spin vibronic (electron-vibration) ground state.

The situation in the critical region has been modelled in more detail and is depicted in Fig. 9.14. Below the critical value the normal conversion curves are obtained. However, above it the high-spin mole fraction passes through a minimum with limiting values of 1.0 for both low and high temperature. Such behaviour really has been observed [29].

In a more complete treatment, both the cooperativity effects and the vibrational effects are taken into account via the system of equations

$$\langle \sigma \rangle = \frac{-1 + F(\langle \sigma \rangle)}{1 + F(\langle \sigma \rangle)}$$

with

$$F(\langle \sigma \rangle) = \frac{g_{HS}^e}{g_{LS}^e} \left[\frac{1 - \exp(-h\bar{\nu}_{LS}/kT)}{1 - \exp(-h\bar{\nu}_{HS}/kT)} \right]^{3n-6} \times \exp \left\{ - \left[\Delta_0 + \frac{3n-6}{2} h(\bar{\nu}_{HS} - \bar{\nu}_{LS}) - 2J\langle \sigma \rangle \right] / kT \right\}$$

The corresponding plots, modelled for certain values of parameters, are given in Fig. 9.15. It can be seen that, in addition to the inverse S-shaped curve (owing to the cooperativity parameter $J > 0$) with increasing abruptness, also a systematic shift of the tangentials is obtained (owing to vibrational effects).

The combined effect of the vibronic states and cooperativity is even more complex and is analysed for some parameter values in Fig. 9.16. While the critical value is overreached, an upturn of the conversion curves is obtained. However, the cooperativity effects alter the conversion curves to the low-spin value at low temperature.

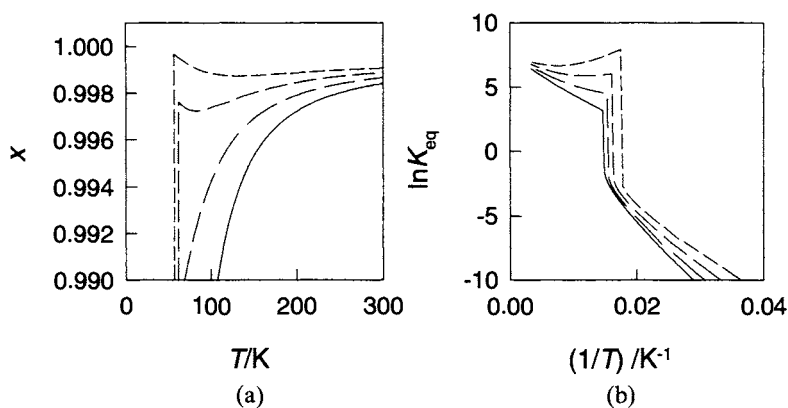


Fig. 9.15. Conversion curve (a) and Arrhenius plot (b) in the presence of cooperativity ($J > 0$): $\bar{\nu}_{LS} = 1.5\bar{\nu}_{HS}$, $g_{HS}^e/g_{LS}^e = 5$, $(\Delta_0/k) = 600$ K; individual curves correspond to $(h\bar{\nu}_{HS}/k) = J/k$, J/k being 100 K (solid), 120 K (long dashed), 140 K (medium dashed) and 160 K (short dashed).

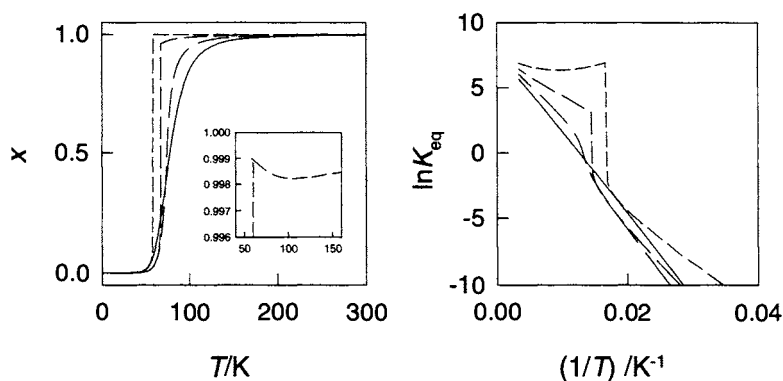


Fig. 9.16. Combined effect of the vibronic states and cooperativity: $\bar{\nu}_{LS} = 1.5\bar{\nu}_{HS}$, $g_{HS}^e/g_{LS}^e = 5$, $(\Delta_0/k) = 600$ K; individual curves correspond to $(h\bar{\nu}_{HS}/k) = J/k$; solid, $J/k = 1$ K (no cooperativity); long dashed, $J/k = 50$ K (slight cooperativity); medium dashed, $J/k = 100$ K (medium cooperativity); short dashed, $J/k = 150$ K (strong cooperativity).

9.2.7 Two-step spin crossover

Some compounds exhibit a spin crossover of the form that the fraction x_{HS} of molecules in the HS state increases with temperature in two steps; a plateau of a few K exists between these steps. This behaviour can be explained by considering two sublattices (A and B) containing the same number of molecules [26]. The Ising-like Hamiltonians corresponding to the respective lattices, in the mean field approach, are defined as follows

$$\hat{H}_A = \frac{4_0}{2} \hat{\sigma}_A - (J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle) \hat{\sigma}_A$$

$$\hat{H}_B = \frac{4_0}{2} \hat{\sigma}_B - (J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle) \hat{\sigma}_B$$

The fictitious spins $\hat{\sigma}_A$ and $\hat{\sigma}_B$ have eigenvalues ± 1 for the LS and HS states and

$$\hat{\sigma} = \hat{\sigma}_A + \hat{\sigma}_B$$

The mole fractions of the HS state are interrelated through

$$\langle \sigma_A \rangle = 2x_A - 1$$

$$\langle \sigma_B \rangle = 2x_B - 1$$

$$\langle \sigma \rangle = 2x_A + 2x_B - 2$$

and

$$x = \frac{1}{2}(x_A + x_B) = \frac{1}{4}(2 + \langle \sigma \rangle)$$

In the above Hamiltonians, J_A and J_B are the intra-sublattice interaction parameters; J_{AB} is the inter-sublattice interaction parameter. Their positive values mean a ferromagnetic interaction whereas negative values refer to antiferromagnetic ones. The corresponding eigenvalues are

$$E_{A+} = \frac{4_0}{2} - (J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle)$$

$$E_{A-} = -\frac{4_0}{2} + (J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle)$$

$$E_{B+} = \frac{\Delta_0}{2} - (J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle)$$

$$E_{B-} = -\frac{\Delta_0}{2} + (J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle)$$

The energy differences become

$$\Delta E_A = E_{A+} - E_{A-} = \Delta_0 - 2(J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle)$$

and

$$\Delta E_B = E_{B+} - E_{B-} = \Delta_0 - 2(J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle)$$

After introducing the degeneracy ratio

$$r = \frac{g_{HS}^e}{g_{LS}^e}$$

the thermal population within the Boltzmann statistics yields

$$K_A = \frac{x_A}{1 - x_A} = r \exp(-\Delta E_A/kT)$$

$$\frac{1 + \langle \sigma_A \rangle}{1 - \langle \sigma_A \rangle} = r \exp\{-[\Delta_0 - 2(J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle)]/kT\}$$

and

$$K_B = \frac{x_B}{1 - x_B} = r \exp(-\Delta E_B/kT)$$

$$\frac{1 + \langle \sigma_B \rangle}{1 - \langle \sigma_B \rangle} = r \exp\{-[\Delta_0 - 2(J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle)]/kT\}$$

This means that the two coupled equations

$$\langle \sigma_A \rangle = \frac{-1 + r \exp\{-[\Delta_0 - 2(J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle)]/kT\}}{1 + r \exp\{-[\Delta_0 - 2(J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle)]/kT\}}$$

$$\langle \sigma_B \rangle = \frac{-1 + r \exp\{-[\Delta_0 - 2(J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle)]/kT\}}{1 + r \exp\{-[\Delta_0 - 2(J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle)]/kT\}}$$

should be fulfilled simultaneously. These equations can be solved by an iterative procedure. The free parameters, to be obtained by the optimisation procedure, cover J_A , J_B , J_{AB} , Δ_0 and eventually r .

The thermal evolution of the conversion parameters $\langle\sigma_A\rangle$ and $\langle\sigma_B\rangle$ is very complex and fully analysed in [26]. There are several critical temperatures when the mean spin values alter their sign:

- (a) T_A^- —sign change of $\langle\sigma_A\rangle$ on heating;
- (b) T_B^- —sign change of $\langle\sigma_B\rangle$ on heating;
- (c) T_A^+ —sign change of $\langle\sigma_A\rangle$ on cooling;
- (d) T_B^+ —sign change of $\langle\sigma_B\rangle$ on cooling;
- (e) T_c —simultaneous sign change of $\langle\sigma_A\rangle$, $\langle\sigma_B\rangle$ and $\langle\sigma\rangle$.

The two-step transition is obtained when the intra-sublattice interactions are ferromagnetic ($J_A, J_B > 0$) and the inter-sublattice interactions are antiferromagnetic ($J_{AB} < 0$). The two-step character of the conversion is provided by $T_B^- \neq T_B^+$ for $|J_A| \geq |J_B|$ and the plateau width is $(T_B^+ - T_B^-)$.

The thermal evolution of the HS state conversion has been modelled for a typical set of parameters: $J_A = J_B > 0$ (the ferromagnetic intra-sublattice interaction) and $J_{AB} < 0$ (the antiferromagnetic inter-sublattice interaction)—see Fig. 9.17. It can be seen that the first (low-temperature) step is more abrupt than the second (high-temperature) one which is smoother.

9.2.8 Spin crossover in dinuclear compounds

Within the Ising-like model the Hamiltonian of a dinuclear system formed of a symmetric pair of metallic centres is

$$\begin{aligned}\hat{H}_{AB} = & \frac{\Delta_0}{2}(\hat{\sigma}_A + \hat{\sigma}_B) - J(\langle\sigma_A\rangle\hat{\sigma}_A + \langle\sigma_B\rangle\hat{\sigma}_B) \\ & - J'(\langle\sigma_A\rangle\hat{\sigma}_B + \langle\sigma_B\rangle\hat{\sigma}_A) - J_{AB}\hat{\sigma}_A \cdot \hat{\sigma}_B\end{aligned}$$

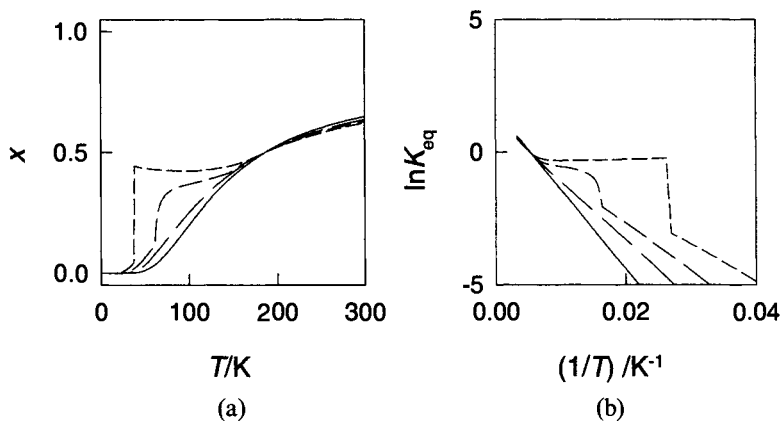


Fig. 9.17. Two-step spin crossover in a mononuclear system: (a) conversion curve, (b) Arrhenius plot; $\Delta_0/k = 300$ K, $g_{HS}^e/g_{LS}^e = 5$; $J_A/k = J_B/k = 50$ K, $J_{AB}/k = -50$ K (solid), -80 K (long dashed), -100 K (medium dashed) and -120 K (short dashed).

The interaction parameters correspond to:

- (a) intra-sublattice interaction, $J = J_{AA} = J_{BB} > 0$ (ferromagnetic);
- (b) inter-sublattice interaction for metallic centres belonging to different molecules, $J' > 0$ (ferromagnetic);
- (c) intramolecular interaction, $J_{AB} < 0$ (antiferromagnetic).

The introduction of the last parameter corresponds to an approach beyond the mean field approximation. The eigenvalues of the above Hamiltonian are received in the space spanned by a direct product $\hat{\sigma}_A \otimes \hat{\sigma}_B$ of interacting centres

$$E_1 = E(\sigma_A = -1, \sigma_B = -1) = -\Delta_0 + mJ_+ - J_{AB}$$

$$E_2 = E(\sigma_A = -1, \sigma_B = +1) = nJ_- + J_{AB}$$

$$E_3 = E(\sigma_A = +1, \sigma_B = -1) = -nJ_- + J_{AB}$$

$$E_4 = E(\sigma_A = +1, \sigma_B = +1) = \Delta_0 - mJ_+ - J_{AB}$$

with

$$J_+ = J + J'$$

$$J_- = J - J'$$

For convenience, two symmetry-adapted parameters were introduced

$$m = \langle \sigma_A \rangle + \langle \sigma_B \rangle$$

$$n = \langle \sigma_A \rangle - \langle \sigma_B \rangle$$

The first parameter is related to the high-spin mole fraction

$$x = \frac{1}{4}(2 + m)$$

The second parameter adopts a meaning of the order parameter. For $n = 0$ the sublattices are equivalent whereas for $n \neq 0$ there is a spontaneous symmetry breaking since the two sublattices are no longer equivalent.

The associated degeneracies of the above states are 1, r , r and r^2 for E_1 to E_4 with

$$r = g_{HS}^e / g_{LS}^e$$

in the first approximation. Then the molecular partition function becomes

$$Z = \exp[-(-\Delta_0 + mJ_+ - J_{AB})/kT] + r \exp[-(nJ_- + J_{AB})/kT] \\ + r \exp[-(-nJ_- + J_{AB})/kT] + r^2 \exp[-(\Delta_0 - mJ_+ - J_{AB})/kT]$$

The thermal averages of the individual spin values are calculated as follows

$$\begin{aligned}\langle\sigma_A\rangle &= \{(-1)\exp(-E_1/kT) + (-1)r\exp(-E_2/kT) \\ &\quad + (+1)r\exp(-E_3/kT) + (+1)r^2\exp(-E_4/kT)\}/Z \\ &= \{-\exp[-(-\Delta_0 + mJ_+ - J_{AB})/kT] - r\exp[-(nJ_- + J_{AB})/kT] \\ &\quad + r\exp[-(-nJ_- + J_{AB})/kT] + r^2\exp[-(\Delta_0 - mJ_+ - J_{AB})/kT]\}/Z\end{aligned}$$

and

$$\begin{aligned}\langle\sigma_B\rangle &= \{(-1)\exp(-E_1/kT) + (+1)r\exp(-E_2/kT) \\ &\quad - (+1)r\exp(-E_3/kT) + (+1)r^2\exp(-E_4/kT)\}/Z \\ &= \{-\exp[-(-\Delta_0 - mJ_+ + J_{AB})/kT] + r\exp[-(-nJ_- - J_{AB})/kT] \\ &\quad - r\exp[-(nJ_- - J_{AB})/kT] + r^2\exp[-(\Delta_0 + mJ_+ + J_{AB})/kT]\}/Z\end{aligned}$$

These expressions can be added and subtracted to yield two coupled equations for the parameters m and n [27]

$$\langle\sigma_A\rangle + \langle\sigma_B\rangle = m = \frac{2r^2\exp[-(\Delta_0 - mJ_+)/kT] - 2\exp[(\Delta_0 - mJ_+)/kT]}{D(m, n)}$$

$$\langle\sigma_A\rangle - \langle\sigma_B\rangle = n = \frac{2r\{\exp[nJ_-/kT] - \exp[-nJ_-/kT]\}}{D(m, n)}$$

with the denominator

$$\begin{aligned}D(m, n) &= r^2\exp[-(\Delta_0 - mJ_+)/kT] + \exp[(\Delta_0 - mJ_+)/kT] \\ &\quad + r\{\exp[nJ_-/kT] + \exp[-nJ_-/kT]\}\exp[-2J_{AB}/kT]\end{aligned}$$

These equations can be solved by an iterative procedure. However, the situation is complicated by the fact that the solutions in the critical region, where a two-step crossover can occur, may depend upon the initial values of the parameters at the beginning of the iteration. The results of modelling are displayed in Fig. 9.18. For typical values of interaction constants the conversion curve obeys a two-step transition, the second step being smoother than the first step.

A piece of software useful for generating the conversion curves for several spin crossover cases is presented in Appendix 6.

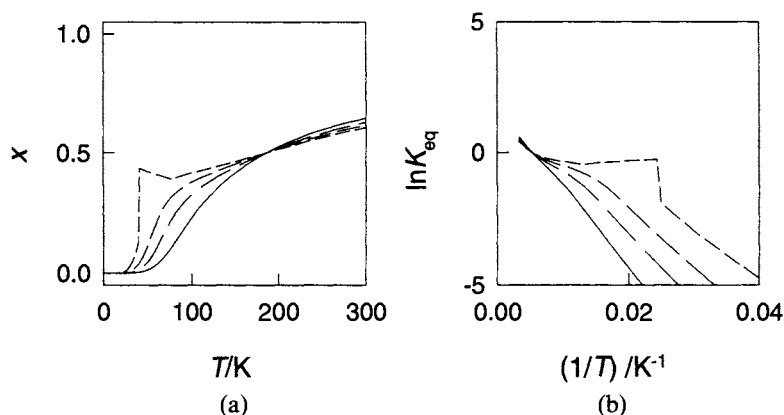


Fig. 9.18. Spin crossover in a dinuclear compound: (a) conversion curve, (b) Arrhenius plot; $\Delta_0/k = 300$ K, $g_{HS}^e/g_{LS}^e = 5$; $J_A/k = J_B/k = 50$ K, $J' = 0$, $J_{AB}/k = -50, -80, -100$ and -120 K.

9.3 PROPERTIES OF SPIN CROSSOVER SYSTEMS

9.3.1 Factors influencing the spin crossover

The spin crossover is influenced by several factors: some of them belong to the sample itself (composition, preparation and handling), some to the physical influences (applied field, pressure, temperature drift). Selected examples of iron(II) spin crossover systems are collected in Table 9.4.

TABLE 9.4
Representative examples of iron(II) spin crossover systems

System ^a	Property	Ref.
[Fe(phen) ₂ (NCS) ₂]	a prototype, abrupt transition	[35]
[Fe(trim) ₂]Cl ₂	continuous transition, no cooperativity	[30]
[Fe(trim) ₂](PhCOO)(ClO ₄)	continuous transition, cooperativity	[30]
[Fe(NH ₂ trz) ₃](BF ₄) ₂	small hysteresis	[8]
[Fe(NH ₂ trz) ₃]Br ₂ · H ₂ O	broad hysteresis	[8]
[Fe(trz)(Htrz) ₂](BF ₄) ₂	broad hysteresis around room temperature	[34,8]
[Fe(trim) ₂]F ₂	incomplete transition, small LS fraction	[29]
[Fe{5NO ₂ -sal-(1,4,7,10)}]	two-step transition	[31]
[(Fe(bt)(NCS) ₂) ₂ bpy]	dinuclear system, two-step transition	[32]
[Fe ₃ (ettrz) ₆ (H ₂ O) ₆](CF ₃ SO ₃) ₆	trinuclear system	[33]

^aLigands: phen = 1,10-phenanthroline; trim = 4'-(4-methylimidazole)-2'-(2''-methylimidazole)imidazole; bt = 2,2'-bis(2-thiazoline); ettrz = 4-ethyl-1,2,4-triazole; bpy = 2,2'-bipyrimidine; NH₂trz = 4-amino-1,2,4-triazole; trz = 1,2,4-triazole; Htrz = 1,2,4-1H-triazole; 5-NO₂-sal-(1,4,7,10) = Schiff base of 5-nitro-salicylaldehyde and 1,4,7,10-tetraazadecane.

Effect of pressure

It is a general feature of spin crossover systems that the metal–ligand distances in the HS state are longer than for the corresponding LS state. This finding follows both from volume measurements and from a direct X-ray structure analysis (Table 9.5). Thus, increasing pressure will favour the LS state and consequently the spin transition will occur at a higher T_c than at normal pressure.

Effect of dilution

The dilution of the spin crossover system in a similar host lattice with bigger ions (e.g. an iron system in the corresponding zinc compound) will create a negative image pressure. The HS state becomes preferentially stabilised and consequently T_c decreases. Simultaneously the conversion curve x_{HS} versus T becomes more gradual. Analogous behaviour is exhibited by $[\text{Fe}_n\text{M}_{1-n}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ systems ($\text{M} = \text{Co}, \text{Zn}$) and $[\text{Fe}_n\text{M}_{1-n}(\text{phen})_2(\text{NCS})_2]$ systems ($\text{M} = \text{Mn}, \text{Co}, \text{Zn}$).

Effect of magnetic field

The influence of the magnetic field on the transition temperature can be estimated from the equation $T_c = \Delta H / \Delta S$, and the shift of the transition temperature due to the change in the magnetic energy is

$$\Delta T_c = \left(\frac{E_{\text{HS}}^{\text{mag}} - E_{\text{LS}}^{\text{mag}}}{S_{\text{HS}} - S_{\text{LS}}} \right)_{T_c}$$

The magnetic energy of a given state is expressed as follows

$$E_s^{\text{mag}} = -\frac{1}{2\mu_0} \chi B^2$$

The molar magnetic susceptibility of the LS state ($^1A_1$) is of the order $\chi_{\text{LS}} \approx 1 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ and that of the HS state ($^5T_2$) is ca $\chi_{\text{HS}} \approx 2.5 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$ (at 150 K). Since, from the calorimetric measurement, the entropy of

TABLE 9.5
Average metal–ligand distances for LS and HS states

Compound	$\bar{R}_{\text{LS}}$ (pm)	$\bar{R}_{\text{HS}}$ (pm)
$[\text{Fe}(\text{phen})_2(\text{NCS})_2]$	199.2	215.6
$[\text{Fe}(\text{bpy})_2(\text{NCS})_2]$	202	214
$[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$	201.3	219.5
$[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{MeOH}$	201.6	219.8

the transition is typically $\Delta S \approx 50 \text{ J K}^{-1} \text{ mol}^{-1}$ then $\Delta T_c \approx -0.04B^2$ which, for the field $B = 5 \text{ T}$, yields an estimate $\Delta T_c \approx -1 \text{ K}$.

Isotope effect

The substitution of an isotope with higher mass increases the reduced mass of the oscillator

$$\frac{1}{\mu_{AB}} = \frac{1}{m_A} + \frac{1}{m_B}$$

The energy of the zero-point vibration is given by the formula

$$\varepsilon_0 = \hbar \sqrt{\frac{k_{AB}}{\mu_{AB}}}$$

and as a consequence of the isotope effect it is reduced. The decrease in the zero-point energy is more pronounced for the LS state since the force constants obey the relationship $k_{\text{LS}} > k_{\text{HS}}$. Consequently the energy gap between the LS and HS states increases and thus the transition temperature will increase.

In fact, the transition temperature increases by 15 K upon the deuteration of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{sol}$ systems. However, deuteration affects not only the reduced mass of the oscillators but also the hydrogen bonds which considerably mediate the interunit communication.

Effect of temperature drift

Normally it is expected that the temperature changes are moderate enough for the spin crossover system to remain in thermodynamic equilibrium. However, rapid cooling may lead to freezing of the HS state so that the transition temperature in the cooling direction apparently decreases.

Effect of temperature cycling

It was reported [8] that the first temperature cycle (a heating/cooling loop) may be irreproducible. A better reproducibility of the hysteresis curve is achieved after several temperature cycles.

Effect of isomerism

The asymmetric bidentate ligands (like 2-pic, pybzim, etc.) can be bonded in two different modes: to form either the meridional (*mer*) or the facial (*fac*) geometrical isomers. The *mer*-isomer possesses the C_{2v} symmetry of the chromophore whereas the *fac*-isomer has the C_{3v} symmetry. These coordination modes can be distinguished from the magnetic perturbation

Mössbauer spectra. Since the formation of different hydrogen bonding networks is predetermined by the presence of these isomers, the spin crossover parameter can alter.

Effect of solvates

Solvate molecules incorporated into the crystal lattice can strongly influence the spin crossover behaviour. A representative series is given by $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{sol}$ complexes (Table 9.6). These systems differ in their structure and the hydrogen bonding network. Consequently the spin crossover behaviour (transition temperature, hysteresis width, abruptness) is different.

Effect of impurities

The liberation of one water molecule from $[\text{Fe}(\text{pybzim})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ has been found to be a reversible process. However, quite different magnetic moments have been reported for these systems at a low temperature (Table 9.7). An apparent incompleteness of the spin transition at a low temperature (a rather high residual magnetic moment) has been reinterpreted in terms of an increasing admixture of Fe(III) impurities with the sample aging. These paramagnetic impurities are detectable by ESR, electron spectra, Mössbauer data and magnetic data.

TABLE 9.6

Effect of solvates on spin-crossover behaviour of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{sol}$ complexes

sol	Property	Structure	Isomer
EtOH	$T_c = 121$ K, continuous	$\text{P2}_1/\text{c}$, $Z = 4$	<i>mer</i>
MeOH	$T_c = 121$ K, continuous	Pbca , $Z = 8$	<i>mer</i>
H_2O	$\Delta T_c = 90$ K, abrupt		
$2\text{H}_2\text{O}$	LS ($^1A_1$) state	P1 , $Z = 2$	<i>fac</i>

TABLE 9.7

Results of various investigations on $[\text{Fe}(\text{pybzim})_3](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ systems^a

n	T/K	$\mu_{\text{eff}}/\mu_{\text{B}}$	T/K	$\mu_{\text{eff}}/\mu_{\text{B}}$
?	90	1.3	295	5.2
1	85.9	3.41	298.5	5.25
1	90.7	2.05	284.4	5.44
1	90.6	1.01	295.2	5.20
2	80	1.3		
2	95.0	1.29	290.3	5.23

^aAccording to data collection in Ref. [13].

Effect of counterions

The influence of non-coordinating anions on spin transition parameters is substantial: the anion substitution can shift the T_c value over 100 K.

Effect of ligands

Ligand substitution brings primary dispositions for spin crossover behaviour. The dominant effect is the balance of the spin pairing energy and the crystal field splitting energy Δ . For instance, the spin properties of some $[\text{Fe}(\text{phen})_2\text{X}_2]$ -type complexes are presented in Table 9.8.

Effect of ligand substituents

The electronic effect of substituents (functional groups) in a certain stereo-specific position at the ligand skeleton is well documented. For example, in $[\text{Fe}(2\text{-Y-phen})_3]\text{X}_2$ -type complexes the spin properties alter within the series of substituents as follows: Y = H—low-spin complex; CH_3O and CH_3 —spin crossover systems; Cl—high-spin complex.

Effect of particle size

A particle size effect is that the HS fraction increases with increasing loads of spin crossover compounds. With increasing degree of milling the transition curve becomes smoother and a larger proportion of the residual HS state is observed. These effects are more connected with the crystal defects introduced by such a treatment; they have less to do with the particle size.

Solvent variation

In solutions, spin crossover is a gradual process. The actual shape of the conversion curve depends heavily upon the solvent used (Fig. 9.19)

Ligand dissociation

Products of ligand dissociation, which may be enhanced at high temperature, are those complexes where an increased number of solvent molecules is ligated. This may lead to a decrease in the crystal field strength Δ , manifesting itself in the stabilisation of the HS state.

TABLE 9.8
Spin properties of $[\text{Fe}(\text{phen})_2\text{X}_2]$ complexes

Ligand	Δ	Property
Cl^-	small	high spin down to low temperature
NCS^-	moderate	spin crossover at 176 K
NCSe^-	moderate	spin crossover at 231 K
CN^-	high	low spin up to high temperature

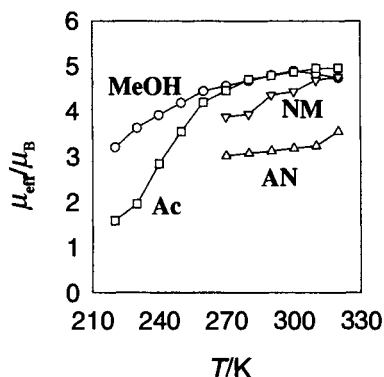


Fig. 9.19. Temperature variation of the effective magnetic moment for $[\text{Fe}(\text{pybzim})_3](\text{ClO}_4)_2$ complex in various solvents: MeOH—methanol, Ac—acetone, NM—nitromethane, AN—acetonitrile.

Deprotonation of ligands

Some ligand bearing acidic hydrogens (like imidazole derivatives) may undergo deprotonation at a suitable pH. The deprotonation is reflected in the strengthening of the metal–ligand bonds and consequently the crystal field strength increases. The greater Δ , the better the stabilisation of the LS state.

Effect of preparation

As an effect of different conditions during preparation a different acidity of some centres can be obtained. For example, the acidity of the imidazole centres can vary over a certain interval; this may be reflected in modified spin crossover behaviour.

The factors influencing spin crossover behaviour are collected in Table 9.9.

9.3.2 Spin crossover and optical properties

The $d-d$ electron transitions for a low-spin iron(II) system cover the spin forbidden $\Delta_1 = {}^1A_1 \rightarrow {}^3T_1$ and $\Delta_2 = {}^1A_1 \rightarrow {}^3T_2$ transitions with low intensity, as well as the spin allowed (orbital forbidden) $\Delta_3 = {}^1A_1 \rightarrow {}^1T_1$ and $\Delta_4 = {}^1A_1 \rightarrow {}^1T_2$ transitions which are well resolved (Fig. 9.20). Typically, $\Delta_1 \approx 10\,000\text{ cm}^{-1}$, $\Delta_3 \approx 18\,000\text{--}19\,500\text{ cm}^{-1}$ and $\Delta_4 \approx 26\,000\text{ cm}^{-1}$ so that the LS system is coloured (purple). In contrast, the HS system exhibits only the single spin-allowed $d-d$ transition $\Delta_5 = {}^5T_2 \rightarrow {}^5E$ with a typical value of $\Delta_5 \approx 12\,000\text{ cm}^{-1}$, which implies that the HS system is colourless (no low-lying metal-to-ligand charge-transfer transitions are assumed).

Upon thermal treatment the high-spin mole fraction increases in accordance with the formula

TABLE 9.9

Factors influencing spin crossover

Influence	Response
increasing temperature	LS to HS transition at T_c
increasing pressure	T_c increases; HS to LS relaxation rate increases
increasing dilution	T_c decreases when the host lattice is bigger
increasing magnetic field	T_c decreases slightly
temperature drift	rapid cooling may freeze the HS state; $T_c^\downarrow$ decreases
temperature cycling	reproducibility of the hysteresis curve increases
light irradiation	LIESST effect: generation of the HS state below T_c
isotope effect	T_c increases; effect on H-bonds
isomerism	different local symmetry; different H-bond networks
paramagnetic impurities	increase in the background susceptibility
presence of solvates	different H-bond networks; different separation of units
counterion substitution	different H-bond networks; different separation of units; different polarisability and permittivity
ligand substitution	different crystal field strength; different networks
increasing particle size	HS fraction increases at constant temperature
degree of milling	smoother transition curve; larger residual HS state
solvent variation	different abruptness and completeness
ligand dissociation	stabilisation of the HS state
deprotonation	stabilisation of the LS state

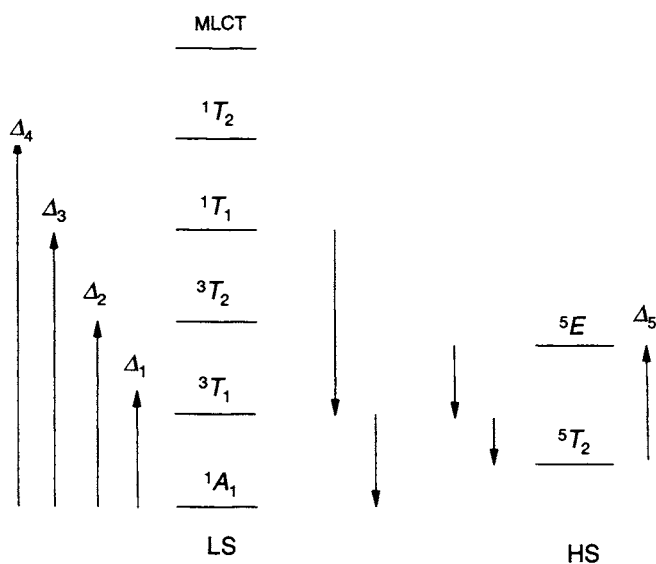


Fig. 9.20. Schematic drawing of energy levels in LS and HS iron(II) complexes.

$$x_{\text{HS}} = \frac{A(\text{HS})}{A(\text{HS}) + A(\text{LS})}$$

where the area fraction $A(\text{LS})$ corresponds to one of the reference absorption bands.

When the purple LS system, being below a thermal spin crossover, is irradiated by an appropriate monochromatic (laser) source, one of the excited states is generated, say $^1T_1$ using green light of $\tilde{\nu} = 19\,500\text{ cm}^{-1}$. A decay of this excited state proceeds through the $^1T_1 \rightarrow ^3T_1 \rightarrow ^5T_2$ pathway ($\Delta S = 1$) so that a metastable HS state is populated. Such a process is referred to as the *light-induced spin transition*. A further transition $^5T_2 \rightarrow ^1A_1$ is extremely slow at low temperature so that the HS state can survive for a long time at a temperature far below T_c of the thermal spin transition. For example, the lifetime of the $^5T_2$ state for the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ complex is ca 40 days at 10 K. Such a phenomenon is termed the *LIESST* (Light Induced Excited Spin State Trapping) effect (see Fig. 9.21). The electron spectrum of the LIESST-generated colourless HS state is identical with that characteristic of the thermally induced HS state (a single $^5T_2 \rightarrow ^5E$ band at $\Delta_5 \approx 12\,200\text{ cm}^{-1}$).

When the colourless crystal in the LIESST-generated HS state is subsequently irradiated by a monochromatic red light of $\tilde{\nu} = 12\,200\text{ cm}^{-1}$, the excited state ^5E of the HS complex is generated. Its decay proceeds through the $^5E \rightarrow ^3T_1 \rightarrow ^1A_1$ pathway and results in the reappearance of the purple LS system. This is referred to as the *reverse LIESST effect*. The electron spectrum of the reverse-LIESST-generated LS state is almost identical to that of the starting LS system at the beginning of the experiment [7].

Spin crossover systems can be utilised for data recording if the following requirements are fulfilled [8]:

- (1) abruptness of the SC, ideally within 5 K;
- (2) transition temperatures close to room temperature;
- (3) thermal hysteresis of the SC, the ideal hysteresis width being $T_c^\uparrow - T_c^\downarrow = 50\text{ K}$;

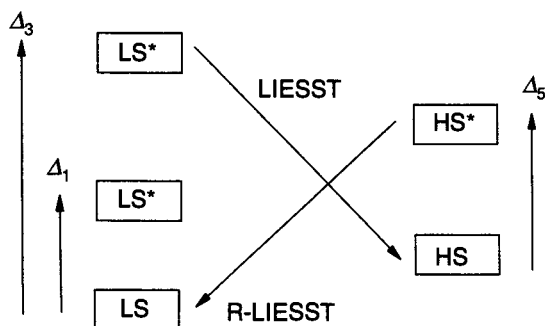


Fig. 9.21. A scheme of the LIESST and reverse LIESST effects.

- (4) thermochromism—a colour change during SC (e.g. LS—purple, HS—colourless) with a pronounced contrast;
- (5) sufficient stability against oxidation and humidity;
- (6) reproducibility of the writing/erasing cycles.

A pronounced change in the absorption spectrum which accompanies the spin transition can be utilised to select an appropriate optical response function (e.g. a difference between HS and LS absorption at a certain wavenumber). The optical response function possesses a shape which copies the shape of the (χT) versus T curve of the magnetic measurements, including the hysteresis width. The hysteresis is utilised as an information-keeping function (memory effect).

SUMMARY

1. Spin crossover (a low-spin to high-spin transition) occurs in many d^4 to d^7 metal complexes and dominates just for iron(II) compounds. It can be monitored by several experimental techniques among which magnetic susceptibility measurements are the most informative.
2. The high-spin mole fraction as a function of temperature can adopt several different profiles: abrupt/gradual, complete/incomplete, one-step/two-step, and with/without hysteresis.
3. Spin crossover is associated with a positive enthalpy change and positive entropy change; thus the change in the Gibbs energy alters the sign at the critical temperature above which the high-spin species becomes thermodynamically more stable. There are several macroscopic (thermodynamic) and microscopic models of spin crossover. Among them the regular solution model and the two-level Ising-like model are formally equivalent. Both deal with the cooperativity parameters which, above a critical value, are responsible for the hysteresis effect. A non-linear dependence of the equilibrium constant of the low-spin to high-spin transition versus inverse temperature (the Arrhenius plot) originates in the non-zero cooperativity parameter.
4. Two-step spin crossover and spin crossover in dinuclear compounds has roots in a proper combination of the inter-sublattice interaction parameter (which is ferromagnetic) and the intra-sublattice one (antiferromagnetic).
5. A large number of different factors influence spin crossover. In addition to temperature-induced spin crossover, light-induced spin transition is also known; this is the basis of the LIESST and reverse-LIESST effects, respectively. Of great interest is the utilisation of thermal hysteresis for data recording and construction of display units.

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Dinuclear Systems

10.1 EXCHANGE INTERACTION

10.1.1 Dominant terms

The essence of exchange interaction is the formation of a weak bond between magnetic moments which may be spread over quite distant centres. Several types of exchange interaction are distinguished (Table 10.1); however, a sharp border between them does not exist [1].

The spin Hamiltonian that describes the exchange interaction in a dinuclear system is

$$\hat{H}_{AB}^{(2)} = -\frac{1}{2} \vec{S}_A \cdot \vec{\overline{D}} \cdot \vec{S}_B [\hbar^{-2}] = \vec{S}_A \cdot \vec{\overline{D}'} \cdot \vec{S}_B [\hbar^{-2}]$$

The Cartesian spin-spin interaction tensor $\vec{\overline{D}'}$, however, can be decomposed into its irreducible components and the spin Hamiltonian rewritten as follows

$$\hat{H}_{AB}^{(2)} = [J'(\vec{S}_A \cdot \vec{S}_B) + \vec{d} \cdot (\vec{S}_A \times \vec{S}_B) + \vec{S}_A \cdot \vec{\overline{D}_0} \cdot \vec{S}_B][\hbar^{-2}]$$

where the first term represents an *isotropic exchange*, the second an *antisymmetric exchange*, and the last an *asymmetric exchange* with:

(1) the scalar (a constant)

$$J' = \frac{1}{3} \text{Tr}(\mathbf{D}') = \frac{1}{3} (D'_{xx} + D'_{yy} + D'_{zz})$$

(2) an antisymmetric vector

$$d_{ab} = \frac{1}{2} (D'_{ab} - D'_{ba}) = -d_{ba}$$

TABLE 10.1
Types of exchange interaction

Type	Nature
1. direct exchange	coupling of localized magnetic moments in insulators through space
2. superexchange	coupling of localized magnetic moments in insulators through diamagnetic groups
3. indirect exchange	coupling of localized magnetic moments in metals with the conduction electrons
4. itinerant exchange	coupling of itinerant electrons in metals
5. double exchange	coupling of two localized magnetic moments through an itinerant electron

(3) and a traceless symmetric tensor

$$D_{0,ab} = \frac{1}{2}(D'_{ab} + D'_{ba}) - J' = D_{0,ba}$$

In the simplest case of isotropic exchange one has

$$\hat{H}_{AB}^{(2)} \approx J'(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}] = -J(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}] = -2J''(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}]$$

(One should be careful in the definition of the constant factor since other numerical and sign conventions are frequent.) Hereafter $\hat{H}_{AB}^{(2)} = -J(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}]$ is assumed.

Restricting ourselves only to pair interactions, the spin Hamiltonian appropriate for the isotropic exchange interaction in polynuclear systems becomes

$$\hat{H}_{\text{poly}}^{(2)} = \sum_A^N \sum_{B < A}^N -J_{AB}(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}]$$

where we adopt one of the possible conventions for the sign and a numerical factor in front of the isotropic exchange constants. The number of magnetic energy levels varies from a few ($M = 2^2 = 4$ for two centres with $S_A = S_B = 1/2$) to several millions ($M = 6^8$ for eight centres with $S_A = 5/2$). The spacing of the magnetic energy levels (density of states) is predetermined by the values of the exchange constants; for J small enough (say $|J| < 5 \text{ cm}^{-1}$) there would be a dense spacing of magnetic energy levels. Thus one can expect that the substance will exhibit a non-linear magnetic

behaviour where the difference between the mean and differential susceptibilities could be substantial.

The spin-spin interaction is not necessarily restricted to quadratic terms in the spin operators. Higher-order terms could be considered, among which the (isotropic) *biquadratic exchange* reads

$$\hat{H}_{AB}^{(4)} = -j(\vec{S}_A \cdot \vec{S}_B)^2[\hbar^{-4}]$$

The terms of exchange interaction are collected in Table 10.2.

10.1.2 Nature of exchange interaction

The Hamiltonian terms that enter the spin-spin interaction tensor $\overline{\overline{D}}$ were derived in Chapter 4. The relevant contributions are:

(1) spin-(own)orbit interaction

$$\hat{H}^{\text{so}} = \hat{H}_N^{1a}(3) = -i \sum_i \sum_N \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 g' Z_N \hat{k}_0^2(\vec{r}_{Ni}) \frac{1}{r_{Ni}^3} \vec{S}_i \cdot (\vec{r}_{Ni} \times \vec{\nabla}_i)$$

(2) spin-other orbit interaction

$$\hat{H}^{\text{soo}} = \hat{H}_{12}^c(1a) = i \sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 g' \frac{1}{r_{ij}^3} \vec{S}_i \cdot (\vec{r}_{ij} \times \vec{\nabla}_j)$$

(3) electron-electron spin-orbit interaction

$$\hat{H}^{\text{eeso}} = \hat{H}_{12}^b(2) = i \sum_i \sum_{j \neq i} \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 g' \frac{1}{r_{ij}^3} \vec{S}_i \cdot (\vec{r}_{ji} \times \vec{\nabla}_i)$$

TABLE 10.2
Terms of exchange interaction

Term	Hamiltonian	Parameters
dinuclear exchange	$\hat{H} = \vec{S}_A \cdot \overline{\overline{D}}' \cdot \vec{S}_B[\hbar^{-2}]$	$\overline{\overline{D}}'$
isotropic exchange	$\hat{H} = J'(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}]$ $= -J(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}]$	$J' = \frac{1}{3}\text{Tr}(\overline{\overline{D}}') = \frac{1}{3}(D'_{xx} + D'_{yy} + D'_{zz})$
antisymmetric exchange	$\hat{H} = \vec{d} \cdot (\vec{S}_A \times \vec{S}_B)[\hbar^{-2}]$	$d_{ab} = \frac{1}{2}(D'_{ab} - D'_{ba}) = -d_{ba}$
asymmetric exchange	$\hat{H} = \vec{S}_A \cdot \overline{\overline{D}}_0 \cdot \vec{S}_B[\hbar^{-2}]$	$D_{0,ab} = \frac{1}{2}(D'_{ab} + D'_{ba}) - J' = D_{0,ba}$
biquadratic exchange	$\hat{H} = -j(\vec{S}_A \cdot \vec{S}_B)^2[\hbar^{-4}]$	j

(4) spin-spin dipolar interaction

$$\hat{H}^{\text{dip}} = \hat{H}_{12}^c(2) = \sum_i \sum_{j < i} \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 4 \left[\frac{1}{r_{ij}^3} (\vec{s}_i \cdot \vec{s}_j) - \frac{3}{r_{ij}^5} (\vec{s}_i \cdot \vec{r}_{ji})(\vec{s}_j \cdot \vec{r}_{ji}) \right]$$

(5) spin-spin contact interaction

$$\hat{H}^{\text{con}} = \hat{H}_{12}^c(3) = - \sum_i \sum_{j < i} \left(\frac{\mu_0}{4\pi} \right) \mu_B^2 \frac{32\pi}{3} \delta(\vec{r}_{ji}) \vec{s}_i \cdot \vec{s}_j$$

where the symbols used (with dimensionless spin operators) were defined in Table 4.6. One then has a first-order contribution (by means of perturbation theory) where the spin-spin dipolar and spin-spin contact terms contribute

$$E_{ij}^{(1)} = \langle \Psi_0 | (\hat{H}_{ij}^{\text{dip}} + \hat{H}_{ij}^{\text{con}}) | \Psi_0 \rangle = -\frac{1}{2} \vec{s}_i \cdot \overline{\vec{D}}_{ij}^{(1)} \cdot \vec{s}_j$$

and a second-order contribution where the spin-orbit terms appear

$$\begin{aligned} E_{ij}^{(2)} &= \sum_{K=1}^{\infty} \frac{\langle \Psi_0 | (\hat{H}_{ij}^{\text{so}} + \hat{H}_{ij}^{\text{soo}} + \hat{H}_{ij}^{\text{eso}}) | \Psi_K \rangle \langle \Psi_K | (\hat{H}_{ij}^{\text{dip}} + \hat{H}_{ij}^{\text{con}} + \hat{H}_{ij}^{\text{eso}}) | \Psi_0 \rangle}{E_0 - E_K} \\ &= -\frac{1}{2} \vec{s}_i \cdot \overline{\vec{D}}_{ij}^{(2)} \cdot \vec{s}_j \end{aligned}$$

It is assumed that the spin-(own)orbit term and the dipolar term are dominating. The interelectron terms contain a factor of

$$F = \frac{\mu_0}{4\pi} \mu_B^2 g^2 r_{ij}^{-3}$$

When the distances are given in atomic units (1 bohr = 0.529 Å = 0.529 × 10⁻¹⁰ m), then (F/hc) = 0.256 cm⁻¹ and rapidly escapes with increasing distance.

An estimate of the dipolar contribution can be made as follows. For separated spins (spin magnetic moments) the classical expression for the interaction energy between two magnetic moments is

$$E_{AB}^{\text{dip}} = \frac{\mu_0}{4\pi} \frac{r_{AB}^2 \vec{\mu}_A \cdot \vec{\mu}_B - 3(\vec{\mu}_A \cdot \vec{r}_{AB})(\vec{\mu}_B \cdot \vec{r}_{AB})}{r_{AB}^5}$$

for

$$\vec{\mu}_A = -g_A \mu_B \vec{s}_A [\hbar^{-1}]$$

yielding the D' -tensor components

$$D'_{ABab} = \frac{\mu_0}{4\pi} g_A g_B \mu_B^2 \left\langle \Psi_0 \left| \frac{r_{AB}^2 \delta_{ab} - 3r_{ABa} r_{ABb}}{r_{AB}^5} \right| \Psi_0 \right\rangle_{\text{space}}$$

At a distance of $5 \text{ \AA}$ (9.45 bohr) the numerical factor brings only $(F/hc) = 3.03 \times 10^{-4} \text{ cm}^{-1}$. However, there are many neighbours in the solid state: an inclusion of localised dipolar interactions between a magnetic centre and the rest of 250 atoms within $5 \times 5 \times 5$ cubic cells brings $(J^{\text{dip}}/hc) = 0.488 \text{ cm}^{-1}$, whereas the interaction with 2000 atoms within $10 \times 10 \times 10$ cubic cells yields $(J^{\text{dip}}/hc) = 0.727 \text{ cm}^{-1}$.

10.1.3 Magnetic orbitals

In analysing the exchange interaction the concept of magnetic orbitals is useful [2]. Under the magnetic orbitals we assume the basis set functions (appropriate localised orbitals) centred at different centres which obey the characteristic equations

$$(\hat{T}_1 + \hat{V}_{A1})|\varphi_A(1)\rangle = \varepsilon_A|\varphi_A(1)\rangle$$

$$(\hat{T}_1 + \hat{V}_{B1})|\varphi_B(1)\rangle = \varepsilon_B|\varphi_B(1)\rangle$$

and analogously for the second electron

$$(\hat{T}_2 + \hat{V}_{A2})|\varphi_A(2)\rangle = \varepsilon_A|\varphi_A(2)\rangle$$

$$(\hat{T}_2 + \hat{V}_{B2})|\varphi_B(2)\rangle = \varepsilon_B|\varphi_B(2)\rangle$$

The magnetic orbitals either can form an orthogonal set or they have a non-zero overlap integral

$$s = \langle \varphi_A(1) | \varphi_B(1) \rangle = \langle \varphi_A(2) | \varphi_B(2) \rangle$$

whereas they are normalised

$$1 = \langle \varphi_A(1) | \varphi_A(1) \rangle = \langle \varphi_B(1) | \varphi_B(1) \rangle$$

The total Hamiltonian of a dinuclear system (in the Born–Oppenheimer approximation when the nuclear motion is frozen) becomes

$$\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{V}_{A1} + \hat{V}_{A2} + \hat{V}_{B1} + \hat{V}_{B2} + \hat{V}_{12} + (\hat{V}_{AB})$$

The last term describes an internuclear repulsion which does not operate on the electron variables; it is omitted hereafter.

The total electronic wave function consists of the spatial and the spin parts

$$\Psi(1, 2) = \Theta(1, 2)\chi(S, M_S)$$

The spin part describes either a spin singlet

$$\chi(0, 0) = [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$$

or a spin triplet

$$\chi(1, +1) = \alpha(1)\alpha(2)$$

$$\chi(1, 0) = [\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}$$

$$\chi(1, -1) = \beta(1)\beta(2)$$

In constructing the spatial part of the electronic wave function the Valence-Bond (VB) method is useful. This method (similar to the Heitler-London approach) postulates that a linear combination of several product functions (called “covalent structures” or “ionic structures”) is appropriate

$$\Theta(1, 2) = C_1\Phi_1 + C_2\Phi_2 + \dots$$

When only the “covalent structures” are involved

$$\Phi_1 = \varphi_A(1)\varphi_B(2)$$

$$\Phi_2 = \varphi_B(1)\varphi_A(2)$$

we speak of a *Limited VB method* (LVB). For equivalent centres the symmetry arguments imply

$$|C_1| = |C_2|$$

Consequently two normalised, symmetry-adapted spatial functions result

$$\Theta_1(^1\Gamma_g) = (\Phi_1 + \Phi_2)[2(1 + s^2)]^{-1/2}$$

$$\Theta_2(^3\Gamma_u) = (\Phi_1 - \Phi_2)[2(1 - s^2)]^{-1/2}$$

The matrix elements of the total Hamiltonian among the product functions are

$$h_{11} = \langle \Phi_1 | \hat{H} | \Phi_1 \rangle = \langle \Phi_2 | \hat{H} | \Phi_2 \rangle = 2\varepsilon_0 + 2\alpha + j$$

and

$$h_{12} = \langle \Phi_1 | \hat{H} | \Phi_2 \rangle = \langle \Phi_2 | \hat{H} | \Phi_1 \rangle = 2\varepsilon_0 s^2 + 2\beta s + k$$

with

$$\varepsilon_0 = \varepsilon_A = \varepsilon_B$$

where we introduce the following integrals

(a) one-electron, two-centre Coulomb integral (negative)

$$\alpha = \langle \varphi_A(1) | \hat{V}_{B1} | \varphi_A(1) \rangle = \langle \varphi_B(1) | \hat{V}_{A1} | \varphi_B(1) \rangle$$

(b) one-electron, two-centre resonance integral (negative)

$$\begin{aligned} \beta &= \langle \varphi_A(1) | \hat{V}_{B1} | \varphi_B(1) \rangle = \langle \varphi_B(1) | \hat{V}_{B1} | \varphi_A(1) \rangle \\ &= \langle \varphi_A(1) | \hat{V}_{A1} | \varphi_B(1) \rangle = \langle \varphi_B(1) | \hat{V}_{A1} | \varphi_A(1) \rangle \end{aligned}$$

(c) two-electron, two-centre Coulomb integral (positive)

$$j = \langle \varphi_A(1)\varphi_B(2) | \hat{V}_{12} | \varphi_A(1)\varphi_B(2) \rangle$$

(d) two-electron, two-centre exchange integral (positive)

$$k = \langle \varphi_A(1)\varphi_B(2) | \hat{V}_{12} | \varphi_A(2)\varphi_B(1) \rangle$$

For completeness, we introduce two remaining integrals which will be met later, namely

(e) two-electron, one-centre Coulomb integral (positive)

$$j_0 = \langle \varphi_A(1)\varphi_A(2) | \hat{V}_{12} | \varphi_A(1)\varphi_A(2) \rangle$$

(f) two-electron, two-centre hybrid integral (positive)

$$h = \langle \varphi_A(1)\varphi_A(2) | \hat{V}_{12} | \varphi_A(1)\varphi_B(2) \rangle$$

The secular equation to be fulfilled reads

$$\det \begin{pmatrix} h_{11} - E & h_{12} - Es_{12} \\ h_{12} - Es_{12} & h_{11} - E \end{pmatrix} = 0$$

having the solutions

$$E_{1,2} = \frac{h_{11} \pm h_{12}}{1 \pm s_{12}}$$

The non-orthogonality integral reduces to

$$s_{12} = \langle \varphi_A(1)\varphi_B(2) | \varphi_B(1)\varphi_A(2) \rangle = s^2$$

and the solutions are explicitly expressed as follows

$$E_1(^1\Gamma_g) = (V_{AB}) + 2\varepsilon_0 + \frac{2\alpha + j + 2\beta s + k}{1 + s^2}$$

and

$$E_2(^3\Gamma_u) = (V_{AB}) + 2\varepsilon_0 + \frac{2\alpha + j - 2\beta s - k}{1 - s^2}$$

The energy difference of the singlet and triplet states defines the exchange coupling constant

$$J(\text{LVB}) = E_1(^1\Gamma_g) - E_2(^3\Gamma_u) = \frac{2k - 4\alpha s^2 + 4\beta s - 2js^2}{1 - s^4}$$

Since

$$s^4 \ll 1$$

this factor can be neglected and hence the exchange coupling constant becomes expressed as

$$J(\text{LVB}) \approx (2k - 4\alpha s^2) + (4\beta s - 2js^2) = J_f + J_a$$

Normally the second term dominates; it is negative and brings an antiferromagnetic contribution to the exchange coupling constant

$$J_a = 4\beta s - 2js^2 < 0$$

The first term, on the other hand, is positive, yielding a ferromagnetic contribution

$$J_f = 2k - 4\alpha s^2 > 0$$

The ferromagnetic term of the coupling constant can dominate only when the overlap integral in J_a is low; this is well fulfilled for orthogonal orbitals. Thus the unpaired electrons can reside on the orthogonal orbitals, as is documented by simple systems like free Mn^{2+} ion (five unpaired electrons) or O_2 molecule (two unpaired electrons). However, the exchange integral

$$k = \left\langle \varphi_A(1)\varphi_B(2) \left| \hat{V}_{12} \right| \varphi_A(2)\varphi_B(1) \right\rangle = \int \int_{V_1 V_2} \hat{V}_{12} \rho^*(2)\rho(1) dV_1 dV_2$$

should adopt a certain magnitude which requires a considerable overlap density

$$\rho(1) = \varphi_A^*(1)\varphi_B(1)$$

somewhere in the internuclear space.

In addition to the “covalent structures” one can include the “ionic structures” (sometimes called the charge-transfer configurations)

$$\Phi_3 = \varphi_A(1)\varphi_A(2)$$

$$\Phi_4 = \varphi_B(1)\varphi_B(2)$$

A linear combination of four product functions (Φ_1 to Φ_4) will yield four spatial wave functions: $\Theta_a(^1\Gamma_g)$, $\Theta_b(^3\Gamma_u)$, $\Theta_c(^1\Gamma_u)$ and $\Theta_d(^1\Gamma_g)$. Because of the symmetry arguments, only $\Theta_a(^1\Gamma_g)$ and $\Theta_d(^1\Gamma_g)$ arise from the mixing of the configurations

$$\Theta_a(^1\Gamma_g) = N_a[(\Phi_1 + \Phi_2) + \lambda_a(\Phi_3 + \Phi_4)]$$

$$\Theta_b(^3\Gamma_u) = \Theta_2(^3\Gamma_u) = N_b(\Phi_1 - \Phi_2) = (\Phi_1 - \Phi_2)[2(1 - s^2)]^{-1/2}$$

$$\Theta_c(^1\Gamma_u) = \Theta_3(^1\Gamma_u) = N_c[(\Phi_3 - \Phi_4)] = (\Phi_3 - \Phi_4)[2(1 - s^2)]^{-1/2}$$

$$\Theta_d(^1\Gamma_g) = N_d[(\Phi_1 + \Phi_2) + \lambda_d(\Phi_3 + \Phi_4)]$$

The remaining matrix elements among the product functions for the complete solution are expressed as follows

$$h_{33} = \left\langle \Phi_3 \left| \hat{H} \right| \Phi_3 \right\rangle = \left\langle \Phi_4 \left| \hat{H} \right| \Phi_4 \right\rangle = 2\varepsilon_0 + 2\alpha + j_0$$

$$h_{34} = \left\langle \Phi_3 \left| \hat{H} \right| \Phi_4 \right\rangle = 2\varepsilon_0 s^2 + 2\beta s + k$$

and

$$\begin{aligned} h_{13} &= \langle \Phi_1 | \hat{H} | \Phi_3 \rangle = \langle \Phi_2 | \hat{H} | \Phi_3 \rangle = \langle \Phi_1 | \hat{H} | \Phi_4 \rangle = \langle \Phi_2 | \hat{H} | \Phi_4 \rangle \\ &= 2\varepsilon_0 s + \alpha s + \beta + h \end{aligned}$$

Then the secular equation adopts the form of

$$\det \begin{pmatrix} h_{11} - E & h_{12} - Es^2 & h_{13} - Es & h_{13} - Es \\ h_{12} - Es^2 & h_{11} - E & h_{13} - Es & h_{13} - Es \\ h_{13} - Es & h_{13} - Es & h_{33} - E & h_{34} - Es^2 \\ h_{13} - Es & h_{13} - Es & h_{34} - Es^2 & h_{33} - E \end{pmatrix} = 0$$

A truncated problem within the “ionic structures”

$$\det \begin{pmatrix} h_{33} - E & h_{34} - Es^2 \\ h_{34} - Es^2 & h_{33} - E \end{pmatrix} = 0$$

has the solutions

$$E_{3,4} = \frac{h_{33} \pm h_{34}}{1 \pm s^2}$$

and explicitly

$$E_3(^1\Gamma_g) = (V_{AB}) + 2\varepsilon_0 + \frac{2\alpha + j_0 + 2\beta s + k}{1 + s^2}$$

$$E_4(^1\Gamma_u) = (V_{AB}) + 2\varepsilon_0 + \frac{2\alpha + j_0 - 2\beta s - k}{1 - s^2}$$

Then the energy separation of the two $^1\Gamma_g$ states before their “interaction” or mixing is

$$\Delta = E_3 - E_1 = \frac{j_0 - j}{1 + s^2} > 0$$

The off-diagonal matrix element connecting these states can be evaluated with the help of the wave functions

$$\Theta_1(^1\Gamma_g) = (\Phi_1 + \Phi_2)[2(1 + s^2)]^{-1/2}$$

$$\Theta_3(^1\Gamma_g) = (\Phi_3 + \Phi_4)[2(1 + s^2)]^{-1/2}$$

as follows

$$\begin{aligned} H_{13} &= \langle \Theta_1 | \hat{H} | \Theta_3 \rangle = \langle (\Phi_1 + \Phi_2) | \hat{H} | (\Phi_3 + \Phi_4) \rangle [2(1 + s^2)]^{-1} \\ &= \frac{4h_{13}}{2(1 + s^2)} \end{aligned}$$

and the non-orthogonality integral is

$$S_{13} = \langle \Theta_1 | \Theta_3 \rangle = \frac{4s}{2(1 + s^2)}$$

The secular equation in the new basis set of symmetry-adapted VB-functions Θ_1 , Θ_3 , Θ_2 and Θ_4 is

$$\det \begin{pmatrix} E_1 - E & H_{13} - S_{13}E & 0 & 0 \\ H_{13} - S_{13}E & E_3 - E & 0 & 0 \\ 0 & 0 & E_2 - E & 0 \\ 0 & 0 & 0 & E_4 - E \end{pmatrix} = 0$$

and hence the quadratic equation

$$(E_1 - E)(E_3 - E) - (H_{13} - S_{13}E)^2 = 0$$

determines the two energies of the $^1\Gamma_g$ states (Fig. 10.1)

$$\begin{aligned} E_{a,d} &= \frac{E_3 + E_1 - 2H_{13}S_{13} \pm \sqrt{(E_3 + E_1 - 2H_{13}S_{13})^2 - 4(1 - S_{13}^2)(E_1E_3 - H_{13}^2)}}{2(1 - S_{13}^2)} \\ &= \frac{E_3 + E_1 - 2H_{13}S_{13} \pm \sqrt{(E_3 - E_1)^2 + 4(H_{13} - S_{13}E_3)(H_{13} - S_{13}E_1)}}{2(1 - S_{13}^2)} \end{aligned}$$

For small “interaction”, when

$$\Delta^2 \gg |4(H_{13} - S_{13}E_3)(H_{13} - S_{13}E_1)|$$

the expansion of the square root is possible according to the formula

$$\sqrt{1+x} = 1 + \frac{x}{2} - \dots$$

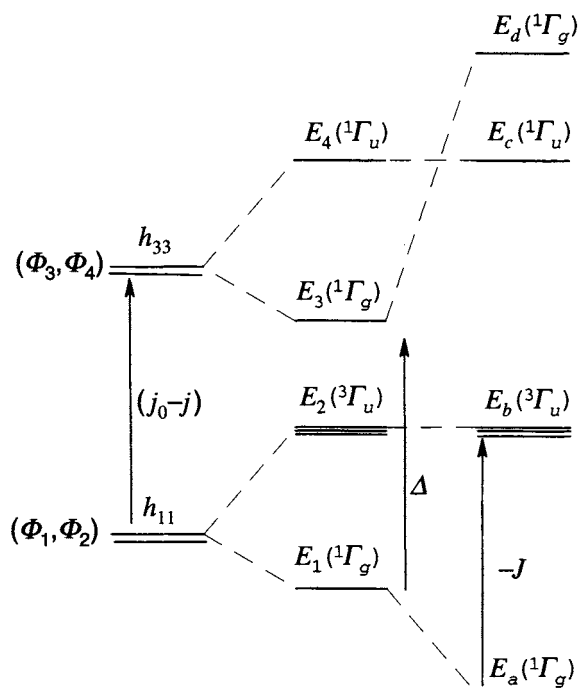


Fig. 10.1. Energy terms for the natural (non-orthogonal) magnetic orbitals via the VB method.

yielding

$$\begin{aligned}
 & \sqrt{\Delta^2 + 4(H_{13} - S_{13}E_3)(H_{13} - S_{13}E_1)} \\
 &= \Delta \sqrt{1 + \frac{4(H_{13} - S_{13}E_3)(H_{13} - S_{13}E_1)}{\Delta^2}} \\
 &= \Delta \left[1 + \frac{4(H_{13} - S_{13}E_3)(H_{13} - S_{13}E_1)}{2\Delta^2} \dots \right] \\
 &\approx \Delta + \frac{2(H_{13} - S_{13}E_3)(H_{13} - S_{13}E_1)}{\Delta}
 \end{aligned}$$

Finally, the energy of the lowest singlet state is

$$\begin{aligned}
 E_a(¹\Gamma_g) &\approx \frac{E_1 - H_{13}S_{13}}{1 - S_{13}^2} - \frac{(H_{13} - S_{13}E_1)(H_{13} - S_{13}E_3)}{\Delta(1 - S_{13}^2)} \\
 &= E_1 - \frac{(H_{13} - S_{13}E_1)^2}{\Delta(1 - S_{13}^2)}
 \end{aligned}$$

and, after substituting for H_{13} and S_{13} , one gets

$$E_a(^1\Gamma_g) \approx E_1 - \frac{4(h_{13} - sE_1)^2}{\Delta(1-s^2)^2}$$

Finally

$$E_a(^1\Gamma_g) \approx (V_{AB}) + 2\varepsilon_0 + \frac{2\alpha + j + 2\beta s + k}{1+s^2} - \frac{4[(\beta - \alpha s)(1-s^2) + h(1+s^2) - (j+k)s]^2}{\Delta(1-s^2)^2(1+s^2)^2}$$

As a consequence of the lowering of the $^1\Gamma_g$ state (after the “interaction” with the “ionic structures”) the exchange coupling constant relaxes to

$$J(\text{VB}) = E_a(^1\Gamma_g) - E_b(^3\Gamma_u) \approx \frac{2k - 4\alpha s^2 + 4\beta s - 2js^2}{1-s^4} - \frac{4}{j_0 - j} \frac{[(\beta - \alpha s)(1-s^2) + h(1+s^2) - (j+k)s]^2}{(1-s^2)^2(1+s^2)}$$

The last term (including its minus sign) is necessarily negative and brings an additional contribution to the antiferromagnetic term [3].

In practice two types of magnetic orbitals are distinguished:

- (a) *natural magnetic orbitals* (NMO), which form a non-orthogonal set; these are represented by appropriate atomic orbitals, hybrid orbitals or localised orbitals;
- (b) *orthogonalised magnetic orbitals* (OMO); these can be constructed from ordinary molecular orbitals by certain localisation schemes (the localisation, however, is only approximate and those orbitals have some tails on the counter-centre).

Due to the vanishing overlap integral for the orthogonalised magnetic orbitals, the expression for the exchange coupling constant simplifies to

$$J(\text{OMO}) = 2k - \frac{4(\beta + h)^2}{j_0 - j}$$

However, the integrals have a different meaning and different values as compared to the case of the natural magnetic orbitals. For a large energy gap between the “covalent” and “ionic” structures, $\Delta = j_0 - j$, the antiferromagnetic term in $J_a(\text{OMO})$ disappears and the only surviving contribution is the ferromagnetic term $J_f(\text{OMO}) = 2k$.

10.1.4 Molecular orbital approach

In the simplest case there are two localised “magnetically active” orbitals φ_A and φ_B that can be combined into two molecular orbitals (MO)

$$\phi_g(i) = (2 + 2s)^{-1/2}[\varphi_A(i) + \varphi_B(i)]$$

$$\phi_u(i) = (2 - 2s)^{-1/2}[\varphi_A(i) - \varphi_B(i)]$$

The basis set orbitals are normalised but non-orthogonal, i.e.

$$1 = \langle \varphi_A | \varphi_A \rangle = \langle \varphi_B | \varphi_B \rangle$$

$$s = \langle \varphi_A | \varphi_B \rangle = \langle \varphi_B | \varphi_A \rangle$$

Their different occupation by electron defines the six electron configurations: $(\phi_g)^2$, $(\phi_g)^\uparrow(\phi_u)^\uparrow$, $(\phi_g)^\uparrow(\phi_u)^\downarrow$, $(\phi_g)^\downarrow(\phi_u)^\uparrow$, $(\phi_g)^\downarrow(\phi_u)^\downarrow$ and $(\phi_u)^2$. The corresponding spatial parts of the electronic wave functions are expressed as follows

$$\begin{aligned}\Theta_1(\Gamma_g) &= \phi_g(1)\phi_g(2) \\ &= (2 + 2s)^{-1} \{ [\varphi_A(1)\varphi_B(2) + \varphi_B(1)\varphi_A(2)] \\ &\quad + [\varphi_A(1)\varphi_A(2) + \varphi_B(1)\varphi_B(2)] \} \\ &= (2 + 2s)^{-1} \{ \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 \}\end{aligned}$$

$$\begin{aligned}\Theta_2(\Gamma_u) &= \phi_g(1)\phi_u(2) = (2 + 2s)^{-1/2}(2 - 2s)^{-1/2} \\ &\quad \times \{ [\varphi_A(1)\varphi_B(2) - \varphi_B(1)\varphi_A(2)] - [\varphi_A(1)\varphi_A(2) - \varphi_B(1)\varphi_B(2)] \} \\ &= [4(1 - s^2)]^{-1/2} \{ \Phi_1 - \Phi_2 - \Phi_3 + \Phi_4 \}\end{aligned}$$

$$\begin{aligned}\Theta_3(\Gamma_g) &= \phi_u(1)\phi_u(2) \\ &= (2 - 2s)^{-1} \{ [\varphi_A(1)\varphi_B(2) + \varphi_B(1)\varphi_A(2)] \\ &\quad - [\varphi_A(1)\varphi_A(2) + \varphi_B(1)\varphi_B(2)] \} \\ &= (2 - 2s)^{-1} \{ \Phi_1 + \Phi_2 - \Phi_3 - \Phi_4 \}\end{aligned}$$

A comparison with the VB method shows that the MO method includes both the “covalent structures” (Φ_1 , Φ_2) and the “ionic structures” (Φ_3 , Φ_4), but with the same weights. This leads to a drawback which will be discussed later.

The full molecular wave function is given by the antisymmetrised product (a Slater determinant), for instance

$$\begin{aligned}
 \Psi_1(^1\Gamma_g) &= \hat{A}\{\phi_g(1)\alpha(1) \cdot \phi_g(2)\beta(2)\} \\
 &= (1/\sqrt{2})[\phi_g(1)\alpha(1) \cdot \phi_g(2)\beta(2) - \phi_g(2)\alpha(2) \cdot \phi_g(1)\beta(1)] \\
 &= [\phi_g(1)\phi_g(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)](1/\sqrt{2}) \\
 &= [\phi_g(1)\phi_g(2)]\chi(0, 0) = \Theta_1\chi(0, 0)
 \end{aligned}$$

and the corresponding energy becomes

$$\begin{aligned}
 E_1(^1\Gamma_g) &= \langle \Psi_1(^1\Gamma_g) | \hat{H} | \Psi_1(^1\Gamma_g) \rangle = \langle \Theta_1 | \hat{H} | \Theta_1 \rangle \\
 &= \langle \phi_g(1)\phi_g(2) | \hat{H} | \phi_g(1)\phi_g(2) \rangle
 \end{aligned}$$

The evaluation of this expression leads to the final formula

$$E_1(^1\Gamma_g) = (V_{AB}) + 2\varepsilon_0 + 2\frac{\alpha + \beta}{1 + s} + \frac{j_0 + j + 2k + 4h}{2(1 + s)^2}$$

where we have used the one-electron and two-electron integrals introduced above. Analogously, one gets

$$E_2(^3\Gamma_u) = (V_{AB}) + 2\varepsilon_0 + \frac{\alpha + \beta}{1 + s} + \frac{\alpha - \beta}{1 - s} + \frac{j_0 + j - 2k}{2(1 + s)(1 - s)}$$

and

$$E_3(^1\Gamma_g) = (V_{AB}) + 2\varepsilon_0 + 2\frac{\alpha - \beta}{1 - s} + \frac{j_0 + j + 2k - 4h}{2(1 - s)^2}$$

The exchange coupling constant evaluated at this level of approximation reads

$$J(\text{MO}) = E_1(^1\Gamma_g) - E_2(^3\Gamma_u) = \frac{2\beta - 2\alpha s}{(1 + s)(1 - s)} + \frac{2k + 2h(1 - s) - s(j_0 + j)}{(1 + s)^2(1 - s)}$$

which is a sum of the ferromagnetic

$$J_f = \frac{2k + 2h(1 - s) - 2\alpha s(1 + s)}{(1 + s)(1 - s^2)}$$

and antiferromagnetic

$$J_a = \frac{2\beta(1+s) - s(j_0 + j)}{(1+s)(1-s^2)}$$

contributions.

The main drawback of this simple MO approach lies in the fact that no proper limiting behaviour is obtained for separated atoms when the inter-nuclear distance is infinite

$$\lim_{R \rightarrow \infty} E_1(^1\Gamma_g) = \lim_{R \rightarrow \infty} E_2(^3\Gamma_u) = \lim_{R \rightarrow \infty} E_3(^1\Gamma_g) = 2\varepsilon_0 + j_0/2$$

This is a consequence of an unbalanced inclusion of the “ionic structures” by the simple MO method.

An improvement on the MO method is provided by the configuration interaction (CI) method which mixes (or allows to “interact”) the states of the same symmetry

$$\Psi^{CI} = C_1 \cdot \Psi_1(^1\Gamma_g) + C_3 \cdot \Psi_3(^1\Gamma_g)$$

The corresponding secular equation becomes

$$\det \begin{pmatrix} H_{11} - E & H_{13} - ES_{13} \\ H_{13} - ES_{13} & H_{33} - E \end{pmatrix} = 0$$

and owing to the orthogonality of the respective Slater determinants

$$S_{13} = \langle \Psi_1 | \Psi_3 \rangle = 0$$

it has the roots

$$E_{a,d}(^1\Gamma_g) = \frac{H_{11} + H_{33}}{2} \pm \sqrt{\left(\frac{H_{11} - H_{33}}{2}\right)^2 + H_{13}^2}$$

Here

$$H_{11} = E_1(^1\Gamma_g)$$

$$H_{33} = E_3(^1\Gamma_g)$$

and

$$H_{13} = \langle \Psi_1(^1\Gamma_g) | \hat{H} | \Psi_3(^1\Gamma_g) \rangle$$

The last “interaction” matrix element can be evaluated with the help of the Slater rules, yielding

$$H_{13} = \frac{j_0 - j}{2(1 - s^2)}$$

In the limit of the infinite internuclear separation we get

$$\lim_{R \rightarrow \infty} H_{13} = j_0/2$$

and now the roots are correctly separated

$$\lim_{R \rightarrow \infty} E_{a,d}(^1\Gamma_g) = (2\varepsilon_0 + j_0/2) \pm (j_0/2) = \begin{cases} 2\varepsilon_0 + j_0 \\ 2\varepsilon_0 \end{cases}$$

Second-order perturbation theory offers a simpler (but approximate) expression

$$E_a(^1\Gamma_g) \approx H_{11} - \frac{H_{13}^2}{H_{33} - H_{11}}$$

if

$$\Delta = H_{33} - H_{11} > |H_{13}|$$

is fulfilled.

To the second-order perturbative CI the exchange coupling constant becomes expressed as follows (Fig. 10.2)

$$\begin{aligned} J(\text{PCI}) &\approx J(\text{MO}) - \frac{H_{13}^2}{H_{33} - H_{11}} \\ &= \frac{2k + 2h(1 - s) - 2\alpha s(1 + s)}{(1 + s)(1 - s^2)} + \frac{2\beta(1 + s) - s(j_0 - j)}{(1 + s)(1 - s^2)} \\ &\quad + \left(\frac{j_0 - j}{2(1 - s^2)} \right)^2 \left[4 \frac{\beta - \alpha s}{1 - s^2} + 4 \frac{2h(1 + s^2) - s(j_0 + j + 2k)}{(1 - s^2)^2} \right]^{-1} \end{aligned}$$

In the limit of a vanishing overlap between the basis set orbitals one gets

$$J(\text{PCI}) = (2k + 2h) + 2\beta + \frac{1}{16} \frac{(j - j_0)^2}{\beta + 2h}$$

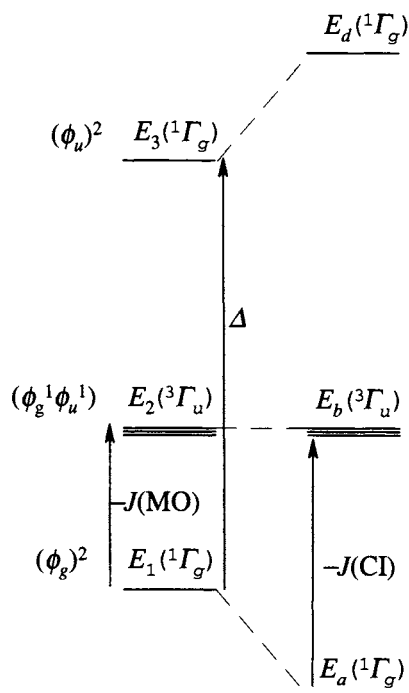


Fig. 10.2. Energy terms for the MO and MO+CI methods.

The complete MO+CI approach is fully equivalent to the complete VB method, as can be proven by substituting for the individual matrix elements. The VB approach, however, is superior since it already includes a part of the electron correlation energy, leading to a lower value of the total energy relative to the MO method. A comparison of these approaches is shown in Tables 10.3 and 10.4.

The above formulae of the LVB, VB, MO and MO+CI methods actually describe the bonding situation in the H_2 molecule when the basis set orbitals are represented by the atomic 1s orbitals.

10.1.5 Two-orbital model

The methodology of a direct evaluation of the exchange coupling constant is best demonstrated when the two-orbital model is reformulated: the MO calculation is done first, then a transformation to the orthogonalised magnetic orbitals is applied and finally a perturbative configuration interaction is used.

TABLE 10.3
Survey of the VB formulae

Product functions	$\Phi_1 = \varphi_A(1)\varphi_B(2)$, $\Phi_2 = \varphi_B(1)\varphi_A(2)$, $\Phi_3 = \varphi_A(1)\varphi_A(2)$, $\Phi_4 = \varphi_B(1)\varphi_B(2)$
Matrix elements $h_{ij} = \langle \Phi_i \hat{H} \Phi_j \rangle$	$h_{11} = h_{22} = (2\varepsilon_0) + 2\alpha + j$ $h_{12} = h_{34} = (2\varepsilon_0 s^2) + 2\beta s + k$ $h_{33} = h_{44} = (2\varepsilon_0) + 2\alpha + j_0$ $h_{13} = (2\varepsilon_0 s) + \alpha s + \beta + h$
Symmetry adapted functions	${}^1\Gamma_g, {}^3\Gamma_u : \Theta_{1,2} = [2(1 \pm s^2)]^{-1/2}(\Phi_1 \pm \Phi_2)$ ${}^1\Gamma_g, {}^1\Gamma_u : \Theta_{3,4} = [2(1 \pm s^2)]^{-1/2}(\Phi_3 \pm \Phi_4)$
LVB energies	$E_{1,2} = \frac{h_{11} \pm h_{12}}{1 \pm s^2} = (2\varepsilon_0) + \frac{2\alpha + j \pm 2\beta s \pm k}{1 \pm s^2}$ $E_{3,4} = \frac{h_{33} \pm h_{34}}{1 \pm s^2} = (2\varepsilon_0) + \frac{2\alpha + j_0 \pm 2\beta s \pm k}{1 \pm s^2}$
Interaction matrix elements $H_{ij} = \langle \Theta_i \hat{H} \Theta_j \rangle$	$H_{13} = \frac{2h_{13}}{1 + s^2}$ $S_{13} = \frac{2s}{1 + s^2}$
Coupling constant	$J(\text{LVB}) = \frac{2k - 4\alpha s^2}{1 - s^4} + \frac{4\beta s - 2js^2}{1 - s^4}$ $J(\text{VB}) \approx J(\text{LVB})$ $- \frac{4}{j_0 - j} \frac{[(\beta - \alpha s)(1 - s^2) + h(1 + s^2) - (j + k)s]^2}{(1 - s^2)^2(1 + s^2)}$

There are three relevant configuration functions in the case of a two-orbital model

$$\Psi_1({}^1\Gamma_g) = \begin{bmatrix} 0 \\ \uparrow\downarrow \end{bmatrix} = |\phi_1 \bar{\phi}_1|$$

$$\Psi_2({}^3\Gamma_u) = \begin{bmatrix} \uparrow \\ \uparrow \end{bmatrix} = |\phi_1 \phi_2|$$

$$\Psi_3({}^1\Gamma_g) = \begin{bmatrix} \uparrow\downarrow \\ 0 \end{bmatrix} = |\phi_2 \bar{\phi}_2|$$

The corresponding energies are expressed with the help of the Slater rules (the identical determinants) as follows

TABLE 10.4
Survey of the MO formulae

Molecular orbitals (LCAO)	$\phi_g(i) = (2 + 2s)^{-1/2}[\varphi_A(i) + \varphi_B(i)]$ $\phi_u(i) = (2 - 2s)^{-1/2}[\varphi_A(i) - \varphi_B(i)]$
Symmetry-adapted functions in terms of product functions	${}^1\Gamma_g : \Theta_{1,3} = [2(1 \pm s)]^{-1}[(\Phi_1 + \Phi_2) \pm (\Phi_3 + \Phi_4)]$ ${}^3\Gamma_u : \Theta_2 = [4(1 + s)(1 - s)]^{-1/2}[(\Phi_1 - \Phi_2) - (\Phi_3 - \Phi_4)]$
Energies in terms of MO and AO integrals	$E_1 = 2h_{11} + J_{11} = (2\varepsilon_0) + 2\frac{\alpha + \beta}{1 + s} + \frac{j_0 + j + 2k + 4h}{2(1 + s)^2}$ $E_2 = h_{11} + h_{22} + J_{12} = (2\varepsilon_0) + \frac{\alpha + \beta}{1 + s} + \frac{\alpha - \beta}{1 - s} + \frac{j_0 + j - 2k}{2(1 + s)(1 - s)}$ $E_3 = 2h_{22} + J_{22} = (2\varepsilon_0) + 2\frac{\alpha - \beta}{1 - s} + \frac{j_0 + j + 2k - 4h}{2(1 - s)^2}$
Energies in terms of VB integrals	$E_{1,3}^{\text{MO}} = \frac{1 + s^2}{(1 \pm s)^2} \frac{1}{2} [E_1^{\text{VB}} + E_3^{\text{VB}} \pm 2H_{13}^{\text{VB}}]$
Interaction matrix elements $H_{ij} = \langle \Theta_i \hat{H} \Theta_j \rangle$	$H_{13} = K_{12} = \frac{j_0 - j}{2(1 - s^2)}$ $S_{13} = 0$
Coupling constant	$J(\text{MO}) = h_{11} - h_{22} + J_{11} - J_{12}$ $= \frac{2k + 2h(1 - s) - 2\alpha s(1 + s)}{(1 + s)(1 - s^2)} + \frac{2\beta(1 + s) - (j_0 + j)s}{(1 + s)(1 - s^2)}$ $J(\text{PCI}) \approx J(\text{MO})$ $+ \frac{(j_0 - j)^2}{16[(\beta - \alpha s)(1 - s^2) + 2h(1 + s^2) - s(j_0 + j + 2k)]}$

$$E_1 = 2h_{11} + J_{11}$$

$$E_2 = h_{11} + h_{22} + J_{12} - K_{12}$$

$$E_3 = 2h_{22} + J_{22}$$

and the interaction matrix element is

$$H_{13} = \langle \Psi_1 | \hat{H} | \Psi_3 \rangle = K_{12}$$

(the determinants differ in two spin-orbitals). The one- and two-electron integrals can be further expanded into the basis set of atomic orbitals, hence

$$h_{11} = \langle \phi_1(1) | \hat{h}(1) | \phi_1(1) \rangle = \frac{\alpha + \beta}{1 + s}$$

$$h_{22} = \langle \phi_2(1) | \hat{h}(1) | \phi_2(1) \rangle = \frac{\alpha - \beta}{1 - s}$$

$$J_{11} = \langle \phi_1(1)\phi_1(2) | \hat{g}(1, 2) | \phi_1(1)\phi_1(2) \rangle = \frac{j_0 + j + 2k + 4h}{2(1 + s)^2}$$

$$J_{22} = \langle \phi_2(1)\phi_2(2) | \hat{g}(1, 2) | \phi_2(1)\phi_2(2) \rangle = \frac{j_0 + j + 2k - 4h}{2(1 - s)^2}$$

$$J_{12} = \langle \phi_1(1)\phi_2(2) | \hat{g}(1, 2) | \phi_1(1)\phi_2(2) \rangle = \frac{j_0 + j - 2k}{2(1 + s)(1 - s)}$$

$$K_{12} = \langle \phi_1(1)\phi_2(2) | \hat{g}(1, 2) | \phi_2(1)\phi_1(2) \rangle = \frac{j_0 - j}{2(1 + s)(1 - s)}$$

The zero-order contribution to the exchange coupling constant is given by

$$J^{(0)} = J(\text{MO}) = h_{11} - h_{22} + J_{11} - J_{12} + K_{12}$$

The second-order perturbation configuration interaction brings a correction

$$J^{(2)} = J(\text{PCI}) = \frac{\langle \Psi_1 | \hat{H}' | \Psi_3 \rangle^2}{E_1 - E_3} = \frac{K_{12}^2}{2h_{11} + J_{11} - (2h_{22} + J_{22})}$$

The second step is the generation of the orthogonalised magnetic orbitals (OMOs). These are given by a transformation of the frontier molecular orbitals (the HOMO–LUMO pair) as

$$|a\rangle = (\phi_1 + \phi_2)/\sqrt{2}$$

$$|b\rangle = (\phi_1 - \phi_2)/\sqrt{2}$$

These orbitals constitute new reference Slater determinants

$$\Xi_1 = [\uparrow \downarrow] = |a\bar{b}|$$

$$\Xi_2 = [\downarrow \uparrow] = |b\bar{a}|$$

which yield the symmetry-adapted configuration functions for the lowest singlet and triplet states

$$\Psi_1(^1\Gamma_g) = (\mathcal{E}_1 + \mathcal{E}_2)/\sqrt{2}$$

$$\Psi_2(^3\Gamma_u) = (\mathcal{E}_1 - \mathcal{E}_2)/\sqrt{2}$$

The corresponding matrix elements involving OMOs are evaluated as

$$H_{11} = \langle \mathcal{E}_1 | \hat{H} | \mathcal{E}_1 \rangle = h_{aa} + h_{bb} + J_{ab}$$

$$H_{22} = \langle \mathcal{E}_2 | \hat{H} | \mathcal{E}_2 \rangle = h_{aa} + h_{bb} + J_{ab}$$

$$H_{12} = \langle \mathcal{E}_1 | \hat{H} | \mathcal{E}_2 \rangle = K_{ab}$$

The energies of the lowest singlet and triplet states become expressed as follows

$$E_1(^1\Gamma_g) = \langle \Psi_1 | \hat{H} | \Psi_1 \rangle = \frac{1}{2}(H_{11} + H_{22} + 2H_{12}) = h_{aa} + h_{bb} + J_{ab} + K_{ab}$$

$$E_2(^3\Gamma_u) = \langle \Psi_2 | \hat{H} | \Psi_2 \rangle = \frac{1}{2}(H_{11} + H_{22} - 2H_{12}) = h_{aa} + h_{bb} + J_{ab} - K_{ab}$$

To this zero-order approximation the exchange coupling constant results as

$$J^{(0)}(\text{PE}) = J(\text{OMO}) = 2H_{12} = 2K_{ab}$$

This term has been termed the *potential exchange* by Anderson [4]. It includes only the exchange integral over the OMOs. However, when a back transformation into the MO basis is used, then the two-electron Coulomb integrals are involved

$$J^{(0)} = \frac{1}{2}(J_{11} + J_{22}) - J_{12}$$

When the further LCAO expansion is applied then the exchange, Coulomb and hybrid integrals contribute

$$J^{(0)} = \frac{2k + (j_0 + j)s^2 - 4sh}{(1 - s^2)^2}$$

In addition to $|\Xi_1\rangle$ and $|\Xi_2\rangle$ reference determinants there are two excited determinantal functions formed of OMOs, namely

$$\Xi_3 = [\uparrow\downarrow \quad 0] = |a\bar{a}|$$

$$\Xi_4 = [0 \quad \uparrow\downarrow] = |b\bar{b}|$$

These yield two symmetry-adapted configuration functions

$$\Psi_3(^1\Gamma_g) = (\Xi_3 + \Xi_4)/\sqrt{2}$$

$$\Psi_4(^1\Gamma_u) = (\Xi_3 - \Xi_4)/\sqrt{2}$$

with the corresponding energies

$$\begin{aligned} E_3(^1\Gamma_g) &= \langle \Psi_3 | \hat{H} | \Psi_3 \rangle = \frac{1}{2}(H_{33} + H_{44} + 2H_{34}) \\ &= h_{aa} + h_{bb} + \frac{1}{2}(J_{aa} + J_{bb}) + K_{ab} \end{aligned}$$

$$\begin{aligned} E_4(^1\Gamma_u) &= \langle \Psi_4 | \hat{H} | \Psi_4 \rangle = \frac{1}{2}(H_{33} + H_{44} - 2H_{34}) \\ &= h_{aa} + h_{bb} + \frac{1}{2}(J_{aa} + J_{bb}) - K_{ab} \end{aligned}$$

In second-order perturbation theory we have a general formula

$$J^{(2)} = \sum_{K \neq 0} \frac{\langle {}^1\Psi_0 | \hat{H}' | \Psi_K \rangle^2 - \langle {}^3\Psi_0 | \hat{H}' | \Psi_K \rangle^2}{E_0 - E_K}$$

which in our particular case relaxes to

$$\begin{aligned} J^{(2)} &= \sum_{K \neq 0} \frac{\langle (\Xi_1 + \Xi_2)/\sqrt{2} | \hat{H}' | \Psi_K \rangle^2 - \langle (\Xi_1 - \Xi_2)/\sqrt{2} | \hat{H}' | \Psi_K \rangle^2}{E_0 - E_K} \\ &= \sum_{K \neq 0} 2 \frac{\langle \Xi_1 | \hat{H}' | \Psi_K \rangle \langle \Psi_K | \hat{H}' | \Xi_2 \rangle}{E_0 - E_K} \end{aligned}$$

Here

$$E_0 = \langle \Xi_1 | \hat{H} | \Xi_1 \rangle = \langle \Xi_2 | \hat{H} | \Xi_2 \rangle = h_{aa} + h_{bb} + J_{ab}$$

is the mean energy associated with the reference Slater determinants; $E_K = \langle \Psi_K | \hat{H} | \Psi_K \rangle$ is the energy given by the determinantal function $|\Psi_K\rangle$. With the help of the excited symmetry-adapted configuration functions we get

$$J^{(2)} = 2 \frac{\langle \Xi_1 | \hat{H}' | \Psi_3 \rangle \langle \Psi_3 | \hat{H}' | \Xi_2 \rangle}{E_0 - E_3} + 2 \frac{\langle \Xi_1 | \hat{H}' | \Psi_4 \rangle \langle \Psi_4 | \hat{H}' | \Xi_2 \rangle}{E_0 - E_4}$$

The matrix elements are expanded as follows

$$\langle \Xi_1 | \hat{H}' | \Psi_3 \rangle = \frac{1}{\sqrt{2}} \left[\langle |a\bar{b}| | \hat{H}' | |a\bar{a}| \rangle + \langle |a\bar{b}| | \hat{H}' | |b\bar{b}| \rangle \right]$$

and evaluated according to the Slater rules: the determinants, differing in one spin-orbital, yield the Fock matrix elements, namely

$$\langle |a\bar{b}| | \hat{H}' | |a\bar{a}| \rangle = \langle b | \hat{F} | a \rangle$$

$$\langle |a\bar{b}| | \hat{H}' | |b\bar{b}| \rangle = \langle a | \hat{F} | b \rangle$$

with

$$F_{ab} = F_{ba} = \langle a | \hat{F} | b \rangle = \langle a | \hat{h} | b \rangle + \langle aa | \hat{g} | ab \rangle + \langle ba | \hat{g} | bb \rangle$$

Then one can find

$$\langle \Xi_1 | \hat{H}' | \Psi_3 \rangle = \frac{1}{\sqrt{2}} [F_{ba} + F_{ab}]$$

$$\langle \Xi_1 | \hat{H}' | \Psi_4 \rangle = \frac{1}{\sqrt{2}} [F_{ba} - F_{ab}] = 0$$

$$\langle \Psi_3 | \hat{H}' | \Xi_2 \rangle = \frac{1}{\sqrt{2}} [F_{ab} + F_{ba}]$$

$$\langle \Psi_4 | \hat{H}' | \Xi_2 \rangle = \frac{1}{\sqrt{2}} [F_{ab} - F_{ba}] = 0$$

Finally, the PCI contribution to the exchange coupling constant reduces to

$$J^{(2)}(\text{KE}) = 4 \frac{(F_{ab})^2}{E_0 - E_3}$$

This term represents the *kinetic exchange*; it contributes to the antiferromagnetic part of the exchange coupling constant (it is negative). The Fock matrix element can be further expanded into the set of canonical molecular orbitals as

$$\begin{aligned} F_{ab} &= \frac{1}{2} \left\langle (\phi_1 + \phi_2) \left| \hat{F} \right| (\phi_1 - \phi_2) \right\rangle \\ &= \frac{1}{2} (F_{11} + F_{21} - F_{12} - F_{22}) = \frac{1}{2} (F_{11} - F_{22}) \end{aligned}$$

The off-diagonal Fock matrix elements disappear for the canonical MOs and the diagonal ones are equal to the MO orbital energies; hence

$$F_{ab} = \frac{1}{2} (\varepsilon_1 - \varepsilon_2)$$

The important OMO formulae of the two-orbital model are given in Table 10.5. These describe the dominant contributions to the direct exchange.

10.1.6 Three-orbital model

When the magnetic centres are linked by a bridging ligand atom, a three-orbital model is appropriate for such an A–X–B fragment. Three atomic orbitals χ_A , χ_B and χ_X constitute three molecular orbitals (Fig. 10.3)

(a) when $\chi_X = ns$, then

$$\phi_1(1\sigma_g) = N_1[\chi_X + \lambda_1(\chi_A + \chi_B)], \quad \lambda \ll 1$$

$$\phi_2(1\sigma_u) = N_2[\chi_A - \chi_B]$$

$$\phi_3(2\sigma_g) = N_3[(\chi_A + \chi_B)] - \lambda_3\chi_X, \quad \lambda_3 \ll 1$$

(b) when $\chi_X = np$, then

$$\phi_1(1\sigma_u) = N_1[\chi_X + \lambda_1(\chi_A - \chi_B)]$$

$$\phi_2(1\sigma_g) = N_2[\chi_A + \chi_B]$$

$$\phi_3(2\sigma_u) = N_3[(\chi_A - \chi_B)] - \lambda_3\chi_X$$

TABLE 10.5
Survey of the OMO formulae

Orthogonal magnetic orbitals	$ a\rangle = (\phi_1 + \phi_2)/\sqrt{2}$ $ b\rangle = (\phi_1 - \phi_2)/\sqrt{2}$
Reference Slater determinants	$\Xi_1 = \begin{bmatrix} \uparrow & \downarrow \end{bmatrix} = a\bar{b} $ $\Xi_2 = \begin{bmatrix} \downarrow & \uparrow \end{bmatrix} = b\bar{a} $
Excited Slater determinants	$\Xi_3 = \begin{bmatrix} \uparrow\downarrow & 0 \end{bmatrix} = a\bar{a} $ $\Xi_4 = \begin{bmatrix} 0 & \uparrow\downarrow \end{bmatrix} = b\bar{b} $
Lowest states	$\Psi_1(^1\Gamma_g) = (\Xi_1 + \Xi_2)/\sqrt{2}$ $\Psi_2(^3\Gamma_u) = (\Xi_1 - \Xi_2)/\sqrt{2}$ $\Psi_3(^1\Gamma_g) = (\Xi_3 + \Xi_4)/\sqrt{2}$ $\Psi_4(^1\Gamma_u) = (\Xi_3 - \Xi_4)/\sqrt{2}$
OMO energies	$E_0 = \langle \Xi_1 \hat{H} \Xi_1 \rangle = \langle \Xi_2 \hat{H} \Xi_2 \rangle = h_{aa} + h_{bb} + J_{ab}$ $E_1(^1\Gamma_g) = h_{aa} + h_{bb} + J_{ab} + K_{ab}$ $E_2(^3\Gamma_u) = h_{aa} + h_{bb} + J_{ab} - K_{ab}$ $E_3(^1\Gamma_g) = h_{aa} + h_{bb} + \frac{1}{2}(J_{aa} + J_{bb}) + K_{ab}$ $E_4(^1\Gamma_u) = h_{aa} + h_{bb} + \frac{1}{2}(J_{aa} + J_{bb}) - K_{ab}$
Coupling constant	$J^{(0)} = J(\text{OMO}) = 2K_{ab}$ $= \frac{1}{2}(J_{11} + J_{22}) - J_{12} = \frac{2k + (j_0 + j)s^2 - 4sh}{(1 - s^2)^2}$ $J^{(2)} = 4 \frac{(F_{ab})^2}{E_0 - E_3}$

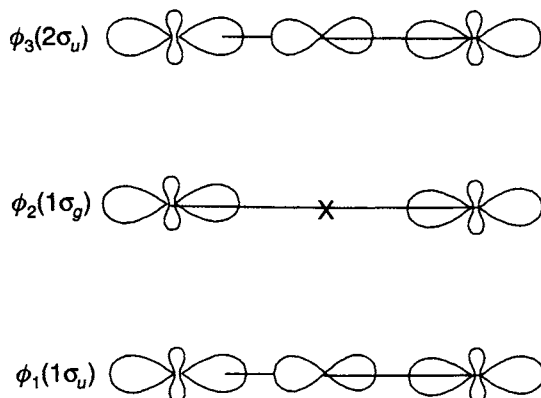


Fig. 10.3. Interaction of three atomic orbitals forming a set of molecular orbitals.

Instead of the pure atomic d -orbitals one can use appropriate hybrid orbitals in the role of χ_A and χ_B . The various occupations of molecular orbitals determine the electron configurations characterised by the configuration functions in the form of the Slater determinants, e.g.

$$\Psi_1(^1\Gamma_g) = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2|$$

$$\Psi_2(^3\Gamma_u) = |\phi_1\bar{\phi}_1\phi_2\phi_3|$$

$$\Psi_3(^1\Gamma_g) = |\phi_1\bar{\phi}_1\phi_3\bar{\phi}_3|$$

$$\Psi_4(^1\Gamma_u) = (|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_3| - |\phi_1\bar{\phi}_1\phi_3\bar{\phi}_2|)/\sqrt{2}$$

$$\Psi_5(^1\Gamma_g) = |\phi_2\bar{\phi}_2\phi_3\bar{\phi}_3|$$

$$\Psi_6(^3\Gamma_u) = |\phi_1\phi_2\bar{\phi}_2\phi_3|$$

There are more configuration functions than in the previous case of the two-orbital model, namely six singlets and three triplets (Table 10.6).

All configuration functions of the same symmetry are further mixed via the CI, e.g.

$$\Psi_a(^1\Gamma_g) = C_1 \cdot \Psi_1(^1\Gamma_g) + C_3 \cdot \Psi_3(^1\Gamma_g) + C_5 \cdot \Psi_5(^1\Gamma_g)$$

leading to the lowering of the singlet ground state

$$E_a(^1\Gamma_g) = E_1(^1\Gamma_g) - \dots$$

and, analogously, the energy of the lowest triplet state is affected by the CI

$$E_b(^3\Gamma_u) = E_2(^3\Gamma_u) - \dots$$

Therefore the exchange coupling constant

$$J(\text{CI}) = E_b(^3\Gamma_u) - E_a(^1\Gamma_g) = J(\text{MO}) + \dots$$

needs to be evaluated beyond the MO approximation.

A new consequence of the three-orbital model is that there are some excited state configuration functions that contribute to the CI expression of the exchange coupling constants. For example, the doubly excited determinantal function over MOs

$$\Psi_5(^1\Gamma_g) = |\phi_2\bar{\phi}_2\phi_3\bar{\phi}_3|$$

TABLE 10.6

List of symmetry-adapted configuration functions for two-orbital and three-orbital models

Configuration functions constructed from Slater determinants	
$m = 2$	
$^1\Gamma_g$	$M_S = 0 \quad \begin{bmatrix} 0 \\ \uparrow\downarrow \end{bmatrix}; \begin{bmatrix} \uparrow\downarrow \\ 0 \end{bmatrix}$
$^1\Gamma_u$	$M_S = 0 \quad \frac{1}{\sqrt{2}} \left(\begin{bmatrix} \downarrow \\ \uparrow \end{bmatrix} - \begin{bmatrix} \uparrow \\ \downarrow \end{bmatrix} \right)$
$^3\Gamma_u$	$M_S = 1 \quad \begin{bmatrix} \uparrow \\ \uparrow \end{bmatrix}$
	$M_S = 0 \quad \frac{1}{\sqrt{2}} \left(\begin{bmatrix} \downarrow \\ \uparrow \end{bmatrix} + \begin{bmatrix} \uparrow \\ \downarrow \end{bmatrix} \right)$
	$M_S = -1 \quad \begin{bmatrix} \downarrow \\ \downarrow \end{bmatrix}$
$m = 3$	
$^1\Gamma_g$	$M_S = 0 \quad \begin{bmatrix} 0 \\ \uparrow\downarrow \\ \uparrow\downarrow \end{bmatrix}, \begin{bmatrix} \uparrow\downarrow \\ 0 \\ \uparrow\downarrow \end{bmatrix}, \begin{bmatrix} \uparrow\downarrow \\ \uparrow\downarrow \\ 0 \end{bmatrix}$
$^1\Gamma_u$	$M_S = 0 \quad \frac{1}{\sqrt{2}} \left(\begin{bmatrix} \downarrow \\ \uparrow \\ \uparrow\downarrow \end{bmatrix} - \begin{bmatrix} \uparrow \\ \downarrow \\ \uparrow\downarrow \end{bmatrix} \right), \frac{1}{\sqrt{2}} \left(\begin{bmatrix} \downarrow \\ \uparrow\downarrow \\ \uparrow \end{bmatrix} - \begin{bmatrix} \uparrow \\ \uparrow\downarrow \\ \downarrow \end{bmatrix} \right), \frac{1}{\sqrt{2}} \left(\begin{bmatrix} \uparrow\downarrow \\ \downarrow \\ \uparrow \end{bmatrix} - \begin{bmatrix} \uparrow\downarrow \\ \uparrow \\ \downarrow \end{bmatrix} \right)$
$^3\Gamma_u$	$M_S = 1 \quad \begin{bmatrix} \uparrow \\ \uparrow \\ \uparrow\downarrow \end{bmatrix}, \begin{bmatrix} \uparrow \\ \uparrow\downarrow \\ \uparrow \end{bmatrix}, \begin{bmatrix} \uparrow\downarrow \\ \uparrow \\ \uparrow \end{bmatrix}$
	$M_S = 0 \quad \frac{1}{\sqrt{2}} \left(\begin{bmatrix} \downarrow \\ \uparrow \\ \uparrow\downarrow \end{bmatrix} + \begin{bmatrix} \uparrow \\ \downarrow \\ \uparrow\downarrow \end{bmatrix} \right), \frac{1}{\sqrt{2}} \left(\begin{bmatrix} \downarrow \\ \uparrow\downarrow \\ \uparrow \end{bmatrix} + \begin{bmatrix} \uparrow \\ \uparrow\downarrow \\ \downarrow \end{bmatrix} \right), \frac{1}{\sqrt{2}} \left(\begin{bmatrix} \uparrow\downarrow \\ \downarrow \\ \uparrow \end{bmatrix} + \begin{bmatrix} \uparrow\downarrow \\ \uparrow \\ \downarrow \end{bmatrix} \right)$
	$M_S = -1 \quad \begin{bmatrix} \downarrow \\ \downarrow \\ \uparrow\downarrow \end{bmatrix}, \begin{bmatrix} \downarrow \\ \uparrow\downarrow \\ \downarrow \end{bmatrix}, \begin{bmatrix} \uparrow\downarrow \\ \downarrow \\ \downarrow \end{bmatrix}$

after introducing OMO transforms to

$$\Psi_5 = |a\bar{a}b\bar{b}|$$

It contributes to $J^{(2)}$ through a term

$$J^{(2)} = 2 \frac{\langle \Xi_1 | \hat{H}' | \Psi_5 \rangle \langle \Psi_5 | \hat{H}' | \Xi_2 \rangle}{E_0 - E_5}$$

The matrix elements are evaluated with the help of the Slater rules (the determinants differing in two spin-orbitals) as

$$\langle \Xi_1 | \hat{H}' | \Psi_5 \rangle = \langle |1\bar{1}a\bar{b}| | \hat{H}' | |b\bar{a}a\bar{b}| \rangle = \langle 1\bar{1} | \hat{g} | b\bar{a} \rangle$$

$$\langle \Psi_5 | \hat{H}' | \Xi_2 \rangle = \langle |b\bar{a}a\bar{b}| | \hat{H}' | |1\bar{1}b\bar{a}| \rangle = \langle |a\bar{b}b\bar{a}| | \hat{H}' | |1\bar{1}b\bar{a}| \rangle = \langle a\bar{b} | \hat{g} | 1\bar{1} \rangle$$

and then

$$J^{(2)}(\text{CT}) = 2 \frac{\langle 1\bar{1} | \hat{g} | b\bar{a} \rangle^2}{E_0 - E_5}$$

Since the involved configuration function corresponds to the ligand-to-metal charge transfer (LMCT), its contribution is called the *charge transfer term*.

When more atomic orbitals are involved, more doubly occupied molecular orbitals (i, j) are present so that there are more LMCT terms of the form

$$J^{(2)}(\text{LMCT}) = 2 \sum_i \sum_j \frac{\langle ij | \hat{g} | ab \rangle \langle ji | \hat{g} | ab \rangle}{\Delta E_{i \rightarrow a} + \Delta E_{j \rightarrow b}}$$

In addition, there are unoccupied molecular orbitals (i^*, j^*) also present, leading to an appearance of the metal-to-ligand charge transfer (MLCT) terms

$$J^{(2)}(\text{MLCT}) = 2 \sum_{i^*} \sum_{j^*} \frac{\langle i^* j^* | \hat{g} | ab \rangle \langle j^* i^* | \hat{g} | ab \rangle}{\Delta E_{a \rightarrow i^*} + \Delta E_{b \rightarrow j^*}}$$

The LMCT and MLCT terms are just the contributions to the *superexchange*: the doubly occupied orbitals and unoccupied orbitals of the bridging ligand mediate the exchange interaction.

10.1.7 CI calculation of coupling constant

Normally $J(\text{MO})$ represents a poor approximation to $J(\text{CI})$. In performing the CI calculations some additional problems arise:

- (a) a rather small J -value is given as the difference of big values of the respective molecular energies;
- (b) the calculations should be done in an extended basis set; consequently the CI calculation involves a large number of configurations;
- (c) the methodology for the closed-shell and the open-shell systems is different (RHF versus ROHF, UHF or the mean Nesbet-type Hamiltonian).

The number of Slater determinants generated from $2m$ available spin-orbitals and n electrons is

$$N_{\text{SD}} = \binom{2m}{n}$$

The number of configuration functions that can be generated from m orbitals for a state with n electrons and total spin S is given by the Weyls formula

$$N = \frac{2S+1}{m+1} \binom{m+1}{n/2-S} \binom{m+1}{n/2+S+1}$$

With increasing number of orbitals, however, N increases rapidly and for $m \gg n \gg S$ it can be estimated as follows

$$N \approx \frac{1}{n^2} \left(\frac{2me}{n} \right)^n$$

In practice the full CI is not performed because of its time consumption and disk capacity requirements, but some approximate versions can be applied at present:

- (a) a limited CI with singly-excited and doubly-excited configurations (CI-SD);
- (b) many-body perturbation theory (MBPT/MP- n), up to a certain order;
- (c) coupled cluster approach (CCA).

10.1.8 Direct calculation of coupling constant

In calculating the energy differences (transition energies) the perturbation theory becomes very effective: calculating the transition energy is much faster than calculating the correlated total molecular energies [5]. In the framework

of formal perturbation theory, operating over the set of the configuration functions, the second-order energy corrections are

$${}^1E^{(2)} = \sum_{K \neq 0} \frac{\langle {}^1\Psi_0 | \hat{H}' | \Psi_K \rangle^2}{E_0 - E_K}$$

and

$${}^3E^{(2)} = \sum_{K \neq 0} \frac{\langle {}^3\Psi_0 | \hat{H}' | \Psi_K \rangle^2}{E_0 - E_K}$$

Then the second-order correction to the exchange coupling constant is

$$J^{(2)} = {}^1E^{(2)} - {}^3E^{(2)} = \sum_{K \neq 0} \frac{\langle {}^1\Psi_0 | \hat{H}' | \Psi_K \rangle^2 - \langle {}^3\Psi_0 | \hat{H}' | \Psi_K \rangle^2}{E_0 - E_K}$$

The configuration functions of the lowest singlet and triplet states are constructed with the help of the OMOs; hence

$$|{}^1\Psi_0({}^1\Gamma_g)\rangle = \left| \dots \bar{i}\bar{i} \left(\frac{a\bar{b} + b\bar{a}}{\sqrt{2}} \right) \right| = \frac{1}{\sqrt{2}}(\Xi_1 + \Xi_2)$$

$$|{}^3\Psi_0({}^3\Gamma_u)\rangle = \left| \dots \bar{i}\bar{i} \left(\frac{a\bar{b} - b\bar{a}}{\sqrt{2}} \right) \right| = \frac{1}{\sqrt{2}}(\Xi_1 - \Xi_2)$$

where the reference Slater determinants involving OMOs occur

$$\Xi_1 = |\dots \bar{i}\bar{i}a\bar{b}|$$

$$\Xi_2 = |\dots \bar{i}\bar{i}b\bar{a}| = -|\dots \bar{i}\bar{i}\bar{a}\bar{b}|$$

Here $(\dots \bar{i}\bar{i})$ represents a subspace of the doubly occupied MOs. Using these Slater determinants, the expression for $J^{(2)}$ can be rewritten in a simpler form

$$J^{(2)} = 2 \sum_{K \neq 0} \frac{\langle \Xi_1 | \hat{H}' | \Psi_K \rangle \langle \Psi_K | \hat{H}' | \Xi_2 \rangle}{E_0 - E_K}$$

Only those configuration functions Ψ_K contribute to the singlet-triplet separation which simultaneously "interact" with the reference Slater determinants Ξ_1 and Ξ_2 involving OMOs.

For a molecule having an inversion centre the calculation is based on the following steps [6, 7].

1. The set of canonical molecular orbitals (CMOs) is generated with any open-shell SCF program. The open shells involve two nearly degenerate MOs of different symmetry

$$\phi_n(\sigma_g) = N(d_A + d_B) + \text{tail}$$

$$\phi_{n+1}(\sigma_u) = N'(d_A - d_B) + (\text{tail})'$$

2. Two OMOs are generated by the transformation

$$|a\rangle = \frac{1}{\sqrt{2}}[\phi_n(\sigma_g) + \phi_{n+1}(\sigma_u)] \approx d_A + \dots$$

$$|b\rangle = \frac{1}{\sqrt{2}}[\phi_n(\sigma_g) - \phi_{n+1}(\sigma_u)] \approx d_B + \dots$$

These orbitals are well localised at the individual centres and are orthogonal

$$\langle a|b\rangle = 0$$

3. Also, the other occupied or unoccupied molecular orbitals can be subjected to localisation by a certain procedure; this may be useful in interpreting the local contributions to the exchange coupling constant.
4. At the SCF level of approximation (in the zeroth order) the singlet-triplet separation is given by the potential exchange

$$J^{(0)} = 2\langle \Xi_1 | \hat{H} | \Xi_2 \rangle = 2K_{ab}$$

and its positive value refers to a ferromagnetic contribution (the ground state is the triplet).

5. The perturbative configuration interaction is applied. This can be done in two ways.
 - (a) The *formal perturbation theory* is used. The basis set is represented by the doubly occupied MOs (indexed as i and j), the singly occupied OMOs (a and b) and the unoccupied MOs (indexed as i^* and j^*). The configuration functions for the excited states $|\Phi_K\rangle$ are represented by Slater determinants generated from single $|\Phi_{i \rightarrow j^*}\rangle$ and double $|\Phi_{i \rightarrow j^*}^{k \rightarrow l^*}\rangle$

excitations. The second-order formulae can be easily obtained with the help of the Slater rules for the evaluation of the respective matrix elements $\langle \Xi_1 | \hat{H}' | \Phi_K \rangle$ and $\langle \Phi_K | \hat{H}' | \Xi_2 \rangle$. Notice that the elements of the Slater determinants should be ordered in the way so that their maximum coincidence is secured. The denominator involves the transition energies $\Delta E_{i \rightarrow j^*}$ and $\Delta E_{i \rightarrow j^*}^{k \rightarrow l^*}$, respectively.

- (b) Alternatively, the *many-body perturbation theory* (MBPT) is applied [8, 9]. The choice of the vacuum state is arbitrary. However, with the $|\dots \bar{i} i a b|$ determinant ($S_z = 1$) as a vacuum state the OMOs $|a\rangle$ and $|b\rangle$ behave as holes (as they are occupied) whereas all unoccupied MOs behave as particles. Then $\Xi_1 = |\dots \bar{i} i \bar{a} b|$ and $\Xi_2 = |\dots \bar{i} i b \bar{a}|$ are the singly excited determinants depicted by oriented lines as [6]

$$|\Xi_1\rangle \Rightarrow \begin{cases} \bar{b} \rightarrow \\ b \leftarrow \end{cases}$$

$$-|\Xi_2\rangle \Rightarrow \begin{cases} \bar{a} \rightarrow \\ a \leftarrow \end{cases}$$

In the framework of a diagrammatic technique (Feynman diagrams, Goldstone diagrams, Hugenholtz diagrams [10–13]) the singlet–triplet energy separation appears as the sum of the diagrams which start from Ξ_1 and lead to Ξ_2 through two successive interaction lines.

One can also use the $|\dots \bar{i} i|$ determinant ($S_z = 0$) as a vacuum state [7]; then $\Xi_1 = |\dots \bar{i} i \bar{a} b|$ and $\Xi_2 = |\dots \bar{i} i b \bar{a}|$ will have two propagating lines

$$|\Xi_1\rangle \Rightarrow \begin{cases} \bar{b} \rightarrow \\ a \rightarrow \end{cases}$$

$$|\Xi_2\rangle \Rightarrow \begin{cases} \bar{a} \rightarrow \\ b \rightarrow \end{cases}$$

Within the Moller–Plesset (MP) partitioning [14] of the Hamiltonian into the unperturbed Hamiltonian and the perturbation the energy denominators will involve the differences in the orbital energies

$$\Delta E_{i \rightarrow j^*} = \varepsilon_i - \varepsilon_{j^*}$$

For the evaluation of the respective matrix elements, the diagrammatic technique becomes very effective when the higher orders of the perturbative CI are involved.

There are seven principal contributions in the second-order perturbative CI to the exchange coupling constant, as follows.

1. *Kinetic exchange* (KE) involves the singly excited ionic structures

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} 0 & & \\ 0 & \uparrow\downarrow & \\ & \uparrow\downarrow & \end{bmatrix} = |\dots b\bar{b}|$$

and

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} 0 & & \\ \uparrow\downarrow & 0 & \\ & \uparrow\downarrow & \end{bmatrix} = |\dots a\bar{a}|$$

Since the determinantal functions differ in one pair of spin-orbitals, their matrix elements are given by the Fock matrix elements; hence

$$\langle \Xi_1 | \hat{H}' | \Phi_{a \rightarrow b} \rangle = \langle |\dots \bar{i}i a \bar{b}| | \hat{H}' | |\dots \bar{i}i b \bar{b}| \rangle = \langle a | \hat{F} | b \rangle = F_{ab}$$

$$\langle \Phi_{\bar{a} \rightarrow \bar{b}} | \hat{H}' | \Xi_2 \rangle = \langle |\dots \bar{i}i b \bar{b}| | \hat{H}' | |\dots \bar{i}i b \bar{a}| \rangle = \langle \bar{b} | \hat{F} | a \rangle = F_{ab}$$

and

$$\langle \Xi_1 | \hat{H}' | \Phi_{\bar{b} \rightarrow \bar{a}} \rangle = \langle |\dots \bar{i}i a \bar{b}| | \hat{H}' | |\dots \bar{i}i a \bar{a}| \rangle = \langle \bar{b} | \hat{F} | \bar{a} \rangle = F_{ab}$$

$$\langle \Phi_{b \rightarrow a} | \hat{H}' | \Xi_2 \rangle = \langle |\dots \bar{i}i a \bar{a}| | \hat{H}' | |\dots \bar{i}i b \bar{a}| \rangle = \langle a | \hat{F} | b \rangle = F_{ab}$$

yielding the overall contribution

$$J^{(2)}(\text{KE}) = 2 \frac{F_{ab} F_{ab}}{\Delta E_{a \rightarrow b}} + 2 \frac{F_{ab} F_{ab}}{\Delta E_{b \rightarrow a}} = 4 \frac{F_{ab}^2}{\Delta E_{a \rightarrow b}}$$

This term can be rewritten as

$$J^{(2)}(\text{KE}) \approx \frac{[\varepsilon(\sigma_g) - \varepsilon(\sigma_u)]^2}{-(J_{aa} - J_{ab})}$$

2. *Hole polarisation* (HP) involves the singly excited configurations relative to $|\Xi_1\rangle$ but the doubly excited ones relative to $|\Xi_2\rangle$, i.e.

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} 0 & & \\ \uparrow & \uparrow\downarrow & \\ & \downarrow & \end{bmatrix} = |\dots b\bar{i}a\bar{b}|$$

and

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} 0 & & \\ \uparrow\downarrow & & \uparrow \\ & \downarrow & \end{bmatrix} = |\dots b\bar{i}a\bar{a}|$$

Then the matrix elements are

$$\langle \Xi_1 | \hat{H}' | \Phi_{i \rightarrow b} \rangle = \langle |\dots \bar{i}a\bar{b}| | \hat{H}' | |\dots b\bar{i}a\bar{b}| \rangle = \langle i | \hat{F} | b \rangle = F_{ib}$$

$$\langle \Phi_{i \rightarrow a}^{\bar{a} \rightarrow \bar{b}} | \hat{H}' | \Xi_2 \rangle = \langle |\dots b\bar{i}a\bar{b}| | \hat{H}' | |\dots \bar{i}b\bar{a}| \rangle = -\langle |\dots a\bar{i}b\bar{b}| | \hat{H}' | |\dots \bar{i}b\bar{a}| \rangle = -\langle i\bar{a} | \hat{g} | a\bar{b} \rangle$$

and

$$\langle \Xi_1 | \hat{H}' | \Phi_{i \rightarrow b}^{\bar{b} \rightarrow \bar{a}} \rangle = \langle |\dots \bar{i}a\bar{b}| | \hat{H}' | |\dots b\bar{i}a\bar{a}| \rangle = \langle i\bar{b} | \hat{g} | b\bar{a} \rangle$$

$$\begin{aligned} \langle \Phi_{i \rightarrow a} | \hat{H}' | \Xi_2 \rangle &= \langle |\dots b\bar{i}a\bar{a}| | \hat{H}' | |\dots \bar{i}b\bar{a}| \rangle = -\langle |\dots a\bar{i}b\bar{a}| | \hat{H}' | |\dots \bar{i}b\bar{a}| \rangle \\ &= -\langle a | \hat{F} | i \rangle = -F_{ia} \end{aligned}$$

giving rise to the contribution

$$\begin{aligned} J^{(2)}(\text{HP}) &= -2 \left\{ \sum_i \frac{F_{ib} \langle ia | \hat{g} | ab \rangle}{\Delta E_{i \rightarrow b}} \right\} - 2 \left\{ \sum_i \frac{F_{ia} \langle ib | \hat{g} | ba \rangle}{\Delta E_{i \rightarrow a}} \right\} \\ &= -4 \sum_i \frac{F_{ia} \langle ib | \hat{g} | ba \rangle}{\Delta E_{i \rightarrow a}} \end{aligned}$$

3. *Particle polarisation (PP)* involves the singly and/or doubly excited configuration functions

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} & \downarrow & \\ \uparrow & & 0 \\ & \uparrow\downarrow & \end{bmatrix} = |\dots a\bar{j}^*|$$

and

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} & \downarrow & \\ 0 & & \uparrow \\ \uparrow\downarrow & & \end{bmatrix} = |\dots b\bar{j}^*|$$

with

$$\langle \Xi_1 | \hat{H}' | \Phi_{b \rightarrow j^*} \rangle = \langle | \dots \bar{i} i a \bar{b} | \hat{H}' | | \dots \bar{i} i a \bar{j}^* | \rangle = \langle \bar{b} | \hat{F} | \bar{j}^* \rangle = F_{bj^*}$$

$$\langle \Phi_{\bar{a} \rightarrow j^*}^{b \rightarrow a} | \hat{H}' | \Xi_2 \rangle = \langle | \dots \bar{i} i a \bar{j}^* | \hat{H}' | | \dots \bar{i} i b \bar{a} | \rangle = \langle \bar{a} b | \hat{g} | \bar{j}^* a \rangle$$

and

$$\langle \Xi_1 | \hat{H}' | \Phi_{b \rightarrow j^*}^{a \rightarrow b} \rangle = \langle | \dots \bar{i} i a \bar{b} | \hat{H}' | | \dots \bar{i} i b \bar{j}^* | \rangle = \langle \bar{b} a | \hat{g} | \bar{j}^* b \rangle$$

$$\langle \Phi_{\bar{a} \rightarrow j^*} | \hat{H}' | \Xi_2 \rangle = \langle | \dots \bar{i} i b \bar{j}^* | \hat{H}' | | \dots \bar{i} i b \bar{a} | \rangle = \langle \bar{a} | \hat{F} | \bar{j}^* \rangle = F_{aj^*}$$

Then

$$\begin{aligned} J^{(2)}(\text{PP}) &= 2 \left\{ \sum_{j^*} \frac{F_{bj^*} \langle ab | \hat{g} | j^* a \rangle}{\Delta E_{b \rightarrow j^*}} \right\} + 2 \left\{ \sum_{j^*} \frac{F_{aj^*} \langle ba | \hat{g} | j^* b \rangle}{\Delta E_{a \rightarrow j^*}} \right\} \\ &= 4 \sum_{j^*} \frac{F_{aj^*} \langle ba | \hat{g} | j^* b \rangle}{\Delta E_{a \rightarrow j^*}} \end{aligned}$$

4. *Double spin polarisation (DSP)* covers the doubly excited configurations of two types:

(a) configurations of the type

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} \downarrow & \downarrow \\ \uparrow & \uparrow \\ \downarrow & \downarrow \end{bmatrix} = | \dots \bar{j}^* \bar{i} a b |$$

with matrix elements

$$\begin{aligned} \langle \Xi_1 | \hat{H}' | \Phi_{i \rightarrow j^*}^{\bar{b} \rightarrow b} \rangle &= \langle | \dots \bar{i} i a \bar{b} | \hat{H}' | | \dots \bar{j}^* \bar{i} a b | \rangle = \langle \bar{i} b | \hat{g} | \bar{j}^* b \rangle - \langle \bar{i} b | \hat{g} | b \bar{j}^* \rangle \\ &= -\langle \bar{i} b | \hat{g} | b \bar{j}^* \rangle \end{aligned}$$

$$\begin{aligned} \langle \Phi_{i \rightarrow j^*}^{\bar{a} \rightarrow a} | \hat{H}' | \Xi_2 \rangle &= \langle | \dots \bar{j}^* \bar{i} a b | \hat{H}' | | \dots \bar{i} i b \bar{a} | \rangle \\ &= -\langle | \dots \bar{j}^* \bar{i} a b | \hat{H}' | | \dots \bar{i} i \bar{a} b | \rangle = -(\langle \bar{i} \bar{a} | \hat{g} | \bar{j}^* a \rangle - \langle \bar{i} \bar{a} | \hat{g} | a \bar{j}^* \rangle) \\ &= \langle \bar{i} a | \hat{g} | a \bar{j}^* \rangle \end{aligned}$$

Then

$$J^{(2)}(\text{DSP})_a = -2 \left\{ \sum_i \sum_{j^*} \frac{\langle ib | \hat{g} | bj^* \rangle \langle ia | \hat{g} | aj^* \rangle}{\Delta E_{i \rightarrow j^*} + \Delta E_{b \rightarrow b}} \right\}$$

(b) configurations of the type

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} \uparrow \\ \downarrow \quad \downarrow \\ \uparrow \end{bmatrix} = |\dots ij^* \bar{a} \bar{b}|$$

yielding

$$\begin{aligned} \langle \Xi_1 | \hat{H}' | \Phi_{i \rightarrow j^*}^{a \rightarrow \bar{a}} \rangle &= \langle |\dots \bar{i} \bar{a} \bar{b}| | \hat{H}' | |\dots ij^* \bar{a} \bar{b}| \rangle \\ &= \langle \bar{i} a | \hat{g} | j^* \bar{a} \rangle - \langle \bar{i} a | \hat{g} | \bar{a} j^* \rangle = -\langle ia | \hat{g} | aj^* \rangle \\ \langle \Phi_{i \rightarrow j^*}^{b \rightarrow \bar{b}} | \hat{H}' | \Xi_2 \rangle &= \langle |\dots ij^* \bar{a} \bar{b}| | \hat{H}' | |\dots \bar{i} \bar{a} \bar{b}| \rangle \\ &= -\langle |\dots ij^* \bar{a} \bar{b}| | \hat{H}' | |\dots \bar{i} \bar{a} \bar{b}| \rangle \\ &= -(\langle \bar{i} b | \hat{g} | j^* \bar{b} \rangle - \langle \bar{i} b | \hat{g} | \bar{b} j^* \rangle) = \langle ib | \hat{g} | bj^* \rangle \end{aligned}$$

and

$$J^{(2)}(\text{DSP})_b = -2 \left\{ \sum_i \sum_{j^*} \frac{\langle ia | \hat{g} | aj^* \rangle \langle ib | \hat{g} | bj^* \rangle}{\Delta E_{i \rightarrow j^*} + \Delta E_{a \rightarrow \bar{a}}} \right\}$$

The final contribution is

$$J^{(2)}(\text{DSP}) = -4 \sum_i \sum_{j^*} \frac{\langle ib | \hat{g} | bj^* \rangle \langle ia | \hat{g} | aj^* \rangle}{\Delta E_{i \rightarrow j^*}}$$

where the singlet-triplet transition energy $\Delta E_{i \rightarrow j^*}$ appears.

5. *Metal-to-ligand charge transfer (MLCT)* term involves the biexcited configurations

$$\begin{bmatrix} j^* \\ i^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} \downarrow \\ \uparrow \\ 0 \quad 0 \\ \uparrow \downarrow \end{bmatrix} = |\dots i^* \bar{j}^*|$$

with

$$\langle \Xi_1 | \hat{H}' | \Phi_{a \rightarrow i^*}^{\bar{b} \rightarrow j^*} \rangle = \langle a\bar{b} | \hat{g} | i^* j^* \rangle$$

$$\langle \Phi_{b \rightarrow i^*}^{\bar{a} \rightarrow j^*} | \hat{H}' | \Xi_2 \rangle = \langle b\bar{a} | \hat{g} | i^* j^* \rangle$$

so that

$$J^{(2)}(\text{MLCT}) = 2 \sum_{i^*} \sum_{j^*} \frac{\langle a\bar{b} | \hat{g} | i^* j^* \rangle \langle b\bar{a} | \hat{g} | i^* j^* \rangle}{\Delta E_{a \rightarrow i^*} + \Delta E_{b \rightarrow j^*}}$$

6. *Ligand-to-metal charge transfer (LMCT)* term arises from the configurations

$$\begin{bmatrix} i^* \\ a, b \\ i \\ j \end{bmatrix} = \begin{bmatrix} 0 & \\ \uparrow\downarrow & \uparrow\downarrow \\ & \downarrow \\ & \uparrow \end{bmatrix} = | \dots j\bar{a}b\bar{i}a\bar{b} |$$

with

$$\begin{aligned} \langle \Xi_1 | \hat{H}' | \Phi_{j \rightarrow \bar{a}}^{i \rightarrow b} \rangle &= \langle | \dots j\bar{j}\bar{i}\bar{a}\bar{b} | \hat{H}' | | \dots j\bar{a}b\bar{i}a\bar{b} | \rangle = \langle i\bar{j} | \hat{g} | b\bar{a} \rangle - \langle i\bar{j} | \hat{g} | \bar{a}b \rangle \\ &= \langle i\bar{j} | \hat{g} | ba \rangle \end{aligned}$$

$$\begin{aligned} \langle \Phi_{i \rightarrow a}^{\bar{j} \rightarrow \bar{b}} | \hat{H}' | \Xi_2 \rangle &= \langle | \dots j\bar{a}b\bar{i}a\bar{b} | \hat{H}' | | \dots j\bar{j}\bar{i}\bar{a}\bar{b} | \rangle = \langle i\bar{j} | \hat{g} | a\bar{b} \rangle - \langle i\bar{j} | \hat{g} | \bar{b}a \rangle \\ &= \langle i\bar{j} | \hat{g} | ab \rangle \end{aligned}$$

and then

$$J^{(2)}(\text{LMCT}) = 2 \sum_i \sum_j \frac{\langle i\bar{j} | \hat{g} | ab \rangle \langle i\bar{j} | \hat{g} | ba \rangle}{\Delta E_{i \rightarrow b} + \Delta E_{j \rightarrow a}}$$

7. *Simultaneous excitation and polarisation (SE + P)* contribution is given by four types of excited configurations, namely

(a)

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} \uparrow & \\ \uparrow\downarrow & 0 \\ & \downarrow \end{bmatrix} = | \dots j^* \bar{i} a \bar{a} |$$

with the matrix elements

$$\begin{aligned}\langle \Xi_1 | \hat{H}' | \Phi_{i \rightarrow j^*}^{\bar{b} \rightarrow \bar{a}} \rangle &= \langle | \dots \bar{i} \bar{i} a \bar{b} | \hat{H}' | | \dots j^* \bar{i} a \bar{a} | \rangle = \langle \bar{i} \bar{b} | \hat{g} | j^* \bar{a} \rangle \\ \langle \Phi_{i \rightarrow j^*}^{b \rightarrow a} | \hat{H}' | \Xi_2 \rangle &= \langle | \dots j^* \bar{i} a \bar{a} | \hat{H}' | | \dots \bar{i} \bar{b} \bar{a} | \rangle \\ &= \langle i \bar{b} | \hat{g} | j^* a \rangle - \langle i \bar{b} | \hat{g} | a j^* \rangle\end{aligned}$$

and a contribution

$$J^{(2)}(\text{SE} + \text{P})_a = 2 \sum_i \sum_{j^*} \frac{\langle i \bar{b} | \hat{g} | j^* a \rangle (\langle i \bar{b} | \hat{g} | j^* a \rangle - \langle i \bar{b} | \hat{g} | a j^* \rangle)}{\Delta E_{i \rightarrow j^*} + \Delta E_{b \rightarrow a}}$$

(b)

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} \downarrow \\ \uparrow \downarrow & 0 \\ \uparrow \end{bmatrix} = | \dots \bar{i} j^* a \bar{a} |$$

with the matrix elements

$$\begin{aligned}\langle \Xi_1 | \hat{H}' | \Phi_{i \rightarrow j^*}^{\bar{b} \rightarrow \bar{a}} \rangle &= \langle | \dots \bar{i} \bar{i} a \bar{b} | \hat{H}' | | \dots \bar{i} j^* a \bar{a} | \rangle = \langle \bar{i} \bar{b} | \hat{g} | j^* \bar{a} \rangle - \langle \bar{i} \bar{b} | \hat{g} | \bar{a} j^* \rangle \\ \langle \Phi_{b \rightarrow a}^{\bar{i} \rightarrow j^*} | \hat{H}' | \Xi_2 \rangle &= \langle | \dots \bar{i} j^* a \bar{a} | \hat{H}' | | \dots \bar{i} \bar{b} \bar{a} | \rangle = \langle \bar{b} \bar{i} | \hat{g} | a j^* \rangle\end{aligned}$$

and

$$J^{(2)}(\text{SE} + \text{P})_b = 2 \sum_i \sum_{j^*} \frac{(\langle i \bar{b} | \hat{g} | j^* a \rangle - \langle i \bar{b} | \hat{g} | a j^* \rangle) \langle \bar{b} \bar{i} | \hat{g} | a j^* \rangle}{\Delta E_{i \rightarrow j^*} + \Delta E_{b \rightarrow a}}$$

(c)

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} \uparrow \\ 0 & \uparrow \downarrow \\ \downarrow \end{bmatrix} = | \dots j^* \bar{i} b \bar{b} |$$

with the matrix elements

$$\begin{aligned}\langle \Xi_1 | \hat{H}' | \Phi_{i \rightarrow j^*}^{a \rightarrow b} \rangle &= \langle | \dots \bar{i} \bar{i} a \bar{b} | \hat{H}' | | \dots j^* \bar{i} b \bar{b} | \rangle = \langle i a | \hat{g} | j^* b \rangle - \langle i a | \hat{g} | b j^* \rangle \\ \langle \Phi_{\bar{a} \rightarrow \bar{b}}^{i \rightarrow j^*} | \hat{H}' | \Xi_2 \rangle &= \langle | \dots j^* \bar{i} b \bar{b} | \hat{H}' | | \dots \bar{i} \bar{b} \bar{a} | \rangle = \langle \bar{a} \bar{i} | \hat{g} | \bar{b} j^* \rangle\end{aligned}$$

and

$$J^{(2)}(\text{SE} + \text{P})_c = 2 \sum_i \sum_{j^*} \frac{(\langle ia|\hat{g}|j^*b \rangle - \langle ia|\hat{g}|bj^* \rangle)(\langle ai|\hat{g}|bj^* \rangle)}{\Delta E_{i \rightarrow j^*} + \Delta E_{a \rightarrow b}}$$

(d)

$$\begin{bmatrix} j^* \\ a, b \\ i \end{bmatrix} = \begin{bmatrix} \downarrow \\ 0 \uparrow \downarrow \\ \uparrow \end{bmatrix} = |\dots \bar{i} \bar{j}^* b \bar{b}|$$

with the matrix elements

$$\langle \Xi_1 | \hat{H}' | \Phi_{i \rightarrow j^*}^{a \rightarrow b} \rangle = \langle |\dots \bar{i} \bar{a} \bar{b}| \hat{H}' | |\dots \bar{i} \bar{j}^* b \bar{b}| \rangle = \langle \bar{i} \bar{a} | \hat{g} | \bar{j}^* b \rangle$$

$$\langle \Phi_{i \rightarrow j^*}^{\bar{a} \rightarrow \bar{b}} | \hat{H}' | \Xi_2 \rangle = \langle |\dots \bar{i} \bar{j}^* b \bar{b}| \hat{H}' | |\dots \bar{i} \bar{b} \bar{a}| \rangle = \langle \bar{i} \bar{a} | \hat{g} | \bar{j}^* \bar{b} \rangle - \langle \bar{i} \bar{a} | \hat{g} | \bar{b} \bar{j}^* \rangle$$

and

$$J^{(2)}(\text{SE} + \text{P})_d = 2 \sum_i \sum_{j^*} \frac{\langle ia|\hat{g}|j^*b \rangle (\langle ia|\hat{g}|j^*b \rangle - \langle ia|\hat{g}|bj^* \rangle)}{\Delta E_{i \rightarrow j^*} + \Delta E_{a \rightarrow b}}$$

These four terms can be combined into a single contribution

$$J^{(2)}(\text{SE} + \text{P}) = \sum_i \sum_{j^*} \frac{\langle ai|\hat{g}|bj^* \rangle (8\langle ai|\hat{g}|bj^* \rangle - 4\langle ab|\hat{g}|ij^* \rangle - 4\langle ab|\hat{g}|j^*i \rangle)}{\Delta E_{i \rightarrow j^*} + \Delta E_{a \rightarrow b}}$$

This holds true since for real orbitals the indices of the first and the second electron in a two-electron integral can be interchanged so that

$$\begin{aligned} \langle ij|\hat{g}|kl \rangle &= \langle il|\hat{g}|kj \rangle = \langle ji|\hat{g}|lk \rangle = \langle jk|\hat{g}|li \rangle \\ &= \langle kl|\hat{g}|ij \rangle = \langle kj|\hat{g}|il \rangle = \langle lk|\hat{g}|ji \rangle = \langle li|\hat{g}|jk \rangle \end{aligned}$$

All the second-order contributions are summarised in Table 10.7.

There are several critical points which should be briefly discussed. First, we applied a non-degenerate perturbation theory although the reference determinantal functions involving OMOs, $|\Xi_1\rangle$ and $|\Xi_2\rangle$ are degenerate. This point can be improved upon by considering a quasi-degenerate perturbation theory as proposed elsewhere [6, 7]. The effective Hamiltonian matrix in the nearly degenerate subspace $S \in I, J$ adopts the form of

TABLE 10.7

Second-order PCI contributions to the exchange coupling constant

Name	Excited determinants	Contribution ^a
Potential exchange	none	PE = $2\langle ab \hat{g} ba\rangle$
Kinetic exchange	$ a\bar{a} $ $ b\bar{b} $	KE = $4\frac{(F_{ab})^2}{\Delta E_{a\rightarrow b}}$
Hole polarisation	$ b\bar{i}a\bar{b} $ $ b\bar{i}a\bar{a} $	HP = $-4\sum_i \frac{F_{ia}\langle ib \hat{g} ba\rangle}{\Delta E_{i\rightarrow a}}$
Particle polarisation	$ aj^* $ $ bj^* $	PP = $4\sum_{j^*} \frac{F_{aj^*}\langle ba \hat{g} j^*b\rangle}{\Delta E_{a\rightarrow j^*}}$
Double-spin polarisation	$ \bar{j}^*i\bar{a}b $ $ ij^*a\bar{b} $	DSP = $-4\sum_i \sum_{j^*} \frac{\langle ib \hat{g} bj^*\rangle\langle ia \hat{g} aj^*\rangle}{\Delta E_{i\rightarrow j^*}}$
Metal-to-ligand charge transfer	$ i^*j^* $	MLCT = $2\sum_{i^*} \sum_{j^*} \frac{\langle ab \hat{g} i^*j^*\rangle\langle ba \hat{g} i^*j^*\rangle}{\Delta E_{a\rightarrow i^*} + \Delta E_{b\rightarrow j^*}}$
Ligand-to-metal charge transfer	$ j\bar{a}b\bar{i}a\bar{b} $	LMCT = $2\sum_i \sum_j \frac{\langle ij \hat{g} ab\rangle\langle ij \hat{g} ba\rangle}{\Delta E_{i\rightarrow a} + \Delta E_{j\rightarrow b}}$
Simultaneous excitation + polarisation	$ \bar{j}^*i\bar{a}\bar{a} $ $ \bar{j}^*a\bar{a} $ $ \bar{j}^*i\bar{b}\bar{b} $ $ \bar{j}^*b\bar{b} $	SE + P = $\sum_i \sum_{j^*} (\Delta E_{i\rightarrow j^*} + \Delta E_{a\rightarrow b})^{-1} \langle ai \hat{g} bj^*\rangle$ $\times (8\langle ai \hat{g} bj^*\rangle - 4\langle ab \hat{g} ij^*\rangle - 4\langle ab \hat{g} j^*i\rangle)$

^a A different sign of the HP and PP terms has been found with respect to the original references [6, 7].

$$H_{IJ}^{\text{eff}} = \langle I|\hat{H}|J\rangle + \sum_{K \neq I, J} \frac{\langle I|\hat{H}|K\rangle\langle K|\hat{H}|J\rangle}{E_I^0 - E_K^0}$$

and it needs to be diagonalised.

Second, the excitation energy $\Delta E_{a\rightarrow b}$ is zero for degenerate levels. This drawback can be overcome by considering

$$\Delta E_{a\rightarrow b} \approx -(J_{aa} - J_{ab})$$

Third, there are possibly substantial contributions from higher orders of the perturbation theory. Some attempts to include partly the higher-order

terms have been made [6, 7]. However, the convergence of the perturbation series becomes questionable.

Finally, there are contributions arising not only from the electron correlation but also from the terms originating in the spin-spin Hamiltonians derived from the relativistic quantum mechanics of many-body systems.

10.2 ISOTROPIC EXCHANGE IN DINUCLEAR SYSTEMS

10.2.1 *A prototype*

The exchange coupling in the $S_A = S_B = 1/2$ system (e.g. copper(II) acetate) represents a prototype for exchange interaction. The coupling of spin angular momenta leads to the singlet ground state ($S = 0$) and a triplet excited state ($S = 1, M_S = 0, \pm 1$) when the exchange constant, according to our definition, is negative: $J < 0$ (antiferromagnetic coupling). For $J > 0$ (ferromagnetic coupling) the ordering of the energy levels is reversed (Fig. 10.4). The situation somewhat resembles the behaviour already described for zero-field splitting systems.

The expression for the magnetisation and the magnetic susceptibility can be derived in two ways, as follows.

1. The exact derivation utilises the energy levels written as

i	S	M_S	$\varepsilon_{S,M_S}(B)$
1	0	0	0
2	1	-1	$-J - \mu_B g B$
3		0	$-J$
4		+1	$-J + \mu_B g B$

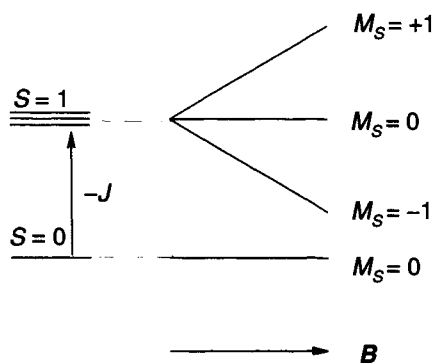


Fig. 10.4. Energy levels in a dinuclear system, $S_A = S_B = 1/2$.

Consequently, the partition function is

$$Z = 1 + \exp[(J + \mu_B g B)/kT] + \exp[J/kT] + \exp[(J - \mu_B g B)/kT]$$

It determines the magnetisation and the differential magnetic susceptibility according to the equations

$$M = N_A \frac{1}{Z} T_1$$

$$\tilde{\chi} = \frac{N_A \mu_0}{kT} \frac{1}{Z} (T_2 Z - T_1^2)$$

with the terms

$$\begin{aligned} T_1 &= \sum_i \left(-\frac{\partial \varepsilon_i}{\partial B} \right) \exp(-\varepsilon_i/kT) \\ &= \mu_B g \{ \exp[(J + \mu_B g B)/kT] - \exp[(J - \mu_B g B)/kT] \} \end{aligned}$$

and

$$\begin{aligned} T_2 &= \sum_i \left(\frac{\partial \varepsilon_i}{\partial B} \right)^2 \exp(-\varepsilon_i/kT) \\ &= (\mu_B g)^2 \{ \exp[(J + \mu_B g B)/kT] + \exp[(J - \mu_B g B)/kT] \} \end{aligned}$$

2. An approximate derivation utilises the van Vleck equation in which the van Vleck coefficients occur

i	$\varepsilon_i^{(0)}$	$\varepsilon_i^{(1)}$	$\varepsilon_i^{(2)}$
1	0	0	0
2	$-J$	$-\mu_B g$	0
3	$-J$	0	0
4	$-J$	$+\mu_B g$	0

However, one can shift the energy origin arbitrarily and thus the coefficient $\varepsilon_i^{(0)}$ can be substituted for

$$\varepsilon_i^{(0)} \rightarrow \varepsilon_i^{(0)} + J$$

yielding the mean susceptibility

$$\bar{\chi} = N_A \mu_0 \frac{0 \cdot \exp(-J/kT) + \frac{\mu_B^2 g^2}{kT} \cdot \exp(0) + 0 \cdot \exp(0) + \frac{\mu_B^2 g^2}{kT} \cdot \exp(0)}{\exp(-J/kT) + 3 \cdot \exp(0)}$$

and finally

$$\bar{\chi} = \frac{N_A \mu_0 \mu_B^2 g^2}{k} \frac{2}{T (3 + \exp(-J/kT))}$$

This is the *Bleaney–Bowers equation* for the dimeric $S_A = S_B = 1/2$ system. For $J > 0$ the magnetic susceptibility increases monotonically on temperature lowering (a ferromagnetic coupling of spin magnetic moments). For $J < 0$, on the other hand, it passes through a maximum at $T_{\max}$ which is related to the coupling constant through

$$|J|/k = 1.599 T_{\max}$$

and then decreases to zero (Fig. 10.5).

10.2.2 Homospin dinuclear systems

For the exchange coupling of homospin systems the allowed molecular states lie between

$$S_{\min} = |S_A - S_B|$$

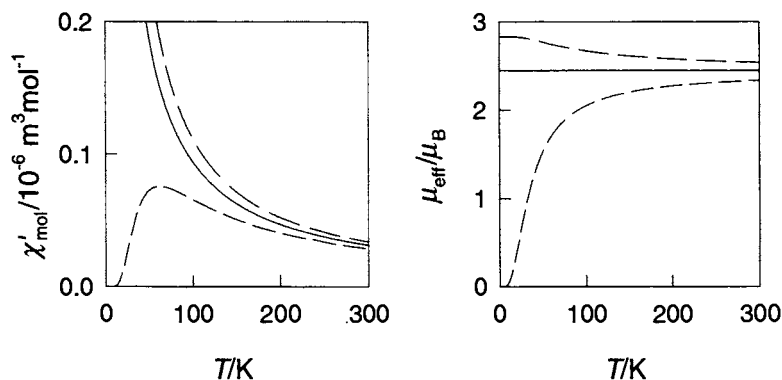


Fig. 10.5. Temperature behaviour of a dimer $S_A = S_B = 1/2$ system: $g = 2.0$, long dashed—ferromagnetic coupling ($J/k = 100$ K); short dashed—antiferromagnetic coupling ($J/k = -100$ K); solid—no coupling ($J = 0$).

and

$$S_{\max} = S_A + S_B$$

Hence

$$S_{\min} \leq S \leq S_{\max}$$

and

$$M_S = -S, -S + 1, \dots, +S - 1, +S$$

The Heisenberg form of the isotropic exchange coupling Hamiltonian

$$\hat{H} = -J(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}]$$

can be rewritten using the relationship

$$\vec{S}^2 = (\vec{S}_A + \vec{S}_B)^2 = \vec{S}_A^2 + \vec{S}_B^2 + 2\vec{S}_A \cdot \vec{S}_B$$

in the form of

$$\hat{H} = -\frac{J}{2}(\vec{S}^2 - \vec{S}_A^2 - \vec{S}_B^2)[\hbar^{-2}]$$

In this fortunate case the zero-field Hamiltonian is diagonal, giving rise to energy levels

$$\varepsilon_S = -\frac{J}{2}[S(S+1) - S_A(S_A+1) - S_B(S_B+1)]$$

The origin of the energy can be shifted arbitrarily, say by a constant factor of $c = -(J/2)[S_A(S_A+1) + S_B(S_B+1)]$. Then one has

$$\varepsilon_S = -\frac{J}{2}S(S+1)$$

Since the (spin) Zeeman operator in the basis set of coupled spin angular momenta functions $|S, M_S\rangle$ is diagonal as well, then the magnetic energy levels are easy to generate (Table 10.8)

$$\varepsilon_{S, M_S}(B) = \varepsilon_S(B=0) + \mu_B g B M_S = -n_S J + \mu_B g B M_S$$

Then the partition function becomes

$$Z = \sum_{S=S_{\min}}^{S_{\max}} Z(S) = \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} \exp[(n_S J - \mu_B g B M_S)/kT]$$

TABLE 10.8

Energy levels ε_S for a dinuclear homospin system in zero field

S	$n_S = S(S+1)/2$	$\varepsilon_S = -n_S J$
0	0	0
1	1	$-J$
2	3	$-3J$
3	6	$-6J$
4	10	$-10J$
5	15	$-15J$
6	21	$-21J$
7	28	$-28J$

In evaluating the magnetic susceptibility one can apply the “magnetisation formula” (Chapter 2). Because the second-order derivatives are zero for the isotropic exchange model, a simplification is obtained

$$M = N_A \frac{1}{Z} T_1$$

and

$$\tilde{\chi} = \frac{N_A \mu_0}{kT} \frac{1}{Z^2} (T_2 Z - T_1^2)$$

The terms of the magnetisation and the susceptibility are (Table 10.9)

$$T_1 = \mu_B g \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S \exp[(n_S J - \mu_B g B M_S)/kT]$$

and

$$T_2 = (\mu_B g)^2 \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S^2 \exp[(n_S J - \mu_B g B M_S)/kT]$$

The corresponding plots for a negative coupling constant are given in Fig. 10.6. It can be seen that the magnetisation, evaluated exactly as a function of the magnetic field, shows some steps. These originate in the fact that with increasing magnetic field a magnetically more productive state becomes the ground state, giving rise to a step increase of the magnetisation. If the coupling constants were positive, no steps on the magnetisation curve would be observable.

TABLE 10.9

Terms of the magnetic susceptibility for dinuclear homospin systems^a

$S_A = S_B$	$S_{\max}$	$Z(S)$	$T_1(S)/(\mu_B g)$	$T_2(S)/(\mu_B g)^2$
1/2	1	1 + exp($x + By$) + exp(x) + exp($x - By$)	+1 · exp($x + By$) -1 · exp($x - By$)	+1 ² · exp($x + By$) +1 ² · exp($x - By$)
1	2	$Z(S - 1)$ + exp($3x + 2By$) + exp($3x + By$) + exp($3x$) + exp($3x - By$) + exp($3x - 2By$)	$T_1(S - 1)$ +2 · exp($3x - 2By$) +1 · exp($3x + By$) -1 · exp($3x - By$) -2 · exp($3x - 2By$)	$T_2(S - 1)$ +2 ² · exp($3x + 2By$) +1 ² · exp($3x + By$) 1 ² · exp($3x - By$) +2 ² · exp($3x - 2By$)
3/2	3	$Z(S - 1)$ + exp($6x + 3By$) + exp($6x + 2By$) + exp($6x + By$) + exp($6x$) + exp($6x - By$) + exp($6x - 2By$) + exp($6x - 3y$)	$T_1(S - 1)$ +3 · exp($6x + 3By$) +2 · exp($6x + 2By$) +1 · exp($6x + By$) -1 · exp($6x - By$) -2 · exp($6x - 2By$) -3 · exp($6x - 3By$)	$T_2(S - 1)$ +3 ² · exp($6x + 3By$) +2 ² · exp($6x + 2By$) +1 ² · exp($6x + By$) +1 ² · exp($6x - By$) +2 ² · exp($6x - 2By$) +3 ² · exp($6x - 3By$)
2	4	$Z(S - 1)$ + exp($10x + 4By$) + exp($10x + 3By$) + exp($10x + 2By$) + exp($10x + By$) + exp($10x$) + exp($10x - By$) + exp($10x - 2By$) + exp($10x - 3By$) + exp($10x - 4By$)	$T_1(S - 1)$ +4 · exp($10x + 4By$) +3 · exp($10x + 3By$) +2 · exp($10x + 2By$) +1 · exp($10x + By$) -1 · exp($10x - By$) -2 · exp($10x - 2By$) -3 · exp($10x - 3By$) -4 · exp($10x - 4By$)	$T_2(S - 1)$ +4 ² · exp($10x + 4By$) +3 ² · exp($10x + 3By$) +2 ² · exp($10x + 2By$) +1 ² · exp($10x + By$) +1 ² · exp($10x - By$) +2 ² · exp($10x - 2By$) +3 ² · exp($10x - 3By$) +4 ² · exp($10x - 4By$)
5/2	5	$Z(S - 1)$ + exp($15x + 5By$) + exp($15x + 4By$) + exp($15x + 3By$) + exp($15x + 2By$) + exp($15x + By$) + exp($15x$) + exp($15x - By$) + exp($15x - 2By$) + exp($15x - 3By$) + exp($15x - 4By$) + exp($15x - 5By$)	$T_1(S - 1)$ +5 · exp($15x + 5By$) +4 · exp($15x + 4By$) +3 · exp($15x + 3By$) +2 · exp($15x + 2By$) +1 · exp($15x + By$) -1 · exp($15x - By$) -2 · exp($15x - 2By$) -3 · exp($15x - 3By$) -4 · exp($15x - 4By$) -5 · exp($15x - 5By$)	$T_2(S - 1)$ +5 ² · exp($15x + 5By$) +4 ² · exp($15x + 4By$) +3 ² · exp($15x + 3By$) +2 ² · exp($15x + 2By$) +1 ² · exp($15x + By$) +1 ² · exp($15x - By$) +2 ² · exp($15x - 2By$) +3 ² · exp($15x - 3By$) +4 ² · exp($15x - 4By$) +5 ² · exp($15x - 5By$)

^a Substitution: $x = J/kT$, $y = \mu_B g/kT$.

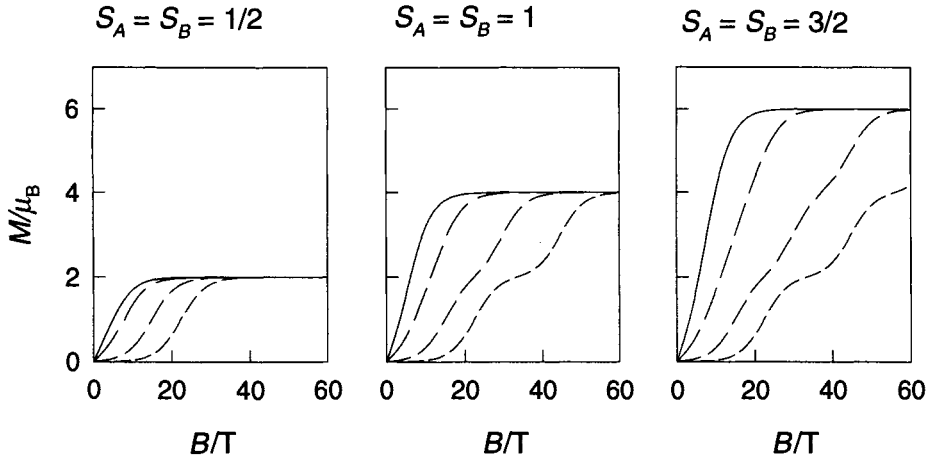


Fig. 10.6. Magnetisation per dimer versus the applied field for dinuclear homospin systems at $T = 4.2$ K; $J/k = -5$ K (solid), $J/k = -10$ K (long dashed), $J/k = -20$ K (medium dashed), $J/k = -30$ K (short dashed).

As a consequence of the non-linear behaviour of the magnetisation, the differential magnetic susceptibility is no longer a constant. It exhibits a wave-type functional dependence on the increasing magnetic field, as shown in Fig. 10.7.

The application of the van Vleck formula is based on the van Vleck coefficients which are simply

$$\varepsilon_i^{(0)}(S, M_S) = -\frac{J}{2} S(S+1)$$

$$\varepsilon_i^{(1)}(S, M_S) = M_S \mu_B g$$

$$\varepsilon_i^{(2)}(S, M_S) = 0$$

Then the van Vleck formula adopts the form of

$$\bar{\chi}_{\text{mol}} = N_A \mu_0 \frac{\sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} \frac{(M_S \mu_B g)^2}{kT} \exp[S(S+1)J/2kT]}{\sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} \exp[S(S+1)J/2kT]}$$

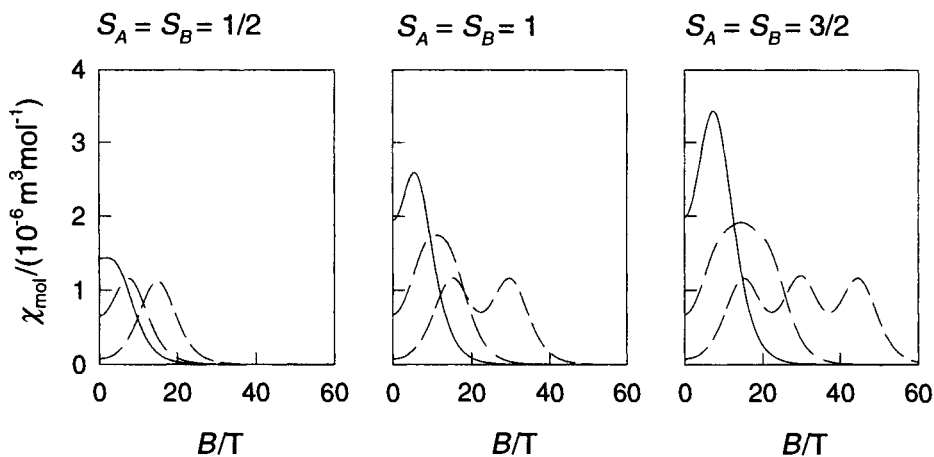


Fig. 10.7. Differential magnetic susceptibility per dimer versus the applied field for dinuclear homospin systems at $T = 4.2$ K; $J/k = -5$ K (solid), $J/k = -10$ K (long dashed), $J/k = -20$ K (medium dashed).

which can be rewritten using the summation

$$\sum_{M_S=-S}^{+S} (M_S)^2 = S(S+1)(2S+1)/3$$

as follows

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{k} \frac{g^2}{3T} \frac{\sum_{S=S_{\min}}^{S_{\max}} S(S+1)(2S+1) \exp[S(S+1)J/2kT]}{\sum_{S=S_{\min}}^{S_{\max}} (2S+1) \exp[S(S+1)J/2kT]}$$

Then the analytical formulae for individual spin combinations exist in the form of

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{k} \frac{2g^2}{T} F(x)$$

for the argument

$$x = J/kT$$

TABLE 10.10

Characteristic susceptibility functions for dinuclear homospin systems $S_A = S_B$

S_A	$F(x)$
1/2	$\frac{\exp(x)}{1 + 3 \exp(x)}$
1	$\frac{\exp(x) + 5 \exp(3x)}{1 + 3 \exp(x) + 5 \exp(3x)}$
3/2	$\frac{\exp(x) + 5 \exp(3x) + 14 \exp(6x)}{1 + 3 \exp(x) + 5 \exp(3x) + 7 \exp(6x)}$
2	$\frac{\exp(x) + 5 \exp(3x) + 14 \exp(6x) + 30 \exp(10x)}{1 + 3 \exp(x) + 5 \exp(3x) + 7 \exp(6x) + 9 \exp(10x)}$
5/2	$\frac{\exp(x) + 5 \exp(3x) + 14 \exp(6x) + 30 \exp(10x) + 55 \exp(15x)}{1 + 3 \exp(x) + 5 \exp(3x) + 7 \exp(6x) + 9 \exp(10x) + 11 \exp(15x)}$
3	$\frac{\exp(x) + 5 \exp(3x) + 14 \exp(6x) + 30 \exp(10x) + 55 \exp(15x) + 273 \exp(21x)}{1 + 3 \exp(x) + 5 \exp(3x) + 7 \exp(6x) + 9 \exp(10x) + 11 \exp(15x) + 13 \exp(21x)}$
7/2	$\frac{\exp(x) + 5 \exp(3x) + 14 \exp(6x) + 30 \exp(10x) + 55 \exp(15x) + 273 \exp(21x) + 476 \exp(28x)}{1 + 3 \exp(x) + 5 \exp(3x) + 7 \exp(6x) + 9 \exp(10x) + 11 \exp(15x) + 13 \exp(21x) + 15 \exp(28x)}$

The explicit form of the characteristic function $F(x)$ is given in Table 10.10.

For ferromagnetic exchange ($J > 0$) the magnetic susceptibility increases monotonically on temperature lowering and, for antiferromagnetic exchange ($J < 0$), it passes through a maximum. The relationships between $T_{\max}$ and $|J|$ are listed in Table 10.11.

TABLE 10.11

Temperature of maximum susceptibility for antiferromagnetically coupled spin dimers

$S_A = S_B$	$ J /kT_{\max}$
1/2	1.599
1	0.976
3/2	0.648
2	0.462
5/2	0.347
3	0.134
7/2	0.0945

10.2.3 Heterospin dinuclear systems

There are 21 combinations of heterospin dinuclear systems between $S_A = 1/2$ and $S_B = 7/2$ local spins. The zero-field energy levels of the coupled systems can be generated in the same way as in the previous case of homospin systems. The result is

$$\varepsilon_S = -\frac{J}{2}[S(S+1) - S_A(S_A+1) - S_B(S_B+1)]$$

which, after an appropriate shift of the origin, can be simplified to

$$\varepsilon_S = -\frac{J}{2}S(S+1)$$

The exchange Hamiltonian in the presence of the magnetic field is enriched by the (spin) Zeeman term, hence

$$\hat{H} = -J(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}] + \mu_B \vec{B} \cdot \vec{g}_A \cdot \vec{S}_A[\hbar^{-1}] + \mu_B \vec{B} \cdot \vec{g}_B \cdot \vec{S}_B[\hbar^{-1}]$$

where we use the uncoupled spin operators. Such a Hamiltonian will generate the matrix elements in the basis set of uncoupled spin states $i = |S_A, M_{SA}\rangle |S_B, M_{SB}\rangle$

$$H_{ij} = \langle i | \hat{H} | j \rangle$$

In order to obtain the magnetic energy levels this Hamiltonian matrix must be diagonalised. Its order is $N = (2S_A + 1)(2S_B + 1)$.

Another possibility is to pass into the basis set of coupled spin functions $I = |S, M_S\rangle$ in which the Hamiltonian

$$\hat{H} = -\frac{J}{2}(\vec{S}^2 - \vec{S}_A^2 - \vec{S}_B^2)[\hbar^{-2}] + \mu_B \vec{B} \cdot \vec{g}_S \cdot \vec{S}[\hbar^{-1}]$$

generates a diagonal zero-field matrix

$$H_{IJ} = \langle I | \hat{H}^{(0)} | J \rangle \delta_{S,S'} \delta_{M_S,M'_S}$$

The Zeeman term is added as a perturbation and the magnetic energy levels are given by the diagonalisation of such a matrix. What we need is a transformation of the Zeeman term from the local spin functions into the basis set of molecular spin functions

$$\hat{H}^Z = \mu_B \vec{B} \cdot (\vec{g}_A \cdot \vec{S}_A + \vec{g}_B \cdot \vec{S}_B)[\hbar^{-1}] \rightarrow \mu_B \vec{B} \cdot \vec{g}_S \cdot \vec{S}[\hbar^{-1}]$$

In other words, we seek the expression of the molecular-state g -factor in terms of the local g -factors

$$\bar{g}_S = f(\bar{g}_A, \bar{g}_B)$$

For this purpose the Zeeman term is rewritten in the form of

$$\hat{H}^Z = \mu_B \vec{B} \cdot (\bar{g}_+ \cdot \vec{S} + \bar{g}_- \cdot \vec{V})(1/2)[\hbar^{-1}]$$

where we introduce the vector operators

$$\vec{S} = \vec{S}_A + \vec{S}_B$$

$$\vec{V} = \vec{S}_A - \vec{S}_B$$

and

$$\bar{g}_+ = \bar{g}_A + \bar{g}_B$$

$$\bar{g}_- = \bar{g}_A - \bar{g}_B$$

Using the Wigner–Eckart theorem, one can express the matrix elements of the operator $\vec{V}$ through the relationship

$$\langle SM | \vec{V} | S'M' \rangle = \langle SM | \vec{S} | S'M' \rangle \frac{\langle S \| \vec{V} \| S \rangle}{\langle S \| \vec{S} \| S \rangle} \delta_{S,S'} = c \langle SM | \vec{S} | S'M' \rangle$$

where the proportionality coefficient

$$c = \frac{\langle S \| \vec{V} \| S \rangle}{\langle S \| \vec{S} \| S \rangle} \delta_{S,S'}$$

is given by the reduced matrix elements. Therefore the Zeeman term adopts the form of

$$\hat{H}^Z = \mu_B \vec{B} \cdot \frac{(\bar{g}_+ + c\bar{g}_-)}{2} \cdot \vec{S}[\hbar^{-1}] = \mu_B \vec{B} \cdot \left(\frac{1+c}{2} \bar{g}_A + \frac{1-c}{2} \bar{g}_B \right) \cdot \vec{S}[\hbar^{-1}]$$

Hence, the g -factor for a given molecular state becomes

$$\begin{aligned}\bar{g}_S &= \frac{1+c}{2}\bar{g}_A + \frac{1-c}{2}\bar{g}_B = c_A\bar{g}_A + c_B\bar{g}_B = c_A\bar{g}_A + (1-c_A)\bar{g}_B \\ &= \frac{1}{2}(\bar{g}_+ + c\bar{g}_-)\end{aligned}$$

In order to evaluate the proportionality coefficient, let us recall that the denominator is simply

$$\langle S \| \vec{S} \| S' \rangle = \delta_{S,S'} \sqrt{S(S+1)(2S+1)} [\hbar]$$

(see Table 1.15). In expressing the numerator, we deal with the first-rank irreducible tensor operators $\vec{S}_A = \hat{T}_1$ and $\vec{S}_B = \hat{T}_1$. Their matrix elements (Section 1.5.4) are expressed as follows

$$\begin{aligned}\langle S_A S_B S \| \vec{S}_A \| S_A S_B S \rangle &= \sqrt{S_A(S_A+1)(2S_A+1)(2S+1)} (-1)^{S_A+S_B+S+1} \\ &\quad \times \left\{ \begin{matrix} S & 1 & S \\ S_A & S_B & S_A \end{matrix} \right\} [\hbar]\end{aligned}$$

where the $6j$ -symbol fulfils the identities

$$\left\{ \begin{matrix} S & 1 & S \\ S_A & S_B & S_A \end{matrix} \right\} = \left\{ \begin{matrix} 1 & S & S \\ S_B & S_A & S_A \end{matrix} \right\} = \left\{ \begin{matrix} S_B & S_A & S \\ 1 & S & S_A \end{matrix} \right\}$$

and is evaluated according to

$$\left\{ \begin{matrix} a & b & c \\ 1 & c & b \end{matrix} \right\} = (-1)^{a+b+c+1} \frac{2[b(b+1) + c(c+1) - a(a+1)]}{[2b(2b+1)(2b+2)2c(2c+1)(2c+2)]^{1/2}}$$

Consequently

$$\begin{aligned}&\langle S_A S_B S \| \vec{S}_A \| S_A S_B S \rangle \\ &= \sqrt{S_A(S_A+1)(2S_A+1)(2S+1)} (-1)^{S_A+S_B+S+1} (-1)^{S_A+S_B+S+1} \\ &\quad \times \frac{2[S_A(S_A+1) + S(S+1) - S_B(S_B+1)]}{[2S_A(2S_A+1)2(S_A+1)2S(2S+1)2(S+1)]^{1/2}} [\hbar]\end{aligned}$$

yielding

$$\frac{\langle S_A S_B S \| \vec{S}_A \| S_A S_B S \rangle}{\langle S \| \vec{S} \| S \rangle} = \frac{[S_A(S_A+1) + S(S+1) - S_B(S_B+1)]}{2[S(S+1)]}$$

Analogously

$$\begin{aligned} \langle S_A S_B S \| \vec{S}_B \| S_A S_B S \rangle &= \sqrt{S_B(S_B + 1)(2S_B + 1)(2S + 1)}(-1)^{S_A + S_B + S + 1} \\ &\quad \times \left\{ \begin{matrix} S & 1 & S \\ S_B & S_A & S_B \end{matrix} \right\} [\hbar] \end{aligned}$$

gives

$$\frac{\langle S_A S_B S \| \vec{S}_B \| S_A S_B S \rangle}{\langle S \| \vec{S} \| S \rangle} = \frac{[S_B(S_B + 1) + S(S + 1) - S_A(S_A + 1)]}{2[S(S + 1)]}$$

The proportionality coefficient becomes expressed as

$$c = \frac{\langle S_A S_B S \| \vec{S}_A \| S_A S_B S \rangle - \langle S_A S_B S \| \vec{S}_B \| S_A S_B S \rangle}{\langle S \| \vec{S} \| S \rangle}$$

and the final result is (Table 10.12)

$$c = \frac{S_A(S_A + 1) - S_B(S_B + 1)}{S(S + 1)}$$

Then the molecular-state g -factor becomes expressed as

$$\bar{g}_S = \frac{(\bar{g}_+ + c\bar{g}_-)}{2} = \frac{1}{2}(\bar{g}_A + \bar{g}_B) + \frac{S_A(S_A + 1) - S_B(S_B + 1)}{S(S + 1)} \frac{1}{2}(\bar{g}_A - \bar{g}_B)$$

For the special case of $S_A = S_B$ we get

$$\bar{g}_S = \frac{1}{2}(\bar{g}_A + \bar{g}_B), \quad [\text{for } S_A = S_B]$$

whatever the value of S .

The van Vleck coefficients are now

$$\varepsilon_i^{(0)} = -\frac{J}{2}S(S + 1)$$

$$\varepsilon_i^{(1)} = \mu_B g_S M_S$$

TABLE 10.12

The g -tensor coefficients, c_A , the second-order coefficients, d_S , and the D -tensor coefficients, C_A , C_B and C_{AB} , in dinuclear systems^a

S_A	S_B	S	c_A	d_S	C_A	C_B	C_{AB}
1/2	1/2	0	1/2	+3/4	0	0	0
		1	1/2	-1/4	0	0	1/2
1/2	1	1/2	-1/3	+4/9	0	0	0
		3/2	+1/3	-2/9	0	+1/3	+1/3
1/2	3/2	1	-1/4	+5/16	0	+3/2	-1/4
		2	+1/4	-3/16	0	+1/2	+1/4
1/2	2	3/2	-1/5	+6/25	0	+7/5	-1/5
		5/2	+1/5	-4/25	0	+3/5	+1/5
1/2	5/2	2	-1/6	+7/36	0	+4/3	-1/6
		3	+1/6	-5/36	0	+2/3	+1/6
1/2	3	5/2	-1/7	+8/49	0	+9/7	-1/7
		7/2	+1/7	-6/49	0	+5/7	+1/7
1/2	7/2	3	-1/8	+9/64	0	+5/4	-1/8
		4	+1/8	-7/64	0	+3/4	+1/8
1	1	0	+1/2	+2	0	0	0
		1	+1/2	-1/4	-1/2	-1/2	+1
		2	+1/2	-1/4	+1/6	+1/6	+1/3
1	3/2	1/2	-2/3	+10/9	0	0	0
		3/2	+4/15	-44/225	-4/15	+1/5	+8/15
		5/2	+2/5	-6/25	+1/10	+3/10	+3/10
1	2	1	-1/2	+3/4	+1/10	+21/10	-3/5
		2	+1/6	-5/36	-1/6	+1/2	+1/3
		3	+1/3	-2/9	+1/15	+2/5	+4/15
1	5/2	3/2	-2/5	+14/25	+1/15	+28/15	-7/15
		5/2	+4/35	-124/1225	-4/35	+23/35	+8/35
		7/2	+2/7	-10/49	+1/21	+10/21	+5/21
1	3	2	-1/3	+9/4	+1/21	+12/7	-8/21
		3	+1/12	-11/144	-1/12	+3/4	+1/6
		4	+1/4	-3/16	+1/28	+15/28	+3/14
1	7/2	5/2	-2/7	+18/49	+1/28	+45/28	-9/28
		7/2	+4/63	-236/3969	-4/63	+17/21	+8/63
		9/2	+2/9	-14/81	+1/36	+7/12	+7/36
3/2	3/2	0	1/2	+6	0	0	0
		1	1/2	-1/4	-6/5	-6/5	+17/10
		2	1/2	-1/4	0	0	+1/2
3/2	2	1/2	-1/4	+1/4	+1/5	+1/5	+3/10
		3/2	+1/5	-4/25	-3/5	0	+4/5
		5/2	+13/35	-286/1225	-3/70	+3/14	+29/70
3/2	5/2	7/2	+3/7	-12/49	+1/7	+2/7	+2/7
		1	-3/4	+21/16	+3/10	+14/5	-21/20
		2	+1/12	-11/144	-5/14	+10/21	+37/84
		3	+7/24	-119/576	-1/20	+11/30	+41/120
		4	+3/8	-15/64	+3/28	+5/14	+15/56

(contd.)

TABLE 10.12

The g -tensor coefficients, c_A , the second-order coefficients, d_S , and the D -tensor coefficients, C_A , C_B and C_{AB} , in dinuclear systems^a (*contd.*)

S_A	S_B	S	c_A	d_S	C_A	C_B	C_{AB}
3/2	3	3/2	-3/5	+24/25	+1/5	+12/5	-4/5
		5/2	+1/35	-34/1225	-33/140	+99/140	+37/140
		7/2	+5/21	-80/441	-1/21	+10/21	+2/7
		9/2	+1/3	-2/9	+1/12	+5/12	+1/4
3/2	7/2	2	-1/2	+3/4	+1/7	+15/7	-9/14
		3	0	0	-1/6	+5/6	+1/6
		4	+1/5	-4/25	-3/70	+39/70	+17/70
		5	+3/10	-21/100	+1/15	+7/15	+7/30
2	2	0	1/2	+15/4	0	0	0
		1	1/2	-1/4	-21/10	-21/10	+13/5
		2	1/2	-1/4	-3/14	-3/14	+5/7
		3	1/2	-1/4	+1/10	+1/10	+2/5
		4	1/2	-1/4	+3/14	+3/14	+2/7
2	5/2	1/2	-4/3	+28/9	0	0	0
		3/2	+2/15	-26/225	-1/10	-4/15	+17/15
		5/2	+12/35	-276/1225	-3/14	+1/10	+39/70
		7/2	+26/63	-962/3969	+1/21	+2/9	+23/63
		9/2	+4/9	-20/81	+1/6	+5/18	+5/18
2	3	1	-1	+2	+3/5	+18/5	-8/5
		2	0	0	-4/7	+3/7	+4/7
		3	+1/4	-3/16	-11/60	+19/60	+13/30
		4	+7/20	-91/400	+3/140	+9/28	+23/70
		5	+2/5	-6/25	+2/15	+1/3	+4/15
2	7/2	3/2	-4/5	+36/25	+2/5	+3	-6/5
		5/2	-2/35	+74/1225	-51/140	+3/4	+43/140
		7/2	+4/21	-68/441	-16/105	+7/15	+12/35
		9/2	+10/33	-230/1089	+1/132	+53/132	+13/44
		11/2	+4/11	-28/121	+6/55	+21/55	+14/55
5/2	5/2	0	1/2	+35/4	0	0	0
		1	1/2	-1/4	-16/5	-16/5	+37/10
		2	1/2	-1/4	-10/21	-10/21	+41/42
		3	1/2	-1/4	-1/45	-1/45	+47/90
		4	1/2	-1/4	+1/7	+1/7	+5/14
5/2	3	5	1/2	-1/4	+2/9	+2/9	+5/18
		1/2	-5/3	+40/9	0	0	0
		3/2	+1/15	-14/225	-22/15	-3/5	+23/15
		5/2	+11/35	-264/1225	-29/70	-3/70	+51/70
		7/2	+25/63	-950/3969	-4/63	+1/7	+29/63
5/2	7/2	9/2	+43/99	-2408/9801	+19/198	+5/22	+67/198
		11/2	+5/11	-30/121	+2/11	+3/11	+3/11
		1	-5/4	+45/16	+1	+9/2	-9/4
		2	-1/12	+13/144	-17/21	+5/14	+61/84
		3	+5/24	-95/576	-1/3	+1/4	+13/24
		4	+13/40	-351/1600	-29/385	+423/1540	1233/3080

TABLE 10.12

The g -tensor coefficients, c_A , the second-order coefficients, d_S , and the D -tensor coefficients, C_A , C_B and C_{AB} , in dinuclear systems^a (*contd.*)

S_A	S_B	S	c_A	d_S	C_A	C_B	C_{AB}
3	3	5	+23/60	-851/3600	+1/15	+3/10	+19/60
		6	+5/12	-35/144	+5/33	+7/22	+35/132
		0	1/2	+12	0	0	0
		1	1/2	-1/4	-9/2	-9/2	+5
		2	1/2	-1/4	-11/4	-11/4	+9/7
		3	1/2	-1/4	-1/6	-1/6	+2/3
		4	1/2	-1/4	+9/154	+9/154	+34/77
		5	1/2	-1/4	+1/6	+1/6	+1/3
		6	1/2	-1/4	+5/22	+5/22	+3/11
		7/2	-2	+6	0	0	0
3	7/2	3/2	0	0	-2	-1	+2
		5/2	+2/7	-10/49	-9/14	-3/14	+13/14
		7/2	+8/21	-104/441	-4/21	+1/21	+4/7
		9/2	+14/33	-266/1089	+1/66	+1/6	+9/22
		11/2	+64/143	-5056/20449	+18/143	+3/13	+46/143
		13/2	+6/13	-42/169	+5/26	+7/26	+7/26
		7/2	1/2	+63/4	0	0	0
		1	1/2	-1/4	-6	-6	+13/2
		2	1/2	-1/4	-8/7	-8/7	+23/14
		3	1/2	-1/4	-1/3	-1/3	+5/6
7/2	7/2	4	1/2	-1/4	-3/77	-3/77	+83/154
		5	1/2	-1/4	+4/39	+4/39	+31/78
		6	1/2	-1/4	+2/11	+2/11	+7/22
		7	1/2	-1/4	+3/13	+3/13	+7/26

^aNote: $c_B = 1 - c_A$.

However, some second-order van Vleck coefficients are non-zero due to the fact that certain magnetic states are coupled through the Zeeman operator

$$\langle S, M_S | \hat{H}^Z | S', M_S \rangle \neq 0$$

Interestingly, the formula for the molecular-state g -factor g_S is similar to that obtained for the atomic-term g -factor g_J when spin-orbit coupling was considered (Section 8.5.2); hence

$$g_J = \frac{1}{2}(g_e + g_L) + \frac{S(S+1) - L(L+1)}{J(J+1)} \frac{1}{2}(g_e - g_L), \quad [\text{in an atom}]$$

for $g_L = 1$ and $g_e = 2$. This is because the spin-orbit coupling in an atom is, in fact, a kind of isotropic coupling of angular momenta. For this reason we

can utilise a formal analogy of the intraatomic spin-orbit coupling and the interatomic spin-spin coupling in deriving the matrix elements of the Zeeman operator. In an atom there is

$$\begin{aligned} & \langle LSJ'M | \hat{H}_z^Z | LSJM \rangle \\ &= \mu_B B_z \left[g_e \langle LSJ'M | \hat{J}_z | LSJM \rangle + (g_L - g_e) \langle LSJ'M | \hat{L}_z | LSJM \rangle \right] [\hbar^{-1}] \end{aligned}$$

Since the first term vanishes, the off-diagonal matrix elements are

$$\begin{aligned} & \langle LSJ'M | \hat{H}_z^Z | LSJM \rangle \\ &= (g_L - g_e) \mu_B B_z \langle LSJ'M | \hat{L}_z | LSJM \rangle [\hbar^{-1}] \\ &= -(g_L - g_e) \mu_B B_z \left\{ \frac{[J^2 - (L - S)^2][(L + S + 1)^2 - J^2](J^2 - M^2)}{4J^2(4J^2 - 1)} \right\}^{1/2} \end{aligned}$$

for

$$J' = J - 1$$

In a dinuclear molecule there is

$$\begin{aligned} \langle S_A S_B S' M | \hat{H}_z^Z | S_A S_B S M \rangle &= \mu_B B_z \left[g_B \langle S_A S_B S' M | \hat{S}_z | S_A S_B S M \rangle \right. \\ &\quad \left. + (g_A - g_B) \langle S_A S_B S' M | \hat{S}_{A,z} | S_A S_B S M \rangle \right] [\hbar^{-1}] \end{aligned}$$

The first term again vanishes for the off-diagonal matrix elements and thus it is

$$\begin{aligned} & \langle S_A S_B S' M | \hat{H}_z^Z | S_A S_B S M \rangle \\ &= (g_A - g_B) \mu_B B_z \langle S_A S_B S' M | \hat{S}_{A,z} | S_A S_B S M \rangle [\hbar^{-1}] \\ &= -(g_A - g_B) \mu_B B_z \left\{ \frac{[S^2 - (S_A - S_B)^2][(S_A + S_B + 1)^2 - S^2](S^2 - M^2)}{4S^2(4S^2 - 1)} \right\}^{1/2} \end{aligned}$$

for

$$S' = S - 1$$

The energy contribution in second-order perturbation theory is

$$\begin{aligned}
 E_2(S, M) &= - \sum_{S' \neq S} \frac{\langle S' M | \hat{H}^Z | S M \rangle^2}{E_0(S') - E_0(S)} [\hbar^{-2}] \\
 &= -[(g_A - g_B)\mu_B B_z]^2 \sum_{S' \neq S} \frac{\langle S' M | \hat{S}_{A,z} | S M \rangle^2}{E_0(S') - E_0(S)} [\hbar^{-2}]
 \end{aligned}$$

and this is helpful in identifying the second-order van Vleck coefficients. The energy differences entering the denominator are

$$E_0(S+1) - E_0(S) = -\frac{J}{2}(S+1)(S+2) + \frac{J}{2}S(S+1) = -J(S+1)$$

$$E_0(S-1) - E_0(S) = -\frac{J}{2}(S-1)S + \frac{J}{2}S(S+1) = JS$$

and the matrix element of the Zeeman operator occurring in the numerator is expressed as

$$\begin{aligned}
 \langle S_A S_B, S+1, M | \hat{S}_{A,z} | S_A S_B S M \rangle &= \langle S_A S_B, S, M | \hat{S}_{A,z} | S_A S_B, S+1, M \rangle \\
 &= -[(S+1)^2 - M^2]^{1/2} f(S_A, S_B, S+1) [\hbar]
 \end{aligned}$$

with the spin function

$$f(S_A, S_B, S) = \left\{ \frac{[S^2 - (S_A - S_B)^2][(S_A + S_B + 1)^2 - S^2]}{4S^2(4S^2 - 1)} \right\}^{1/2}$$

Then the second-order van Vleck coefficients are

$$\begin{aligned}
 \varepsilon_{S,M}^{(2)} &= -[(g_A - g_B)\mu_B]^2 \\
 &\times \left\{ \frac{[f(S_A, S_B, S+1)]^2[(J+1)^2 - M^2]}{-J(S+1)} - \frac{[f(S_A, S_B, S)]^2[J^2 - M^2]}{-JS} \right\}
 \end{aligned}$$

and these are summed up as follows

$$\begin{aligned} \sum_{M=-S}^{+S} \varepsilon_{S,M}^{(2)} &= \frac{[(g_A - g_B)\mu_B]^2}{J} \\ &\times \{ [f(S_A, S_B, S+1)]^2(S+1) - [f(S_A, S_B, S)]^2 S \} \left\{ \sum_{M=-S}^{+S} 1 \right\} \\ &+ \frac{[(g_A - g_B)\mu_B]^2}{J} \left\{ -\frac{[f(S_A, S_B, S+1)]^2}{S+1} + \frac{[f(S_A, S_B, S)]^2}{S} \right\} \\ &\left\{ \sum_{M=-S}^{+S} M^2 \right\} \end{aligned}$$

which yields

$$\begin{aligned} \sum_{M=-S}^{+S} \varepsilon_{S,M}^{(2)} &= \frac{[(g_A - g_B)\mu_B]^2}{3J} (2S+1) \\ &\times \{ [f(S_A, S_B, S+1)]^2(2S+3) - [f(S_A, S_B, S)]^2(2S-1) \} \end{aligned}$$

With the van Vleck coefficients determined, the construction of the susceptibility function is an easy task

$$\chi_{\text{mol}} = N_A \mu_0 \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M=-S}^{+S} \left[\frac{(\varepsilon_{S,M}^{(1)})^2}{kT} - 2\varepsilon_{S,M}^{(2)} \right] \exp[-\varepsilon_{S,M}^{(0)}/kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M=-S}^{+S} \exp[-\varepsilon_{S,M}^{(0)}/kT]}$$

Since the zero-field energies are degenerate, we can write

$$\chi_{\text{mol}} = \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} (2S+1) \chi_S \exp[JS(S+1)/2kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} (2S+1) \exp[JS(S+1)/2kT]}$$

with the molecular-state increments

$$\chi_S = \frac{N_A \mu_0}{2S+1} \left[\frac{1}{kT} \sum_{M=-S}^{+S} (\varepsilon_{S,M}^{(1)})^2 - 2 \sum_{M=-S}^{+S} \varepsilon_{S,M}^{(2)} \right]$$

Using the summation of the first-order coefficients

$$\sum_{M=-S}^{+S} (\varepsilon_{S,M}^{(1)})^2 = \mu_B^2 g_S^2 \frac{S(S+1)(2S+1)}{3}$$

and the above summation of the second-order coefficients, we get

$$\begin{aligned} \chi_S = \frac{N_A \mu_0 \mu_B^2}{2S+1} & \left\langle \frac{1}{kT} g_S^2 \frac{S(S+1)(2S+1)}{3} - 2 \frac{(g_A - g_B)^2}{3J} (2S+1) \right. \\ & \times \left. \{ [f(S_A, S_B, S+1)]^2 (2S+3) - [f(S_A, S_B, S)]^2 (2S-1) \} \right\rangle \end{aligned}$$

or

$$\begin{aligned} \chi_S = \frac{N_A \mu_0 \mu_B^2}{3} & \left\langle \frac{S(S+1)}{kT} g_S^2 - 2 \frac{(g_A - g_B)^2}{J} \right. \\ & \times \left. \{ [f(S_A, S_B, S+1)]^2 (2S+3) - [f(S_A, S_B, S)]^2 (2S-1) \} \right\rangle \end{aligned}$$

The factor containing the spin function $f(S_A, S_B, S)$ is evaluated as

$$\begin{aligned} d_S &= [f(S_A, S_B, S+1)]^2 (2S+3) - [f(S_A, S_B, S)]^2 (2S-1) \\ &= \left\{ \frac{[(S+1)^2 - (S_A - S_B)^2][(S_A + S_B + 1)^2 - (S+1)^2]}{4(S+1)^2[4(S+1)^2 - 1]} \right\} (2S+3) \\ &\quad - \left\{ \frac{[S^2 - (S_A - S_B)^2][(S_A + S_B + 1)^2 - S^2]}{4S^2(4S^2 - 1)} \right\} (2S-1) \end{aligned}$$

and is tabulated in Table 10.12. Now the susceptibility function adopts a form which is analogous to the case of multiplets of intermediate width, hence

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{3kT} \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} a_S (c_S + 2d_S/x) \exp[-b_S x]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} a_S \exp[-b_S x]}$$

with

$$a_S = 2S + 1$$

$$b_S = \frac{1}{2}(S + 1) - b_{S_{\min}}$$

$$c_S = g_S^2 S(S + 1)$$

and the coefficient d_S evaluated above; the argument is

$$x = J/kT$$

The formula just derived for the magnetic susceptibility of heterospin systems is applicable also to the special case of homospin systems when the g -factors differ from each other. Notice that

$$g_S = \frac{1}{2}(g_A + g_B), \quad [\text{for } S = 0]$$

Let us consider, as an example, the simplest heterospin dimer with $S_A = 1/2$ (say Cu^{II}) and $S_B = 1$ (say Ni^{II}). According to the above formulae the molecular-state g -factors are

$$g_{1/2} = (4g_{\text{Ni}} - g_{\text{Cu}})/3$$

$$g_{3/2} = (2g_{\text{Ni}} - g_{\text{Cu}})/3$$

and the non-zero off-diagonal matrix elements are

$$\begin{aligned} \langle S_A S_B S' M | \hat{H}_z^Z | S_A S_B S M \rangle &= \langle 1/2, 1, 1/2, \pm 1/2 | \hat{H}_z^Z | 1/2, 1, 3/2, \pm 1/2 \rangle \\ &= (g_{\text{Ni}} - g_{\text{Cu}})(\sqrt{2}/3)\mu_B B = -\sqrt{2}g'\mu_B B \end{aligned}$$

where we introduce

$$g' = (g_{\text{Cu}} - g_{\text{Ni}})/3$$

Then the Hamiltonian matrix takes the form

$$\mathbf{H} = \begin{matrix} & |1/2, -1/2\rangle |1/2, +1/2\rangle & |3/2, -3/2\rangle & |3/2, -1/2\rangle & |3/2, +1/2\rangle & |3/2, +3/2\rangle \\ \begin{pmatrix} -\frac{1}{2}\beta g_{1/2} & 0 & 0 & -g'\beta\sqrt{2} & 0 & 0 \\ 0 & +\frac{1}{2}\beta g_{1/2} & 0 & 0 & -g'\beta\sqrt{2} & 0 \\ 0 & 0 & -\frac{3}{2}J - \frac{3}{2}\beta g_{3/2} & 0 & 0 & 0 \\ -g'\beta\sqrt{2} & 0 & 0 & -\frac{3}{2}J - \frac{1}{2}\beta g_{3/2} & 0 & 0 \\ 0 & -g'\beta\sqrt{2} & 0 & 0 & -\frac{3}{2}J + \frac{1}{2}\beta g_{3/2} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{3}{2}J + \frac{3}{2}\beta g_{3/2} \end{pmatrix} \end{matrix}$$

with

$$\beta = \mu_B B$$

The increment in the energy, in second-order perturbation theory, is

$$E_2(1/2, 1/2) = -\frac{(-g'\beta\sqrt{2})^2}{-(3/2)J - 0} = \frac{4g'^2\beta^2}{3J}$$

and thus the second-order van Vleck coefficient for this energy level is

$$\varepsilon_1^{(2)} = \frac{4g'^2\mu_B^2}{3J}$$

The other second-order van Vleck coefficients can be enumerated analogously (Table 10.13). Then the magnetic susceptibility becomes expressed as

$$\bar{\chi}_{\text{mol}} = N_A \mu_0 \mu_B^2 \frac{2 \left[\frac{g_{1/2}^2}{kT} \frac{1}{4} - 2 \frac{4g'^2}{3J} \right] \exp(0) + \left[4 \frac{g_{3/2}^2}{kT} \frac{5}{4} + 2 \cdot 2 \frac{4g'^2}{3J} \right] \exp(3J/2kT)}{2 \exp(0) + 4 \exp(3J/2kT)}$$

which can be simplified to

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{4kT} \frac{g_{1/2}^2 - (32g'^2/3x) + [10g_{3/2}^2 + (32g'^2/3x)] \exp(3x/2)}{1 + 2 \exp(3x/2)}$$

for the argument

$$x = J/kT$$

TABLE 10.13

Van Vleck coefficients for the dimer $S_A = 1/2$, $S_B = 1$

$i = S, M_S\rangle$	$\varepsilon_i^{(0)}$	$\varepsilon_i^{(1)}$	$\varepsilon_i^{(2)}$
1 = $ 1/2, -1/2\rangle$	0	$-(1/2)\mu_B g_{1/2}$	$+(4/3)\mu_B^2 g^2/J$
2 = $ 1/2, +1/2\rangle$	0	$+(1/2)\mu_B g_{1/2}$	$+(4/3)\mu_B^2 g^2/J$
3 = $ 3/2, -3/2\rangle$	$-(3/2)J$	$-(3/2)\mu_B g_{3/2}$	0
4 = $ 3/2, -1/2\rangle$	$-(3/2)J$	$-(1/2)\mu_B g_{3/2}$	$-(4/3)\mu_B^2 g^2/J$
5 = $ 3/2, +1/2\rangle$	$-(3/2)J$	$+(1/2)\mu_B g_{3/2}$	$-(4/3)\mu_B^2 g^2/J$
6 = $ 3/2, +3/2\rangle$	$-(3/2)J$	$+(3/2)\mu_B g_{3/2}$	0

Evidently, the exchange coupling constant should be far from zero; otherwise the susceptibility formula derived with the help of the perturbation theory diverges.

According to Fig. 10.8, the effective magnetic moment is almost constant at low temperature where only one state, either $S = 1/2$ or $S = 3/2$, is populated. With increasing temperature the population of both states becomes nearly equal and thus the same limiting value is reached.

10.3 NON-ISOTROPIC EXCHANGE IN DINUCLEAR SYSTEMS

The isotropic exchange discussed so far represents only a portion of the total exchange interaction operating in binuclear and oligonuclear systems.

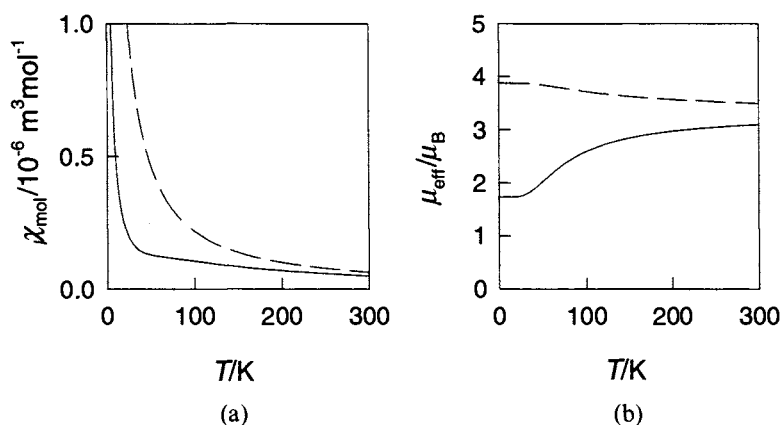


Fig. 10.8. Temperature variation of the magnetic susceptibility (a) and the effective magnetic moment (b) for a heterospin system $S_A = 1/2$ and $S_B = 1$: $g_A = 2.0$, $g_B = 2.0$, solid—antiferromagnetic coupling ($J/k = -100$ K); dashed—ferromagnetic coupling ($J/k = +100$ K).

The zero-field Hamiltonian appropriate for an exchange interaction in the dinuclear system adopts the form of

$$\hat{H}_{AB}^{(0)} = [-J_{AB}(\vec{S}_A \cdot \vec{S}_B) + \vec{S}_A \cdot \vec{\bar{D}}_{AB} \cdot \vec{S}_B + \vec{d}_{AB} \cdot (\vec{S}_A \times \vec{S}_B)][\hbar^{-2}] \\ - j_{AB}(\vec{S}_A \cdot \vec{S}_B)^2[\hbar^{-4}]$$

where isotropic, asymmetric, antisymmetric and eventually biquadratic terms occur. The local anisotropies are included in the one-centre terms

$$\hat{H}_A^{(0)} + \hat{H}_B^{(0)} = [\vec{S}_A \cdot \vec{\bar{D}}_A \cdot \vec{S}_A + \vec{S}_B \cdot \vec{\bar{D}}_B \cdot \vec{S}_B][\hbar^{-2}]$$

and the (spin) Zeeman operator reads

$$\hat{H}^Z = [\mu_B \vec{B} \cdot (\vec{g}_A \cdot \vec{S}_A + \vec{g}_B \cdot \vec{S}_B)][\hbar^{-1}]$$

In electron spin resonance also the hyperfine (superhyperfine) terms should be considered

$$\hat{H}_A^{\text{hf}} + \hat{H}_B^{\text{hf}} = \left[\sum_N \vec{I}_N \cdot (\vec{\bar{T}}_{N,A} \cdot \vec{S}_A + \vec{\bar{T}}_{N,B} \cdot \vec{S}_B) \right][\hbar^{-2}]$$

We have assumed that no angular momentum contribution assists. Then the basis set of spin functions consists of the uncoupled set $|S_A, M_{SA}\rangle |S_B, M_{SB}\rangle$, or the coupled set $|S_A, S_B, S, M_S\rangle$; its size is $N = (2S_A + 1)(2S_B + 1)$. Additionally, the orbital angular momentum can be added and then the basis set becomes a direct product of all orbital and spin functions. In a special case, spin delocalisation (double exchange) operates.

There are two physical limiting cases according to which we should accommodate the computational strategy.

1. In the *strong exchange limit* the reference states are represented by the set of coupled spin functions $|S_A, S_B, S, M_S\rangle$ and the zero-field energies are represented by the eigenvalues of the isotropic exchange operator $\hat{H}_{AB}^{(0)} = [-J_{AB}(\vec{S}_A \cdot \vec{S}_B)][\hbar^{-2}]$. The effect of the other operators (asymmetric exchange, antisymmetric exchange, biquadratic exchange, Zeeman operator) is treated by perturbation theory, provided that their influence is secondary relative to that of the leading isotropic exchange term.
2. In the *weak exchange limit* the effect of isotropic exchange is small. This is well fulfilled when the magnetic centres are rather far from each other (say 800 pm apart). Thus the eigenvectors $|S, M_S\rangle$ of $\vec{S}^2$ and $\hat{S}_z$ do not give a correct description of the spin states; the proper molecular states are obtained by the diagonalisation of the full Hamiltonian matrix. In fact, the variation method is applied.

10.3.1 Asymmetric exchange

The asymmetry effects are covered by the pair-interaction D -tensor

$$\hat{H}_{AB}^{\text{asym}} = (\vec{S}_A \cdot \vec{\bar{D}}_{AB} \cdot \vec{S}_B)[\hbar^{-2}]$$

and a set of the local D -tensors

$$\hat{H}_A^{\text{asym}} + \hat{H}_B^{\text{asym}} = (\vec{S}_A \cdot \vec{\bar{D}}_A \cdot \vec{S}_A + \vec{S}_B \cdot \vec{\bar{D}}_B \cdot \vec{S}_B)[\hbar^{-2}]$$

These can be combined into a single molecular-state term

$$\begin{aligned} \hat{H}_S^{\text{asym}} &= (\vec{S}_A \cdot \vec{\bar{D}}_{AB} \cdot \vec{S}_B + \vec{S}_A \cdot \vec{\bar{D}}_A \cdot \vec{S}_A + \vec{S}_B \cdot \vec{\bar{D}}_B \cdot \vec{S}_B)[\hbar^{-2}] \\ &= (\vec{S} \cdot \vec{\bar{D}}_S \cdot \vec{S})[\hbar^{-2}] \end{aligned}$$

All the involved D -tensors are symmetric and traceless, each having five independent components.

We seek an expression of the molecular-state D -tensor in the form of

$$\vec{\bar{D}}_S = C_A \vec{\bar{D}}_A + C_B \vec{\bar{D}}_B + C_{AB} \vec{\bar{D}}_{AB}$$

where the combination coefficients (C_A, C_B, C_{AB}) depend only upon the spin numbers (S_A, S_B, S). The above asymmetric-exchange Hamiltonian can be rewritten in the form of

$$\begin{aligned} \hat{H}_S^{\text{asym}} &= \frac{1}{4} [(\vec{S} \cdot \vec{\bar{D}}_+ \cdot \vec{S}) + (\vec{V} \cdot \vec{\bar{D}}_+ \cdot \vec{V}) + 2(\vec{S} \cdot \vec{\bar{D}}_- \cdot \vec{V}) \\ &\quad + (\vec{S} \cdot \vec{\bar{D}}_{AB} \cdot \vec{S}) - (\vec{V} \cdot \vec{\bar{D}}_{AB} \cdot \vec{V})][\hbar^{-2}] \end{aligned}$$

using the spin vectors

$$\vec{S} = \vec{S}_A + \vec{S}_B$$

$$\vec{V} = \vec{S}_A - \vec{S}_B$$

and

$$\vec{\bar{D}}_+ = \vec{\bar{D}}_A + \vec{\bar{D}}_B$$

$$\vec{\bar{D}}_- = \vec{\bar{D}}_A - \vec{\bar{D}}_B$$

which can easily be proven. Then the Wigner–Eckart theorem, followed by the replacement theorem, is applied for the matrix elements containing the

vector operator $\vec{V}$, hence

$$(\vec{V} \cdot \vec{\bar{D}}_+ \cdot \vec{V}) \rightarrow c_+(\vec{S} \cdot \vec{\bar{D}}_+ \cdot \vec{S})$$

$$(\vec{V} \cdot \vec{\bar{D}}_{AB} \cdot \vec{V}) \rightarrow c_+(\vec{S} \cdot \vec{\bar{D}}_{AB} \cdot \vec{S})$$

$$(\vec{S} \cdot \vec{\bar{D}}_- \cdot \vec{V}) \rightarrow c_-(\vec{S} \cdot \vec{\bar{D}}_- \cdot \vec{S})$$

so that we get

$$\hat{H}_S^{\text{asym}} = \frac{1}{4} \vec{S} \cdot [(1 + c_+) \vec{\bar{D}}_+ + 2c_- \vec{\bar{D}}_- + (1 - c_+) \vec{\bar{D}}_{AB}] \cdot \vec{S} [\hbar^{-2}]$$

and then

$$C_{AB} = (1 - c_+)/4$$

$$C_A = (1 + c_+)/4 + c_-/2$$

$$C_B = (1 + c_+)/4 - c_-/2$$

The proportionality coefficients are given by the ratio of the reduced matrix elements [15], i.e.

$$c_+ = \frac{\langle S \| \hat{T}_2(\vec{V} \otimes \vec{V}) \| S \rangle}{\langle S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S \rangle}$$

$$c_- = \frac{\langle S \| \hat{T}_2(\vec{S} \otimes \vec{V}) \| S \rangle}{\langle S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S \rangle}$$

Here $\hat{T}_2(\vec{S} \otimes \vec{S})$, $\hat{T}_2(\vec{S} \otimes \vec{V})$ and $\hat{T}_2(\vec{V} \otimes \vec{V})$ mean the second-rank irreducible tensor operators built up of the vector operators. Their reduced matrix elements are evaluated as follows

$$\begin{aligned} & \langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S_A S_B S' \rangle \\ &= \delta_{S, S'} \sqrt{(2S+1)(2S+3)(2S-1)S(S+1)/6} [\hbar^2] \end{aligned}$$

$$\begin{aligned}
& \langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{V}) \| S_A S_B S \rangle \\
&= \langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}_A) \| S_A S_B S \rangle - \langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}_B) \| S_A S_B S \rangle \\
&= \langle S_A S_B S \| [\hat{T}_2(\vec{S}_A \otimes \vec{S}_A) - \hat{T}_2(\vec{S}_B \otimes \vec{S}_B)] \| S_A S_B S \rangle \\
& \langle S_A S_B S \| \hat{T}_2(\vec{V} \otimes \vec{V}) \| S_A S_B S \rangle \\
&= \langle S_A S_B S \| [\hat{T}_2(\vec{S}_A \otimes \vec{S}_A) + \hat{T}_2(\vec{S}_B \otimes \vec{S}_B) - 2\hat{T}_2(\vec{S}_A \otimes \vec{S}_B)] \| S_A S_B S \rangle \\
&= \langle S_A S_B S \| [\hat{T}_2(\vec{S} \otimes \vec{S}) - 4\hat{T}_2(\vec{S}_A \otimes \vec{S}_B)] \| S_A S_B S \rangle
\end{aligned}$$

The actual formula applied to obtain the reduced matrix elements is (see Section 1.5.4)

$$\begin{aligned}
& \langle S_A S_B S \| \hat{T}_2(\vec{X} \otimes \vec{Y}) \| S_A S_B S \rangle = \langle S_A \| \vec{X} \| S_A \rangle \cdot \langle S_B \| \vec{Y} \| S_B \rangle \\
& \times [(2S+1)(2S+1)(2 \cdot 2+1)]^{1/2} \begin{Bmatrix} S_A & S_A & 1 \\ S_B & S_B & 1 \\ S & S & 2 \end{Bmatrix}
\end{aligned}$$

The $9j$ -symbol adopts the special form of

$$\begin{aligned}
\{9j\} &= \begin{Bmatrix} A & A & 1 \\ B & B & 1 \\ S & S & 2 \end{Bmatrix} \\
&= P(-1)^{2S} \frac{\begin{Bmatrix} A & S & B \\ S & A & 1 \end{Bmatrix} \begin{Bmatrix} B & S & A \\ S & B & 1 \end{Bmatrix} + \frac{(-1)^{A+B+S+1}}{3(2S+1)} \begin{Bmatrix} A & B & S \\ B & A & 1 \end{Bmatrix}}{5 \begin{Bmatrix} 2 & S & S \\ S & 1 & 1 \end{Bmatrix}}
\end{aligned}$$

with $P = (-1)^{2A+2B+2S+4}$ which, for $S = A + B$, results in a closed formula

$$\{9j\} = \frac{-3[A(A+1) - B(B+1)]^2 + S(S+1)[S(S+1) + 2A(A+1) + 2B(B+1)]}{2[30(2S+3)(2S-1)S(S+1)(2S+1)A(A+1)(2A+1)B(B+1)(2B+1)]^{1/2}}$$

Then

$$c_+ = 1 - 4 \frac{\langle S_A S_B S \| \hat{T}_2(\vec{S}_A \otimes \vec{S}_B) \| S_A S_B S \rangle}{\langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S_A S_B S \rangle}$$

$$\begin{aligned}
&= 1 - 4 \frac{\langle S_A \| \vec{S}_A \| S_A \rangle \cdot \langle S_B \| \vec{S}_B \| S_B \rangle [(2S+1)(2S+1)(2 \cdot 2+1)]^{1/2}}{\langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S_A S_B S \rangle} \\
&\quad \times \begin{Bmatrix} S_A & S_A & 1 \\ S_B & S_B & 1 \\ S & S & 2 \end{Bmatrix}
\end{aligned}$$

which finally yields the combination coefficient

$$c_+ = 1 + \frac{6[S_A(S_A+1) - S_B(S_B+1)]^2 - 2S(S+1)[S(S+1) + 2S_A(S_A+1) + 2S_B(S_B+1)]}{(2S+3)(2S-1)S(S+1)}$$

An analogous procedure gives

$$\begin{aligned}
c_- &= \frac{\langle S \| \hat{T}_2(\vec{S} \otimes \vec{V}) \| S \rangle}{\langle S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S \rangle} \\
&= \frac{\langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}_A) \| S_A S_B S \rangle - \langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}_B) \| S_A S_B S \rangle}{\langle S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S \rangle}
\end{aligned}$$

and then

$$\begin{aligned}
c_- &= \frac{\langle S \| \vec{S} \| S \rangle \cdot \langle S_A \| \vec{S}_A \| S_A \rangle [(2S+1)(2S+1)(2 \cdot 2+1)]^{1/2}}{\langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S_A S_B S \rangle} \\
&\quad \times \begin{Bmatrix} S & S & 1 \\ S_A & S_A & 1 \\ S & S & 2 \end{Bmatrix} \\
&\quad - \frac{\langle S \| \vec{S} \| S \rangle \cdot \langle S_B \| \vec{S}_B \| S_B \rangle [(2S+1)(2S+1)(2 \cdot 2+1)]^{1/2}}{\langle S_A S_B S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S_A S_B S \rangle} \\
&\quad \times \begin{Bmatrix} S & S & 1 \\ S_B & S_B & 1 \\ S & S & 2 \end{Bmatrix}
\end{aligned}$$

One can also utilise the results of Table 1.16 (Section 1.5.4), yielding finally the combination coefficient in the form of

$$c_- = \frac{[4S(S+1) - 3][S_A(S_A+1) - S_B(S_B+1)]}{(2S+3)(2S-1)S(S+1)}$$

With the coefficients c_+ and c_- determined [15] the expression of C_A , C_B and C_{AB} is an easy task. The results are tabulated in Table 10.12.

Evaluation involving the combination of the local g -tensors into the molecular-state g -tensor, and that combining the local and pair-interaction D -tensors into the molecular-state D -tensor, are satisfied even when the tensors are neither diagonal nor collinear; care must be taken, however, to refer all the tensors to the same reference system. Therefore the difference in centres means not only that $S_A \neq S_B$; the systems $S_A = S_B$ can be taken as different when otherwise identical tensors are differently oriented.

In the case of a strong exchange limit ($|J_{AB}|$ is large) the classification of the field-dependent molecular states as slightly perturbed zero-field states $|S, M_S\rangle$ is fully justified. Consequently the replacement theorem holds true for $S = S'$ and the irreducible tensor operators containing the operator variable $\vec{V}$ can be substituted for those containing $\vec{S}$ as a variable. The spin Hamiltonian is somewhat different for each manifold of the spin S , hence

$$\begin{aligned} \hat{H}|_{S=S'} &= \frac{1}{2} \mu_B \vec{B} \cdot (\vec{g}_+ + c_- \vec{g}_-) \cdot \vec{S} [\hbar^{-1}] \\ &\quad + \frac{1}{4} \vec{S} \cdot [(1 + c_+) \vec{D}_+ + 2c_- \vec{D}_- + (1 - c_+) \vec{D}_{AB}] \cdot \vec{S} [\hbar^{-2}] \end{aligned}$$

or

$$\begin{aligned} \hat{H}|_{S=S'} &= \mu_B \vec{B} \cdot (c_A \vec{g}_A + c_B \vec{g}_B) \cdot \vec{S} [\hbar^{-1}] \\ &\quad + \vec{S} \cdot [C_A \vec{D}_A + C_B \vec{D}_B + C_{AB} \vec{D}_{AB}] \cdot \vec{S} [\hbar^{-2}] \end{aligned}$$

or alternatively

$$\hat{H}|_{S=S'} = \mu_B \vec{B} \cdot \vec{g}_S \cdot \vec{S} [\hbar^{-1}] + \vec{S} \cdot \vec{D}_S \cdot \vec{S} [\hbar^{-2}]$$

The combination coefficients are different for individual spin states. The situation resembles the case of isolated multiplets (wide multiplets) and thus the Hamiltonian matrix takes a block-diagonal form.

In the case of a weak exchange limit ($|J_{AB}|$ is low) the field-dependent molecular states are far from the zero-field states: the eigenvectors of $\hat{S}^2$ and $\hat{S}_z$ do not give a proper description of the spin states and correct eigenvalues and eigenvectors should be obtained by diagonalisation of the full Hamiltonian matrix. The off-diagonal Hamiltonian contains only the tensor

operators involving the operator variable $\vec{V}$, since the tensor operators involving only $\vec{S}$ have vanishing off-diagonal ($S \neq S'$) matrix elements, hence

$$\hat{H}|_{S \neq S'} = \frac{1}{2} \mu_B \vec{B} \cdot \vec{g}_- \cdot \vec{V} [\hbar^{-1}] + \frac{1}{4} [\vec{V} \cdot (\vec{D}_- - \vec{D}_{AB}) \cdot \vec{V} + 2\vec{S} \cdot \vec{D}_- \cdot \vec{V}] [\hbar^{-2}]$$

In evaluating the matrix elements we need the $3j$ -symbols and the reduced matrix elements

$$\begin{aligned} \langle S' M' | \hat{T}_{1q}(\vec{V}) | S M \rangle &= (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} \langle S' \| \hat{T}_1(\vec{V}) \| S \rangle \\ \langle S' M' | \hat{T}_{2q}(\vec{S} \otimes \vec{V}) | S M \rangle &= (-1)^{S'-M'} \begin{pmatrix} S' & 2 & S \\ -M' & q & M \end{pmatrix} \langle S' \| \hat{T}_2(\vec{S} \otimes \vec{V}) \| S \rangle \\ \langle S' M' | \hat{T}_{2q}(\vec{V} \otimes \vec{V}) | S M \rangle &= (-1)^{S'-M'} \begin{pmatrix} S' & 2 & S \\ -M' & q & M \end{pmatrix} \langle S' \| \hat{T}_2(\vec{V} \otimes \vec{V}) \| S \rangle \end{aligned}$$

The triangular conditions for the $3j$ -symbols yield the restrictions $M' = M$, $M \pm 1$ and $M \pm 2$, respectively, and closed formulae exist for all these $3j$ -symbols [16]. The restriction to $S' = S \pm 1$ and $S' = S \pm 2$ originates in the triangular relationships in the corresponding $6j$ -symbols involved in the reduced matrix elements of the second-rank irreducible tensor operators

$$\{6j\} = \begin{Bmatrix} S' & S & 2 \\ S_1 & S_1 & S_2 \end{Bmatrix} \neq 0$$

and the first-rank irreducible tensor operators, respectively

$$\{6j\} = \begin{Bmatrix} S' & S & 1 \\ S_1 & S_1 & S_2 \end{Bmatrix} \neq 0$$

In the above formulae, spherical components of the irreducible tensor operators occur. In changing to Cartesian components one can use the transformations listed in Table 1.13 (Section 1.5.3); the following relationships hold true:

(a) three components of the first-rank tensor (vector) operator are

$$\hat{T}_x = (1/\sqrt{2})(\hat{T}_{1,-1} - \hat{T}_{1,+1})$$

$$\hat{T}_y = (i/\sqrt{2})(\hat{T}_{1,-1} + \hat{T}_{1,+1})$$

$$\hat{T}_z = \hat{T}_{1,0}$$

(b) five components of the symmetric traceless second-rank tensor are

$$2\hat{T}_{zz} - \hat{T}_{xx} - \hat{T}_{yy} = \sqrt{6}\hat{T}_{2,0}$$

$$\hat{T}_{xz} + \hat{T}_{zx} = \hat{T}_{2,-1} - \hat{T}_{2,+1}$$

$$\hat{T}_{yz} + \hat{T}_{zy} = i(\hat{T}_{2,-1} + \hat{T}_{2,+1})$$

$$\hat{T}_{xx} - \hat{T}_{yy} = \hat{T}_{2,-2} + \hat{T}_{2,+2}$$

$$\hat{T}_{yx} + \hat{T}_{xy} = i(\hat{T}_{2,-2} - \hat{T}_{2,+2})$$

Then the three components of a vector operator $\vec{A}$ are

$$\begin{aligned} \langle S'M' | \hat{A}_x | SM \rangle &= (1/\sqrt{2}) \left[\begin{pmatrix} S' & 1 & S \\ -M' & -1 & M \end{pmatrix} - \begin{pmatrix} S' & 1 & S \\ -M' & +1 & M \end{pmatrix} \right] \\ &\quad \times (-1)^{S'-M'} \langle S' | \hat{T}_1(\vec{A}) | S \rangle \end{aligned}$$

$$\begin{aligned} \langle S'M' | \hat{A}_y | SM \rangle &= (i/\sqrt{2}) \left[\begin{pmatrix} S' & 1 & S \\ -M' & -1 & M \end{pmatrix} + \begin{pmatrix} S' & 1 & S \\ -M' & +1 & M \end{pmatrix} \right] \\ &\quad \times (-1)^{S'-M'} \langle S' | \hat{T}_1(\vec{A}) | S \rangle \end{aligned}$$

$$\langle S'M' | \hat{A}_z | SM \rangle = \begin{pmatrix} S' & 1 & S \\ -M' & 0 & M \end{pmatrix} (-1)^{S'-M'} \langle S' | \hat{T}_1(\vec{A}) | S \rangle$$

and the five components of the symmetric traceless second-rank tensor operator of the variables $\{\vec{A} \otimes \vec{B}\}_2$ are

$$\begin{aligned} \langle S'M' | 3\hat{A}_z\hat{B}_z - \vec{A} \cdot \vec{B} | SM \rangle &= \sqrt{6} \begin{pmatrix} S' & 2 & S \\ -M' & 0 & M \end{pmatrix} (-1)^{S'-M'} \\ &\quad \times \langle S' | \hat{T}_2(\vec{A} \otimes \vec{B}) | S \rangle \end{aligned}$$

$$\begin{aligned} \langle S'M' | \hat{A}_x\hat{B}_z + \hat{A}_z\hat{B}_x | SM \rangle &= \left[\begin{pmatrix} S' & 2 & S \\ -M' & -1 & M \end{pmatrix} - \begin{pmatrix} S' & 2 & S \\ -M' & +1 & M \end{pmatrix} \right] \\ &\quad \times (-1)^{S'-M'} \langle S' | \hat{T}_2(\vec{A} \otimes \vec{B}) | S \rangle \end{aligned}$$

$$\begin{aligned} \langle S'M' | \hat{A}_y \hat{B}_z + \hat{A}_z \hat{B}_y | SM \rangle = & i \left[\begin{pmatrix} S' & 2 & S \\ -M' & -1 & M \end{pmatrix} + \begin{pmatrix} S' & 2 & S \\ -M' & +1 & M \end{pmatrix} \right] \\ & \times (-1)^{S'-M'} \langle S' \| \hat{T}_2(\vec{A} \otimes \vec{B}) \| S \rangle \end{aligned}$$

$$\begin{aligned} \langle S'M' | \hat{A}_x \hat{B}_x - \hat{A}_y \hat{B}_y | SM \rangle = & \left[\begin{pmatrix} S' & 2 & S \\ -M' & -2 & M \end{pmatrix} + \begin{pmatrix} S' & 2 & S \\ -M' & +2 & M \end{pmatrix} \right] \\ & \times (-1)^{S'-M'} \langle S' \| \hat{T}_2(\vec{A} \otimes \vec{B}) \| S \rangle \end{aligned}$$

$$\begin{aligned} \langle S'M' | \hat{A}_y \hat{B}_x + \hat{A}_x \hat{B}_y | SM \rangle = & i \left[\begin{pmatrix} S' & 2 & S \\ -M' & -2 & M \end{pmatrix} - \begin{pmatrix} S' & 2 & S \\ -M' & +2 & M \end{pmatrix} \right] \\ & \times (-1)^{S'-M'} \langle S' \| \hat{T}_2(\vec{A} \otimes \vec{B}) \| S \rangle \end{aligned}$$

The reduced matrix elements, evaluated with the help of Table 1.16, are

$$\begin{aligned} & \langle S+1 \| \hat{T}_1(\vec{V}) \| S \rangle \\ & = \langle S_A S_B, S+1 \| \vec{S}_A \| S_A, S_B, S \rangle - \langle S_A S_B, S+1 \| \vec{S}_B \| S_A, S_B, S \rangle \\ & = \{(S_A - S_B + S + 1)(-S_A + S_B + S + 1)(S_A + S_B - S) \\ & \quad \times (S_A + S_B + S + 2)/(S+1)\}^{1/2} [\hbar] \equiv X[\hbar] \end{aligned}$$

$$\begin{aligned} & \langle S+1 \| \hat{T}_2(\vec{S} \otimes \vec{V}) \| S \rangle \\ & = \langle S_A S_B, S+1 \| \{\vec{S}_A \otimes \vec{S}_A\}_2 \| S_A, S_B, S \rangle \\ & \quad - \langle S_A S_B, S+1 \| \{\vec{S}_B \otimes \vec{S}_B\}_2 \| S_A, S_B, S \rangle \\ & = X \cdot \{S(S+2)/2\}^{1/2} [\hbar^2] \end{aligned}$$

$$\begin{aligned} & \langle S+1 \| \hat{T}_2(\vec{V} \otimes \vec{V}) \| S \rangle \\ & = \langle S_A S_B, S+1 \| \{\vec{S}_A \otimes \vec{S}_A\}_2 \| S_A, S_B, S \rangle \\ & \quad + \langle S_A S_B, S+1 \| \{\vec{S}_B \otimes \vec{S}_B\}_2 \| S_A, S_B, S \rangle \\ & = X \cdot \{[S_A(S_A+1) - S_B(S_B+1)]/[2S(S+2)]\}^{1/2} [\hbar^2] \end{aligned}$$

$$\begin{aligned}
& \langle S + 2 \| \hat{T}_2(\vec{V} \otimes \vec{V}) \| S \rangle \\
&= \langle S_A S_B, S + 2 \| \{ \tilde{S}_A \otimes \tilde{S}_A \}_2 \| S_A, S_B, S \rangle \\
&\quad + \langle S_A S_B, S + 2 \| \{ \tilde{S}_B \otimes \tilde{S}_B \}_2 \| S_A, S_B, S \rangle \\
&= \frac{1}{2} X \cdot \{ (S_A + S_B + S + 3)(S_A - S_B + S + 2) \\
&\quad \times (-S_A + S_B + S + 2)(S_A + S_B - S + 1) / \\
&\quad / [(S + 1)(S + 2)(2S + 3)] \}^{1/2} [\hbar^2]
\end{aligned}$$

These matrix elements differ from those reported by Scaringe et al. [15] since those authors used Rose's definition of the reduced matrix element [17] which absorbs the factor $(2S' + 1)^{-1/2}$, being either $(2S + 3)^{-1/2}$ for $S' = S + 1$ or $(2S + 5)^{-1/2}$ for $S' = S + 2$. The relevant matrix elements are summarised in Table 10.14.

The asymmetric exchange term requires the evaluation of the blocks

$$\mathbf{H}^{\text{asym}} = [\hbar^{-2}] \begin{pmatrix} \langle SM' | \vec{S} \cdot \vec{D}_S \cdot \vec{S} | SM \rangle \\ \langle S'M' | (1/4)[\vec{V} \cdot (\vec{D}_- - \vec{D}_{AB}) \cdot \vec{V} + 2\vec{S} \cdot \vec{D}_- \cdot \vec{V}] | SM \rangle \\ \langle S'M' | (1/4)[\vec{V} \cdot (\vec{D}_- - \vec{D}_{AB}) \cdot \vec{V} + 2\vec{S} \cdot \vec{D}_- \cdot \vec{V}] | SM \rangle \\ \langle SM' | \vec{S} \cdot \vec{D}_S \cdot \vec{S} | SM \rangle \end{pmatrix}$$

We assume a diagonal form of the D -tensors so that the scalar products are expanded as follows

$$\vec{A} \cdot \vec{D} \cdot \vec{B} = D_{xx} \hat{A}_x \hat{B}_x + D_{yy} \hat{A}_y \hat{B}_y + D_{zz} \hat{A}_z \hat{B}_z$$

A diagonal and traceless D -tensor obeys

$$D_{xx} + D_{yy} + D_{zz} = 0$$

and one can proceed with the expression

$$D_{xx} \hat{A}_x \hat{B}_x + D_{yy} \hat{A}_y \hat{B}_y + D_{zz} \hat{A}_z \hat{B}_z = \frac{D}{3} (3\hat{A}_z \hat{B}_z - \vec{A} \cdot \vec{B}) + E(\hat{A}_x \hat{B}_x - \hat{A}_y \hat{B}_y)$$

where the axial zero-field splitting parameter

$$D = \frac{3}{2} D_{zz}$$

TABLE 10.14

Off-diagonal matrix elements of the form $\langle S' M' | \hat{A}_\alpha \hat{B}_\beta | S M \rangle = f(S, M) \cdot \langle S' | \hat{T}_k(\vec{A} \otimes \vec{B}) | S \rangle$

Matrix element	Function $f(S, M)^a$
$\langle S+1, M \hat{A}_z S M \rangle$	$\left\{ \frac{(S-M+1)(S+M+1)}{(2S+3)(2S+1)(S+1)} \right\}^{1/2}$
$\langle S+1, M \pm 1 \hat{A}_x S M \rangle$	$\mp \frac{1}{2} \left\{ \frac{(S \pm M+1)(S \pm M+2)}{(2S+3)(2S+1)(S+1)} \right\}^{1/2}$
$\langle S+1, M \pm 1 \hat{A}_y S M \rangle$	$i \frac{1}{2} \left\{ \frac{(S \pm M+1)(S \pm M+2)}{(2S+3)(2S+1)(S+1)} \right\}^{1/2}_b$
$\langle S+1, M 3\hat{A}_z \hat{B}_z - \vec{A} \cdot \vec{B} S M \rangle$	$M \sqrt{6} \left\{ \frac{3(S-M+1)(S+M+1)}{S(S+1)(2S+1)(S+2)(2S+3)} \right\}^{1/2}$
$\langle S+1, M \pm 1 \hat{A}_x \hat{B}_z + \hat{A}_z \hat{B}_x S M \rangle$	$(S \mp 2M) \left\{ \frac{(S \pm M+1)(S \pm M+2)}{2S(S+1)(2S+1)(S+2)(2S+3)} \right\}^{1/2}$
$\langle S+1, M \pm 1 \hat{A}_y \hat{B}_z + \hat{A}_z \hat{B}_y S M \rangle$	$\mp i (S \mp 2M) \left\{ \frac{(S \pm M+1)(S \pm M+2)}{2S(S+1)(2S+1)(S+2)(2S+3)} \right\}^{1/2}$
$\langle S+1, M \pm 2 \hat{A}_x \hat{B}_x - \hat{A}_y \hat{B}_y S M \rangle$	$\mp \left\{ \frac{(S \pm M+1)(S \pm M+2)(S \pm M+3)(S \mp M)}{2S(S+1)(2S+1)(S+2)(2S+3)} \right\}^{1/2}$
$\langle S+1, M \pm 2 \hat{A}_x \hat{B}_y - \hat{A}_y \hat{B}_x S M \rangle$	$i \left\{ \frac{(S \pm M+1)(S \pm M+2)(S \pm M+3)(S \mp M)}{2S(S+1)(2S+1)(S+2)(2S+3)} \right\}^{1/2}$
$\langle S+2, M 3\hat{A}_z \hat{B}_z - \vec{A} \cdot \vec{B} S M \rangle$	$\sqrt{6} \left\{ \frac{3(S-M+2)(S-M+1)(S+M+1)(S+M+2)}{(2S+1)(2S+2)(2S+3)(S+2)(2S+5)} \right\}^{1/2}$
$\langle S+2, M \pm 1 \hat{A}_x \hat{B}_z + \hat{A}_z \hat{B}_x S M \rangle$	$\mp \left\{ \frac{(S \mp M+1)(S \pm M+3)(S \pm M+2)(S \pm M+1)}{(2S+1)(S+1)(2S+3)(S+2)(2S+5)} \right\}^{1/2}$
$\langle S+2, M \pm 1 \hat{A}_y \hat{B}_z + \hat{A}_z \hat{B}_y S M \rangle$	$\mp i \left\{ \frac{(S \mp M+1)(S \pm M+3)(S \pm M+2)(S \pm M+1)}{(2S+1)(S+1)(2S+3)(S+2)(2S+5)} \right\}^{1/2}$
$\langle S+2, M \pm 2 \hat{A}_x \hat{B}_x - \hat{A}_y \hat{B}_y S M \rangle$	$\left\{ \frac{(S \pm M+4)(S \pm M+3)(S \pm M+2)(S \pm M+1)}{4(2S+1)(S+1)(2S+3)(S+2)(2S+5)} \right\}^{1/2}$
$\langle S+2, M \pm 2 \hat{A}_x \hat{B}_y - \hat{A}_y \hat{B}_x S M \rangle$	$\mp i \left\{ \frac{(S \pm M+4)(S \pm M+3)(S \pm M+2)(S \pm M+1)}{4(2S+1)(S+1)(2S+3)(S+2)(2S+5)} \right\}^{1/2}$

^aFor an indeterminate function the expression is equal to zero.^bDifferent sign from the original reference [15] but identical to that of ref. [19].

and the rhombic zero-field splitting parameter

$$E = \frac{1}{2}(D_{xx} - D_{yy})$$

have been introduced.

The matrix elements of the D -tensors are then evaluated according to

$$\begin{aligned} \langle S'M' | \vec{A} \cdot \vec{D} \cdot \vec{B} | SM \rangle &= \frac{D}{3} \langle S'M' | 3\hat{A}_z\hat{B}_z - \vec{A} \cdot \vec{B} | SM \rangle \\ &+ E \langle S'M' | \hat{A}_x\hat{B}_x - \hat{A}_y\hat{B}_y | SM \rangle \end{aligned}$$

The non-zero matrix elements involving the D -tensors are of the following types. The diagonal blocks ($S' = S$) contain the elements

$$\langle SM' | \vec{S} \cdot \vec{D}_S \cdot \vec{S} | SM \rangle = \frac{D_S}{3} \langle SM' | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle + E_S \langle SM' | \hat{S}_x^2 - \hat{S}_y^2 | SM \rangle$$

(a) The first contribution involves the integral

$$\langle SM' | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle = \sqrt{6} \begin{pmatrix} S & 2 & S \\ -M' & 0 & M \end{pmatrix} (-1)^{S-M'} \langle S || \hat{T}_2(\vec{S} \otimes \vec{S}) || S \rangle$$

with the $3j$ -symbol

$$\begin{pmatrix} S & 2 & S \\ -M & 0 & M \end{pmatrix} = (-1)^{S-M} \frac{3M^2 - S(S+1)}{[S(S+1)(2S+1)(2S-1)(2S+3)]^{1/2}}$$

and with the reduced matrix element

$$\langle S || \hat{T}_2(\vec{S} \otimes \vec{S}) || S \rangle = [S(S+1)(2S+1)(2S-1)(2S+3)/6]^{1/2} [\hbar^2]$$

The result is

$$\langle SM | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle = [3M^2 - S(S+1)] [\hbar^2]$$

Therefore the elements

$$H_{SM,SM}^{\text{asym}}(a) = \frac{D_S}{3} [3M^2 - S(S+1)]$$

fill just the diagonal of the interaction matrix. Obviously, the same result can be obtained by a simpler treatment but the outlined procedure is of general validity and is applicable to more complex situations.

(b) The second contribution involves the integral

$$\begin{aligned} \langle SM' | \hat{S}_x^2 - \hat{S}_y^2 | SM \rangle &= \left[\begin{pmatrix} S & 2 & S \\ -M' & -2 & M \end{pmatrix} + \begin{pmatrix} S & 2 & S \\ -M' & +2 & M \end{pmatrix} \right] \\ &\quad \times (-1)^{S-M'} \langle S \| \hat{T}_2(\vec{S} \otimes \vec{S}) \| S \rangle \end{aligned}$$

and the triangular restriction requires either $M' = M - 2$ or $M' = M + 2$. Then a special formula for the $3j$ -symbol is

$$\begin{aligned} &\begin{pmatrix} S & 2 & S \\ -(M+2) & +2 & M \end{pmatrix} \\ &= (-1)^{S-M} \left\{ \frac{6(S-M-1)(S-M)(S+M+1)(S+M+2)}{4S(S+1)(2S+1)(2S-1)(2S+3)} \right\}^{1/2} \end{aligned}$$

and the final result becomes

$$\begin{aligned} H_{S,M+2,S,M}^{\text{asym}}(b) &= E_S \langle S, M+2 | \hat{S}_x^2 - \hat{S}_y^2 | S, M \rangle [\hbar^{-2}] \\ &= E_S (1/2) \{(S-M-1)(S-M)(S+M+1)(S+M+2)\}^{1/2} \end{aligned}$$

Such matrix elements fill the places shifted by two positions out of the diagonal. Since the interaction matrix is symmetric, the same matrix elements are obtained for $M' = M - 2$.

In creating the diagonal blocks of the interaction matrix we can also utilize the procedure outlined in Section 8.4.1 where the matrices of the zero-field splitting Hamiltonian have been generated for certain values of the spin (Table 8.21). For higher spin values the corresponding matrices can be generated according to Appendix 2. Thus the matrices $\mathbf{H}^{\text{zfs}}(S)$ occupy the diagonal blocks of $\mathbf{H}^{\text{asym}}$.

The asymmetric exchange results in zero-field splitting: the magnetic levels for $S \geq 1$ are split, in the absence of the magnetic field, into a set of Kramers doublet and eventually a single level (for odd-multiplicity systems).

The off-diagonal blocks of the interaction matrix (assuming as above the diagonal and traceless form of the D -tensors) contain the elements

$$\begin{aligned}
 H_{S'M',SM}^{\text{asym}} &= \langle S'M' | (1/4)[\vec{V} \cdot (\bar{\bar{D}}_- - \bar{\bar{D}}_{AB}) \cdot \vec{V} + 2\vec{S} \cdot \bar{\bar{D}}_- \cdot \vec{V}] | SM \rangle [\hbar^{-2}] \\
 &= \frac{D'}{3} \langle S'M' | 3\hat{V}_z^2 - \hat{V}^2 | SM \rangle [\hbar^{-2}] + E' \langle S'M' | \hat{V}_x^2 - \hat{V}_y^2 | SM \rangle [\hbar^{-2}] \\
 &\quad + \frac{D''}{3} \langle S'M' | 3\hat{S}_z \hat{V}_z - \vec{S} \cdot \vec{V} | SM \rangle [\hbar^{-2}] \\
 &\quad + E'' \langle S'M' | \hat{S}_x \hat{V}_x - \hat{S}_y \hat{V}_y | SM \rangle [\hbar^{-2}]
 \end{aligned}$$

where the axial and rhombic zero-field splitting parameters have been introduced

$$D' = \frac{3}{2} \cdot \frac{1}{4} [(D_-)_{zz} - (D_{AB})_{zz}]$$

$$D'' = \frac{3}{2} \cdot \frac{1}{2} (D_-)_{zz}$$

$$E' = \frac{1}{2} \cdot \frac{1}{4} [(D_-)_{xx} - (D_-)_{yy} - (D_{AB})_{xx} + (D_{AB})_{yy}]$$

$$E'' = \frac{1}{2} \cdot \frac{1}{2} [(D_-)_{xx} - (D_-)_{yy}]$$

- (c) Inspection of Table 10.14 brings information that the matrix elements of the axial component fill only the places with $S' = S + 1$ and $M' = M$; hence

$$\begin{aligned}
 H_{S+1,M,S,M}^{\text{asym}}(\text{c}) &= \left[\frac{D'}{3} \langle S+1, M | 3\hat{V}_z^2 - \hat{V}^2 | S, M \rangle \right. \\
 &\quad \left. + \frac{D''}{3} \langle S+1, M | 3\hat{S}_z \hat{V}_z - \vec{S} \cdot \vec{V} | S, M \rangle \right] [\hbar^{-2}] \\
 &= \sqrt{6} \begin{pmatrix} (S+1) & 2 & S \\ -(M) & 0 & M \end{pmatrix} (-1)^{(S+1)-M} \\
 &\quad \times \left[\frac{D'}{3} \langle S+1 || \hat{T}_2(\vec{V} \otimes \vec{V}) || S \rangle + \frac{D''}{3} \langle S+1 || \hat{T}_2(\vec{S} \otimes \vec{V}) || S \rangle \right] [\hbar^{-2}]
 \end{aligned}$$

- (d) Also, the places with $S' = S + 2$ and $M' = M$ are filled by the axial component, i.e.,

$$\begin{aligned} H_{S+2,M,S,M}^{\text{asym}}(\text{d}) &= \frac{D'}{3} \langle S+2, M | 3\hat{V}_z^2 - \hat{V}^2 | S, M \rangle [\hbar^{-2}] \\ &= \frac{D'}{3} \sqrt{6} \begin{pmatrix} (S+2) & 2 & S \\ -(M) & 0 & M \end{pmatrix} (-1)^{(S+2)-M} \\ &\quad \times \langle S+2 \| \hat{T}_2(\vec{V} \otimes \vec{V}) \| S \rangle [\hbar^{-2}] \end{aligned}$$

- (e) The rhombic component fills the places $S' = S + 1$ and $M' = M \pm 2$ so that we have

$$\begin{aligned} H_{S+1,M\pm 2,S,M}^{\text{asym}}(\text{e}) &= \left[E' \langle S+1, M \pm 2 | \hat{V}_x^2 - \hat{V}_y^2 | S, M \rangle \right. \\ &\quad \left. + E'' \langle S+1, M \pm 2 | \hat{S}_x \hat{V}_x - \hat{S}_y \hat{V}_y | S, M \rangle \right] [\hbar^{-2}] \\ &= \begin{pmatrix} (S+1) & 2 & S \\ -(M \pm 2) & \pm 2 & M \end{pmatrix} (-1)^{(S+1)-(M \pm 2)} \\ &\quad \times \left[E' \langle S+1 \| \hat{T}_2(\vec{V} \otimes \vec{V}) \| S \rangle \right. \\ &\quad \left. + E'' \langle S+1 \| \hat{T}_2(\vec{S} \otimes \vec{V}) \| S \rangle \right] [\hbar^{-2}] \end{aligned}$$

- (f) At the same time, the rhombic component fills the places $S' = S + 2$ and $M' = M \pm 2$, and thus

$$\begin{aligned} H_{S+2,M\pm 2,S,M}^{\text{asym}}(\text{f}) &= E' \langle S+2, M \pm 2 | \hat{V}_x^2 - \hat{V}_y^2 | S, M \rangle [\hbar^{-2}] \\ &= E' \begin{pmatrix} (S+2) & 2 & S \\ -(M \pm 2) & \pm 2 & M \end{pmatrix} (-1)^{(S+2)-(M \pm 2)} \\ &\quad \times \langle S+2 \| \hat{T}_2(\vec{V} \otimes \vec{V}) \| S \rangle [\hbar^{-2}] \end{aligned}$$

The non-zero matrix elements for the asymmetric exchange Hamiltonian are collected in Table 10.15. The structure of the interaction matrix copies a scheme in which the above six types of matrix element occur

$$\text{a} \sim D_S$$

$$\text{b} \sim E_S$$

TABLE 10.15

Matrix elements for the asymmetric exchange Hamiltonian^a

Type	Expression
$H_{S,M,S,M}^{\text{asym}}(\text{a})$	$\frac{D_S}{3}[3M^2 - S(S+1)]$
$H_{S,M+2,S,M}^{\text{asym}}(\text{b})$	$E_S(1/2)\{(S-M-1)(S-M)(S+M+1)(S+M+2)\}^{1/2}$
$H_{S+1,M,S,M}^{\text{asym}}(\text{c})$	$\left\{ \frac{D'}{3} \left[\frac{S_A(S_A+1) - S_B(S_B+1)}{2S(S+2)} \right]^{1/2} + \frac{D''}{3} \left[\frac{S(S+2)}{2} \right]^{1/2} \right\}$ $\times \left[\frac{(S_A - S_B + S + 1)(-S_A + S_B + S + 1)(S_A + S_B - S)(S_A + S_B + S + 2)}{(S+1)} \right]^{1/2}$ $\times M \sqrt{6} \left[\frac{3(S-M+1)(S+M+1)}{S(S+1)(2S+1)(S+2)(2S+3)} \right]^{1/2}$
$H_{S+2,M,S,M}^{\text{asym}}(\text{d})$	$\frac{D'}{3} \frac{\sqrt{6}}{2} \left[\frac{3(S-M+2)(S-M+1)(S+M+1)(S+M+2)}{(2S+1)(2S+2)(2S+3)(S+2)(2S+5)} \right]^{1/2}$ $\times \left[\frac{(S_A - S_B + S + 1)(-S_A + S_B + S + 1)(S_A + S_B - S)(S_A + S_B + S + 2)}{(S+1)} \right]^{1/2}$ $\times \left[\frac{(S_A + S_B + S + 3)(S_A - S_B + S + 2)(-S_A + S_B + S + 2)(S_A + S_B - S + 1)}{(S+1)(S+2)(2S+3)} \right]^{1/2}$
$H_{S+1,M\pm 2,S,M}^{\text{asym}}(\text{e})$	$\left\{ E' \left[\frac{S_A(S_A+1) - S_B(S_B+1)}{2S(S+2)} \right]^{1/2} + E'' \left[\frac{S(S+2)}{2} \right]^{1/2} \right\}$ $\times \left[\frac{(S_A - S_B + S + 1)(-S_A + S_B + S + 1)(S_A + S_B - S)(S_A + S_B + S + 2)}{(S+1)} \right]^{1/2}$ $\times (\mp 1) \left[\frac{(S \pm M + 1)(S \pm M + 2)(S \pm M + 3)(S \mp M)}{2S(S+1)(2S+1)(S+2)(2S+3)} \right]^{1/2}$
$H_{S+2,M\pm 2,S,M}^{\text{asym}}(\text{f})$	$E' \frac{1}{2} \left[\frac{(S \pm M + 4)(S \pm M + 3)(S \pm M + 2)(S \pm M + 1)}{(2S+1)(2S+2)(2S+3)(2S+4)(2S+5)} \right]^{1/2}$ $\times \left[\frac{(S_A - S_B + S + 1)(-S_A + S_B + S + 1)(S_A + S_B - S)(S_A + S_B + S + 2)}{(S+1)} \right]^{1/2}$ $\times \left[\frac{(S_A + S_B + S + 3)(S_A - S_B + S + 2)(-S_A + S_B + S + 2)(S_A + S_B - S + 1)}{(S+1)(S+2)(2S+3)} \right]^{1/2}$

^aThe zero-field splitting parameters are in energy units.

$$c \sim D', D''$$

$$d \sim D'$$

$$e \sim E', E''$$

$$f \sim E'$$

The structure of the interaction matrix is

	M'	M	$M + 1$	$M + 2$	$M + 3$
$S' = S$	M	a	0	b	0
	$M + 1$	0	a	0	b
	$M + 2$	b	0	a	0
	$M + 3$	0	b	0	a
$S' = S + 1$	M	c	0	e'	0
	$M + 1$	0	c	0	e'
	$M + 2$	e	0	c	0
	$M + 3$	0	e	0	c
$S' = S + 2$	M	d	0	f'	0
	$M + 1$	0	d	0	f'
	$M + 2$	f	0	d	0
	$M + 3$	0	f	0	d

The matrix elements of the Zeeman operator should be evaluated according to the recipe

$$\mathbf{H}^Z = \mu_B [\hbar^{-1}] \begin{pmatrix} \langle SM' | \vec{B} \cdot \vec{g}_S \cdot \vec{S} | SM \rangle & \langle S'M' | (1/2) \vec{B} \cdot \vec{g}_- \cdot \vec{V} | SM \rangle \\ \langle S'M' | (1/2) \vec{B} \cdot \vec{g}_- \cdot \vec{V} | SM \rangle & \langle SM' | \vec{B} \cdot \vec{g}_S \cdot \vec{S} | SM \rangle \end{pmatrix}$$

Assuming that the g_S -tensor is diagonal, the scalar product will contain only three terms; the diagonal blocks of the Zeeman matrix are evaluated as

$$\begin{aligned} \langle SM' | \vec{B} \cdot \vec{g}_S \cdot \vec{S} | SM \rangle &= \langle SM' | B_x g_x \hat{S}_x + B_y g_y \hat{S}_y + B_z g_z \hat{S}_z | SM \rangle \\ &= B_x g_x \langle SM' | \hat{S}_x | SM \rangle + B_y g_y \langle SM' | \hat{S}_y | SM \rangle + B_z g_z \langle SM' | \hat{S}_z | SM \rangle \end{aligned}$$

(a) For the z-component it holds true that

$$\langle SM' | \hat{S}_z | SM \rangle = \begin{pmatrix} S & 1 & S \\ -M' & 0 & M \end{pmatrix} (-1)^{S-M'} \langle S || \hat{T}_1(\vec{S}) || S \rangle = \delta_{M',M} M [\hbar]$$

and the triangular condition for the $3j$ -symbol yields $M' = M$; hence

$$H_{S,M,S,M}^Z(a) = \mu_B g_z B_z M$$

(b) The remaining components are expressed as follows

$$\begin{aligned} \langle S, M+1 | \hat{S}_x | SM \rangle &= -(1/\sqrt{2}) \begin{pmatrix} S & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} \\ &\times (-1)^{S-(M+1)} \langle S \| \hat{T}_1(\vec{S}) \| S \rangle \end{aligned}$$

$$\begin{aligned} \langle S, M+1 | \hat{S}_y | SM \rangle &= (i/\sqrt{2}) \begin{pmatrix} S & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} \\ &\times (-1)^{S-(M+1)} \langle S \| \hat{T}_1(\vec{S}) \| S \rangle \end{aligned}$$

$$\begin{aligned} \langle S, M-1 | \hat{S}_x | SM \rangle &= (1/\sqrt{2}) \begin{pmatrix} S & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} \\ &\times (-1)^{S-(M-1)} \langle S \| \hat{T}_1(\vec{S}) \| S \rangle \end{aligned}$$

$$\begin{aligned} \langle S, M-1 | \hat{S}_y | SM \rangle &= (i/\sqrt{2}) \begin{pmatrix} S & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} \\ &\times (-1)^{S-(M-1)} \langle S \| \hat{T}_1(\vec{S}) \| S \rangle \end{aligned}$$

Owing to the triangular restriction for the $3j$ -symbols only the elements adjacent to the diagonal, $M' = M \pm 1$, are non-zero within each $S' = S$ block

$$\begin{aligned} H_{S,M+1,S,M}^Z(b) &= \mu_B (-g_x B_x + i g_y B_y) \frac{1}{\sqrt{2}} \begin{pmatrix} S & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} \\ &\times (-1)^{S-(M+1)} \langle S \| \hat{T}_1(\vec{S}) \| S \rangle [\hbar^{-1}] \end{aligned}$$

$$\begin{aligned} H_{S,M-1,S,M}^Z(b') &= \mu_B (g_x B_x + i g_y B_y) \frac{1}{\sqrt{2}} \begin{pmatrix} S & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} \\ &\times (-1)^{S-(M-1)} \langle S \| \hat{T}_1(\vec{S}) \| S \rangle [\hbar^{-1}] \end{aligned}$$

The off-diagonal block is evaluated according to

$$\begin{aligned}
 & \langle S' M' | (1/2) \vec{B} \cdot \vec{g}_- \cdot \vec{V} | S M \rangle \\
 &= (1/2) \langle S' M' | B_x g'_x \hat{V}_x + B_y g'_y \hat{V}_y + B_z g'_z \hat{V}_z | S M \rangle \\
 &= (1/2) \left(B_x g'_x \langle S' M' | \hat{V}_x | S M \rangle + B_y g'_y \langle S' M' | \hat{V}_y | S M \rangle \right. \\
 &\quad \left. + B_z g'_z \langle S' M' | \hat{V}_z | S M \rangle \right)
 \end{aligned}$$

where we use a substitution

$$g'_\alpha \equiv (g_-)_\alpha = g_{A,\alpha} - g_{B,\alpha}$$

(c) The z-component is

$$\langle S+1, M | \hat{V}_z | S M \rangle = \begin{pmatrix} (S+1) & 1 & S \\ -M & 0 & M \end{pmatrix} (-1)^{(S+1)-M} \langle S+1 | \hat{T}_1(\vec{V}) \| S \rangle$$

so that

$$\begin{aligned}
 H_{S+1, M, S, M}^Z(c) &= \frac{1}{2} \mu_B g'_z B_z \begin{pmatrix} (S+1) & 1 & S \\ -M & 0 & M \end{pmatrix} (-1)^{(S+1)-M} \\
 &\quad \times \langle S+1 | \hat{T}_1(\vec{V}) \| S \rangle [\hbar^{-1}]
 \end{aligned}$$

(d) The remaining components are expressed as follows

$$\begin{aligned}
 \langle S+1, M+1 | \hat{V}_x | S M \rangle &= -(1/\sqrt{2}) \begin{pmatrix} (S+1) & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} \\
 &\quad \times (-1)^{(S+1)-(M+1)} \langle S+1 | \hat{T}_1(\vec{V}) \| S \rangle
 \end{aligned}$$

$$\begin{aligned}
 \langle S+1, M+1 | \hat{V}_y | S M \rangle &= (i/\sqrt{2}) \begin{pmatrix} (S+1) & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} \\
 &\quad \times (-1)^{(S+1)-(M+1)} \langle S+1 | \hat{T}_1(\vec{V}) \| S \rangle
 \end{aligned}$$

$$\begin{aligned} \langle S+1, M-1 | \hat{V}_x | SM \rangle &= (1/\sqrt{2}) \begin{pmatrix} (S+1) & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} \\ &\times (-1)^{(S+1)-(M-1)} \langle S+1 \| \hat{T}_1(\vec{V}) \| S \rangle \end{aligned}$$

$$\begin{aligned} \langle S+1, M-1 | \hat{V}_y | SM \rangle &= (i/\sqrt{2}) \begin{pmatrix} (S+1) & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} \\ &\times (-1)^{(S+1)-(M-1)} \langle S+1 \| \hat{T}_1(\vec{V}) \| S \rangle \end{aligned}$$

yielding

$$\begin{aligned} H_{S+1, M+1, S, M}^Z(d) &= \mu_B (-g'_x B_x + i g'_y B_y) \frac{1}{2\sqrt{2}} \begin{pmatrix} (S+1) & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} \\ &\times (-1)^{(S+1)-(M+1)} \langle S+1 \| \hat{T}_1(\vec{V}) \| S \rangle [\hbar^{-1}] \end{aligned}$$

$$\begin{aligned} H_{S+1, M-1, S, M}^Z(d') &= \mu_B (g'_x B_x + i g'_y B_y) \frac{1}{2\sqrt{2}} \begin{pmatrix} (S+1) & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} \\ &\times (-1)^{(S+1)-(M-1)} \langle S+1 \| \hat{T}_1(\vec{V}) \| S \rangle [\hbar^{-1}] \end{aligned}$$

The matrix elements of the Zeeman operator are collected in Table 10.16.

The structure of the Zeeman matrix copies a scheme in which the above four types of matrix elements occur

$$a \sim g_z$$

$$b, b' \sim g_x, g_y$$

$$c \sim g'_z$$

$$d, d' \sim g'_x, g'_y$$

Under the g -tensor we assume the molecular-state tensor composed of the local tensors

$$\bar{\bar{g}}_S = c_A \bar{\bar{g}}_A + (1 - c_A) \bar{\bar{g}}_B$$

TABLE 10.16
Matrix elements of the Zeeman operator for dinuclear systems^a

Type	Expression
$H_{S,M,S,M}^Z(a)$	$\mu_B g_z B_z M$
$H_{S,M+1,S,M}^Z(b)$	$\mu_B (g_x B_x - i g_y B_y) \frac{1}{\sqrt{2}} \left[\frac{(S-M)(S+M+1)}{2S(S+1)(2S+1)} \right]^{1/2} [S(S+1)(2S+1)]^{1/2}$
$H_{S,M-1,S,M}^Z(b')$	$\mu_B (g_x B_x + i g_y B_y) \frac{1}{\sqrt{2}} \left[\frac{(S+M)(S-M+1)}{2S(S+1)(2S+1)} \right]^{1/2} [S(S+1)(2S+1)]^{1/2}$
$H_{S+1,M,S,M}^Z(c)$	$\mu_B g'_z B_z \frac{1}{2} \left[\frac{(S-M+1)(S+M+1)}{(2S+3)(2S+1)(S+1)} \right]^{1/2} \times \left[\frac{(S_A - S_B + S + 1)(-S_A + S_B + S + 1)(S_A + S_B - S)(S_A + S_B + S + 2)}{(S+1)} \right]^{1/2}$
$H_{S+1,M+1,S,M}^Z(d)$	$\mu_B (-g'_x B_x + i g'_y B_y) \frac{1}{2\sqrt{2}} \left[\frac{(S+M+1)(S+M+2)}{2(2S+3)(2S+1)(S+1)} \right]^{1/2} \times \left[\frac{(S_A - S_B + S + 1)(-S_A + S_B + S + 1)(S_A + S_B - S)(S_A + S_B + S + 2)}{(S+1)} \right]^{1/2}$
$H_{S+1,M-1,S,M}^Z(d')$	$\mu_B (g'_x B_x + i g'_y B_y) \frac{1}{2\sqrt{2}} \left[\frac{(S-M+1)(S-M+2)}{2(2S+3)(2S+1)(S+1)} \right]^{1/2} \times \left[\frac{(S_A - S_B + S + 1)(-S_A + S_B + S + 1)(S_A + S_B - S)(S_A + S_B + S + 2)}{(S+1)} \right]^{1/2}$

^a There is $g_\alpha \equiv (g_S)_\alpha = (c_A g_A + c_B g_B)_\alpha$ and $g'_\alpha \equiv (g_-)_\alpha = (g_A - g_B)_\alpha$.

with the combination coefficients according to Table 10.12. The structure of the interaction matrix is

	M'	M	$M + 1$	$M + 2$	$M + 3$
$S' = S$	M	a	b'	0	0
	$M + 1$	b	a	b'	0
	$M + 2$	0	b	a	b'
	$M + 3$	0	0	b	a
$S' = S + 1$	M	c	d'	0	0
	$M + 1$	d	c	d'	0
	$M + 2$	0	d	c	d'
	$M + 3$	0	0	d	c

In order to exemplify the construction of the Hamiltonian matrix let us consider the simplest case of the $S_A = S_B = 1/2$ system with the following order of molecular states: $|0, 0\rangle$, $|1, -1\rangle$, $|1, 0\rangle$ and $|1, +1\rangle$. In constructing the asymmetric exchange Hamiltonian matrix only the block $S' = S = 1$ is filled; hence

$$\mathbf{H}^{\text{asym}} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & (1/3)D_1 & 0 & E_1 \\ 0 & 0 & -(2/3)D_1 & 0 \\ 0 & E_1 & 0 & (1/3)D_1 \end{pmatrix}$$

According to Table 10.12 the molecular-state D -tensor is composed as follows

$$\overline{\overline{D}}_{S=1} = \frac{1}{2} \overline{\overline{D}}_{AB}$$

so that the axial zero-field splitting parameter is

$$D_1 = \frac{3}{2} (D_{S=1})_{zz} = \frac{3}{4} (D_{AB})_{zz}$$

and the rhombic zero-field splitting parameter becomes

$$E_1 = \frac{1}{2} [(D_{S=1})_{xx} - (D_{S=1})_{yy}] = \frac{1}{4} [(D_{AB})_{xx} - (D_{AB})_{yy}]$$

The situation resembles the case of zero-field splitting in mononuclear systems (Section 8.4): the energy levels are split by the axial parameter into a Kramers doublet and a single level; the rhombic parameter removes the degeneracy completely.

The complete Zeeman matrix is evaluated as follows

$$\mathbf{H}^Z = \mu_B \begin{pmatrix} 0 & (1/\sqrt{8})d'^* & (1/2)c & (1/\sqrt{8})d^* \\ (1/\sqrt{8})d' & -a & (1/\sqrt{2})b^* & 0 \\ (1/2)c & (1/\sqrt{2})b & 0 & (1/\sqrt{2})b^* \\ (1/\sqrt{8})d & 0 & (1/\sqrt{2})b & a \end{pmatrix}$$

with

$$a = \mu_B g_z B_z$$

$$b = \mu_B (g_x B_x - i g_y B_y)$$

$$c = \mu_B g'_z B_z$$

$$d = \mu_B (-g'_x B_x + i g'_y B_y)$$

$$d' = \mu_B (g'_x B_x + i g'_y B_y)$$

where, in accordance with Table 10.12, the molecular-state g -tensor is composed as

$$\bar{g}_{S=1} = \frac{1}{2}(\bar{g}_A + \bar{g}_B)$$

Under the assumption that the centres are equivalent (all tensors aligned parallel), there is

$$\bar{g}' = \bar{g}_A - \bar{g}_B = 0$$

and then the Zeeman matrix collapses to

$$\mathbf{H}^Z = \mu_B \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -a & (1/\sqrt{2})b^* & 0 \\ 0 & (1/\sqrt{2})b & 0 & (1/\sqrt{2})b^* \\ 0 & 0 & (1/\sqrt{2})b & a \end{pmatrix}$$

Assuming only axial asymmetry ($E_1 = 0$), the simplified Hamiltonian matrix becomes

$$\mathbf{H} = \mathbf{H}^{\text{iso}} + \mathbf{H}^{\text{asym}} + \mathbf{H}^Z$$

$$= \begin{pmatrix} (3/4)J & 0 & 0 & 0 \\ 0 & (-1/4)J + (1/3)D_1 & \mu_B g_{\perp} B_{\perp} / \sqrt{2} & 0 \\ 0 & -\mu_B g_{\parallel} B_{\parallel} & (-1/4)J - (2/3)D_1 & \mu_B g_{\perp} B_{\perp} / \sqrt{2} \\ 0 & 0 & \mu_B g_{\perp} B_{\perp} / \sqrt{2} & (-1/4)J + (1/3)D_1 + \mu_B g_{\parallel} B_{\parallel} \end{pmatrix}$$

The corresponding secular equation has the set of algebraic roots from which the van Vleck coefficients can be identified individually for the parallel and perpendicular directions, respectively. These are collected in Table 10.17. With the van Vleck coefficients evaluated, then the components of the magnetic susceptibility, as they result from the van Vleck formula, are

$$\chi_{\parallel} = C_0 \frac{g_{\parallel}^2}{T} 2 \frac{\exp(-x/3)}{\exp(2x/3) + 2 \exp(-x/3) + \exp(-J/kT)}$$

$$\chi_{\perp} = C_0 \frac{g_{\perp}^2}{(D_1/k)} 2 \frac{\exp(2x/3) - \exp(-x/3)}{\exp(2x/3) + 2 \exp(-x/3) + \exp(-J/kT)}$$

for the argument

$$x = D_1/kT$$

TABLE 10.17

Eigenvalues and van Vleck coefficients for the $S_A = S_B = 1/2$ system^a

Eigenvalues ε_i	$\varepsilon_i^{(0)}$	$\varepsilon_i^{(1)}$	$\varepsilon_i^{(2)}$
Parallel direction			
1 $(3/4)J$	$+J$	0	0
2 $-(1/4)J + (1/3)D_1 - G_{\parallel}$	$+(1/3)D_1$	$-\mu_B g_{\parallel}$	0
3 $-(1/4)J - (2/3)D_1$	$-(2/3)D_1$	0	0
4 $-(1/4)J + (1/3)D_1 + G_{\parallel}$	$+(1/3)D_1$	$+\mu_B g_{\parallel}$	0
Perpendicular direction			
1 $(3/4)J$	$+J$	0	0
2 $-(1/4)J + (1/3)D_1$	$+(1/3)D_1$	0	0
3 $-(1/4)J - (2/3)D_1 + [D_1 - (D_1^2 + 4G_{\perp}^2)^{1/2}]/2$	$-(2/3)D_1$	0	$-\mu_B^2 g_{\perp}^2 / D_1$
4 $-(1/4)J - (2/3)D_1 + [D_1 + (D_1^2 + 4G_{\perp}^2)^{1/2}]/2$	$+(1/3)D_1$	0	$+\mu_B^2 g_{\perp}^2 / D_1$

^a $G_{\parallel} = \mu_B g_{\parallel} B_{\parallel}$, $G_{\perp} = \mu_B g_{\perp} B_{\perp}$; the zero-order energies are shifted by $(1/4)J$.

The temperature behaviour of the magnetic susceptibility is plotted in Fig. 10.9.

Another example is represented by the $S_A = S_B = 1$ system, e.g. a nickel(II) dimer. Let the nine components of the molecular-spin states be ordered as follows: $|0, 0\rangle$, $|1, -1\rangle$, $|1, 0\rangle$, $|1, +1\rangle$, $|2, -2\rangle$, $|2, -1\rangle$, $|2, 0\rangle$, $|2, +1\rangle$ and $|2, +2\rangle$. The local and molecular-state tensors are related through (Table 10.12)

$$\overline{\overline{D}}_{S=1} = -\frac{1}{2}\overline{\overline{D}}_A - \frac{1}{2}\overline{\overline{D}}_B + \overline{\overline{D}}_{AB} = -\overline{\overline{D}}_A + \overline{\overline{D}}_{AB}$$

$$\overline{\overline{D}}_{S=2} = \frac{1}{6}\overline{\overline{D}}_A + \frac{1}{6}\overline{\overline{D}}_B + \frac{1}{3}\overline{\overline{D}}_{AB} = \frac{1}{3}(\overline{\overline{D}}_A + \overline{\overline{D}}_{AB})$$

$$\overline{\overline{D}}_- = \overline{\overline{D}}_A - \overline{\overline{D}}_B = 0$$

$$\overline{\overline{g}}_S = \frac{1}{2}(\overline{\overline{g}}_A + \overline{\overline{g}}_B)$$

$$\overline{\overline{g}}' \equiv \overline{\overline{g}}_- = (\overline{\overline{g}}_A - \overline{\overline{g}}_B) = 0$$

where the second equality is valid for the equivalent centres with collinear tensors. For the diagonal D -tensors the zero-field splitting parameters are introduced as follows

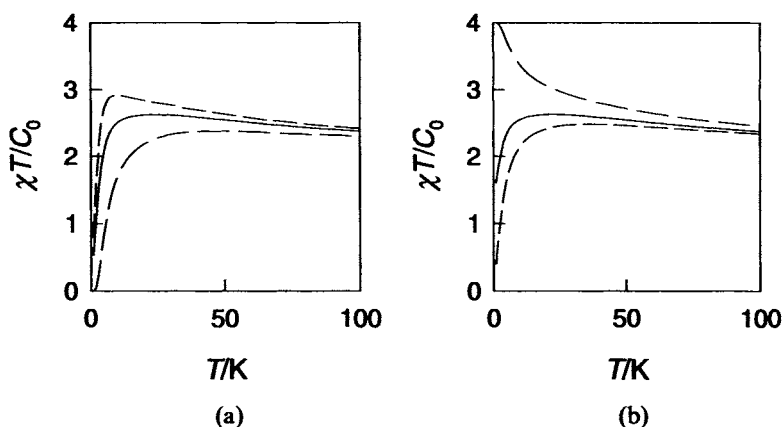


Fig. 10.9. Temperature dependence of the product function (per dimer) for a ferromagnetically coupled $S_A = S_B = 1/2$ system, $J/k = +100$ K, $g_{||} = g_{\perp} = 2.0$; $\chi_{||} T$ —long dashed, $\chi_{\perp} T$ —short dashed, $\chi_{av} T$ —solid; (a) $D_1/k = +10$ K, (b) $D_1/k = -10$ K.

$$D_1 = \frac{3}{2}(D_{S=1})_{zz} = \frac{3}{2}[-(D_A)_{zz} + (D_{AB})_{zz}]$$

$$D_2 = \frac{3}{2}(D_{S=2})_{zz} = \frac{1}{2}[(D_A)_{zz} + (D_{AB})_{zz}]$$

$$E_1 = \frac{1}{2}[(D_{S=1})_{xx} - (D_{S=1})_{yy}] = \frac{1}{2}[-(D_A)_{xx} + (D_A)_{yy} + (D_{AB})_{xx} - (D_{AB})_{yy}]$$

$$E_2 = \frac{1}{2}[(D_{S=2})_{xx} - (D_{S=2})_{yy}] = \frac{1}{6}[(D_A)_{xx} - (D_A)_{yy} + (D_{AB})_{xx} - (D_{AB})_{yy}]$$

The interaction matrix, restricted to the diagonal blocks only, is

$$\mathbf{H}^{\text{asym}} = \begin{pmatrix} 0 & & & & & & & & \\ \hline (1/3)D_1 & 0 & E_1 & & & & & & \\ & 0 & -(2/3)D_1 & 0 & & & & & \\ & E_1 & 0 & (1/3)D_1 & & & & & \\ \hline & & & & 2D_2 & 0 & \sqrt{6}E_2 & 0 & 0 \\ & & & & 0 & -D_2 & 0 & 3E_2 & 0 \\ & & & & \sqrt{6}E_2 & 0 & -2D_2 & 0 & \sqrt{6}E_2 \\ & & & & 0 & 3E_2 & 0 & -D_2 & 0 \\ & & & & 0 & 0 & \sqrt{6}E_2 & 0 & 2D_2 \end{pmatrix}$$

The off-diagonal ($S' = S + 1$ or $S' = S + 2$) matrix elements were neglected in the first approximation. The Zeeman matrix is

$$\mathbf{H}^Z/\mu_B = \begin{pmatrix} 0 & & & & & & & & \\ \hline -g_z B_z & g_x B_x/\sqrt{2} & 0 & & & & & & \\ & g_x B_x/\sqrt{2} & 0 & g_x B_x/\sqrt{2} & & & & & \\ & 0 & g_x B_x/\sqrt{2} & +g_z B_z & & & & & \\ \hline & & & & -2g_z B_z & g_x B_x & 0 & 0 & 0 \\ & & & & g_x B_x & -g_z B_z & g_x B_x\sqrt{6}/2 & 0 & 0 \\ & & & & 0 & g_x B_x\sqrt{6}/2 & 0 & g_x B_x\sqrt{6}/2 & 0 \\ & & & & 0 & 0 & g_x B_x\sqrt{6}/2 & +g_z B_z & g_x B_x \\ & & & & 0 & 0 & 0 & g_x B_x & +2g_z B_z \end{pmatrix}$$

The total Hamiltonian matrix consists of the three contributions

$$\mathbf{H} = \mathbf{H}^{\text{iso}} + \mathbf{H}^{\text{asym}} + \mathbf{H}^Z$$

Assuming only axial anisotropy ($E_1 = E_2 = 0$), the eigenvalues, together with the van Vleck coefficients, are readily obtained (Table 10.18). Substitution

TABLE 10.18

Van Vleck coefficients for asymmetric exchange in the $S_A = S_B = 1$ system

	M	$\varepsilon_i^{(0)}$	$\varepsilon_{i,\parallel}^{(1)}/\mu_B$	$\varepsilon_{i,\perp}^{(1)}/\mu_B$	$\varepsilon_{i,\perp}^{(2)}/\mu_B^2$
$S = 0$	0	0	0	0	0
$S = 1$	-1	$-J + (1/3)D_1$	$-g_{\parallel}$	0	0
	0	$-J - (2/3)D_1$	0	0	$-g_{\perp}^2/D_1$
	+1	$-J + (1/3)D_1$	$+g_{\parallel}$	0	$+g_{\perp}^2/D_1$
$S = 2^a$	-2	$-3J + 2D_2$	$-2g_{\parallel}$	0	$+(1/3)g_{\perp}^2/D_2$
	-1	$-3J - D_2$	$-g_{\parallel}$	0	$+(7/6)g_{\perp}^2/D_2$
	0	$-3J - 2D_2$	0	0	$-3g_{\perp}^2/D_2$
	+1	$-3J - D_2$	$+g_{\parallel}$	0	$+(7/6)g_{\perp}^2/D_2$
	+2	$-3J + 2D_2$	$+2g_{\parallel}$	0	$+(1/3)g_{\perp}^2/D_2$

^aA perturbation formula is used to get the approximate eigenvalues.

into the van Vleck equation yields the parallel and perpendicular magnetic susceptibilities, respectively

$$\chi_{\parallel} = C_0 \frac{g_{\parallel}^2}{T} \frac{2}{Z_0} \{ \exp\{[J - (1/3)D_1]/kT\} + 4 \exp\{[3J - 2D_2]/kT\} + \exp\{[3J + D_2]/kT\} \}$$

$$\chi_{\perp} = \frac{C_0 g_{\perp}^2}{Z_0 (D_1/k)} 2 \{ \exp\{[J + (2/3)D_1]/kT\} - \exp\{[J - (1/3)D_1]/kT\} \}$$

$$+ \frac{C_0 g_{\perp}^2}{Z_0 (D_2/k)} \{ -(4/3) \exp\{[3J - 2D_2]/kT\} - (14/3) \exp\{[3J + D_2]/kT\} + 6 \exp\{[3J + 2D_2]/kT\} \}$$

with the denominator

$$Z_0 = 1 + 2 \exp\{[J - (1/3)D_1]/kT\} + \exp\{[J + (2/3)D_1]/kT\} + 2 \exp\{[3J - 2D_2]/kT\} + 2 \exp\{[3J + D_2]/kT\} + \exp\{[3J + 2D_2]/kT\}$$

The formula just derived for the $S_A = S_B = 1$ system is applied in Fig. 10.10 to a certain set of parameters. A comparison with Figs. 10.5, 10.8 and 10.9 for the $S_A = S_B = 1/2$ system allows some generalisation:

- (a) For ferromagnetically coupled systems ($J > 0$) a plateau is reached at low temperature when the zero-field splitting is irrelevant (when the system exhibits isotropic exchange only).

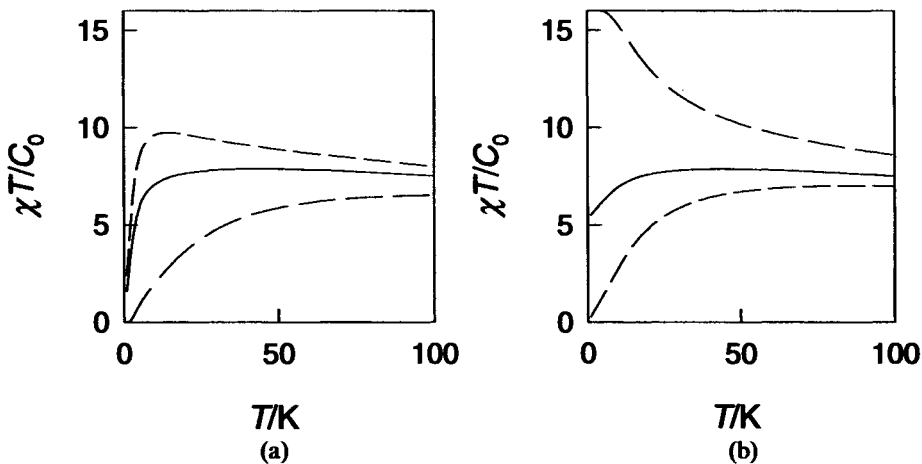


Fig. 10.10. Temperature dependence of the product function (per dimer) for a ferromagnetically coupled $S_A = S_B = 1$ system, $J/k = +100$ K; $\chi_{||}T$ —long dashed, $\chi_{\perp}T$ —short dashed, $\chi_{av}T$ —solid; (a) $D_1/k = D_2/k = +10$ K, (b) $D_1/k = D_2/k = -10$ K.

- (b) For asymmetric exchange the parallel and perpendicular susceptibilities (or product functions) display a considerable difference. For the positive zero-field splitting parameter ($D > 0$) the parallel component of the susceptibility turns to zero on temperature lowering and thus the product function, $\chi_{||}T$, escapes rapidly. The parallel component, on the other hand, is increasing so that the corresponding product function, $\chi_{\perp}T$, passes through a maximum and then turns to zero. The lowest energy state is magnetically low-productive as it is either the singlet state ($M = 0$ for $S_A = S_B$) or a component of the lowest Kramers doublet ($M = -1/2$ for $S_A \neq S_B$)—see Fig. 10.11. Therefore an upturn of $\chi_{av}T$ from the hypothetical plateau occurs.
- (c) For negative zero-field splitting ($D < 0$) the lowest energy state is the magnetically most productive since $M = -(S_A + S_B)$ holds true. The upturn of $\chi_{av}T$ from the hypothetical plateau is rather moderate. Now the perpendicular component, $\chi_{\perp}T$, escapes on cooling whereas the parallel component $\chi_{||}T$ increases.
- (d) For the antiferromagnetically coupled system ($J < 0$) only a slight magnetic anisotropy exists; the difference between $D > 0$ and $D < 0$ is rather low over the whole temperature interval.

10.3.2 Antisymmetric exchange

The antisymmetric term of the exchange interaction is defined through the operator

$$\hat{H}^{\text{anti}} = \vec{d}_{AB} \cdot (\vec{S}_A \times \vec{S}_B) [\hbar^{-2}]$$

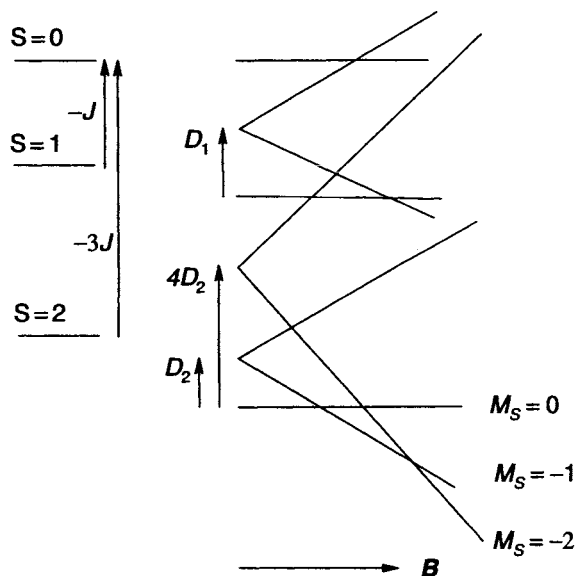


Fig. 10.11. Magnetic energy levels for a ferromagnetically coupled system $S_A = S_B = 1$ with positive zero-field splitting parameters.

The components of the polar vector $\vec{d}_{AB}(d_x, d_y, d_z)$ are related to the anti-symmetric part of the exchange coupling tensor as follows [18, 19]

$$\begin{pmatrix} 0 & d_z & -d_y \\ -d_z & 0 & d_x \\ d_y & -d_x & 0 \end{pmatrix} = \begin{pmatrix} 0 & (D'_{xy} - D'_{yx})/2 & (D'_{xz} - D'_{zx})/2 \\ -(D'_{xy} - D'_{yx})/2 & 0 & (D'_{yz} - D'_{zy})/2 \\ -(D'_{xz} - D'_{zx})/2 & -(D'_{yz} - D'_{zy})/2 & 0 \end{pmatrix}$$

In terms of Cartesian components the antisymmetric exchange term can be written as

$$\hat{H}^{\text{anti}} = \vec{d}_{AB} \cdot \vec{A} = d_{AB,x} \hat{A}_x + d_{AB,y} \hat{A}_y + d_{AB,z} \hat{A}_z$$

with the antisymmetric vector operator

$$\vec{A} = (\vec{S}_A \times \vec{S}_B)[\hbar^{-2}]$$

The cross-product can be expressed with the help of the first-order tensor product

$$\hat{A}_{1,q} = (\vec{S}_A \times \vec{S}_B)_q[\hbar^{-2}] = -i\sqrt{2} \left\{ \hat{T}_{1,q}(\vec{S}_A \otimes \vec{S}_B) \right\}[\hbar^{-2}]$$

for $q = 0, \pm 1$. In order to prove such a transcription one can use the result of Table 1.14 (Section 1.5.3) according to which the compound first-rank tensor

operators are generated from the products of the genuine vector operator components weighed by the vector coupling (Clebsch–Gordan) coefficients. One of the spherical components is expanded as follows

$$\begin{aligned}
 \left\{ \hat{T}_{1,1}(\vec{A} \otimes \vec{B}) \right\} &= \frac{1}{\sqrt{2}} (\hat{A}_{1,1} \hat{B}_{1,0} - \hat{A}_{1,0} \hat{B}_{1,1}) \\
 &= \frac{1}{\sqrt{2}} \left[-\frac{1}{\sqrt{2}} (\hat{A}_x + i\hat{A}_y) \hat{B}_z + \hat{A}_z \frac{1}{\sqrt{2}} (\hat{B}_x + i\hat{B}_y) \right] \\
 &= \frac{1}{2} (\hat{A}_z \hat{B}_x - \hat{A}_x \hat{B}_z) - \frac{i}{2} (\hat{A}_y \hat{B}_z - \hat{A}_z \hat{B}_y) \\
 &= \frac{1}{2} (\hat{C}_y - i\hat{C}_x) = -\frac{i}{\sqrt{2}} (\hat{C}_x + i\hat{C}_y) \frac{1}{\sqrt{2}} = \frac{i}{\sqrt{2}} \hat{C}_{1,1}
 \end{aligned}$$

where the vector resulting from the cross-product is denoted as

$$\vec{C} = \vec{A} \times \vec{B}$$

In transforming the spherical first-rank tensor components into Cartesian ones one can utilise the expressions

$$\hat{O}_{1,1} = -\frac{1}{\sqrt{2}} (\hat{O}_x + i\hat{O}_y)$$

$$\hat{O}_{1,-1} = \frac{1}{\sqrt{2}} (\hat{O}_x - i\hat{O}_y)$$

$$\hat{O}_{1,0} = \hat{O}_z$$

and the back transformations are

$$\hat{O}_x = \frac{1}{\sqrt{2}} (\hat{O}_{1,-1} - \hat{O}_{1,+1})$$

$$\hat{O}_y = \frac{i}{\sqrt{2}} (\hat{O}_{1,-1} + \hat{O}_{1,+1})$$

The other components of the first-order tensor product can be obtained by a similar procedure; hence

$$\begin{aligned}
 \left\{ \hat{T}_{1,-1}(\vec{A} \otimes \vec{B}) \right\} &= \frac{1}{\sqrt{2}} (\hat{A}_{1,0} \hat{B}_{1,-1} - \hat{A}_{1,-1} \hat{B}_{1,0}) \\
 &= \frac{i}{\sqrt{2}} (\hat{C}_x + i\hat{C}_y) \frac{1}{\sqrt{2}} = \frac{i}{\sqrt{2}} \hat{C}_{1,-1}
 \end{aligned}$$

and

$$\left\{ \hat{T}_{1,0}(\vec{A} \otimes \vec{B}) \right\} = \frac{1}{\sqrt{2}} (\hat{A}_{1,1} \hat{B}_{1,-1} - \hat{A}_{1,-1} \hat{B}_{1,1}) = \frac{i}{\sqrt{2}} \hat{C}_z = \frac{i}{\sqrt{2}} \hat{C}_{1,0}$$

so that we get the relationship between the cross-product and the first-order tensor product

$$\left\{ \hat{T}_{1,q}(\vec{A} \otimes \vec{B}) \right\} = \frac{i}{\sqrt{2}} \hat{C}_{1,q} = \frac{i}{\sqrt{2}} (\vec{A} \times \vec{B})_q$$

QED.

The matrix elements of the antisymmetric vector operator, by means of the Wigner–Eckart theorem, are

$$A_{S'M'SM,q} = (-i\sqrt{2})(-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} \langle S' \| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \| S \rangle [\hbar^{-2}]$$

The reduced matrix element is evaluated according to the general decoupling formula

$$\begin{aligned} & \langle S_A S_B S' \| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \| S_A S_B S \rangle \\ &= \langle S_A \| \vec{S}_A \| S_A \rangle \cdot \langle S_B \| \vec{S}_B \| S_B \rangle [(2S+1)(2S'+1)(2 \cdot 1+1)]^{1/2} \\ & \quad \times \begin{Bmatrix} S_A & S_A & 1 \\ S_B & S_B & 1 \\ S' & S & 1 \end{Bmatrix} \end{aligned}$$

This 9j-symbol can be generated by utilizing the special formula [16]

$$\begin{Bmatrix} f & f & 1 \\ d & c & e \\ b & a & e \end{Bmatrix} = \begin{Bmatrix} f & f & 0 \\ d & c & e \\ b & a & e \end{Bmatrix} \frac{d(d+1) + a(a+1) - b(b+1) - c(c+1)}{2[f(f+1)e(e+1)]^{1/2}}$$

whereas the 9j-symbol containing one zero collapses to the 6j-symbol

$$\begin{Bmatrix} f & f & 0 \\ d & c & e \\ b & a & e \end{Bmatrix} = \frac{(-1)^{b+c+e+f}}{[(2e+1)(2f+1)]^{1/2}} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix}$$

Then the 9j-symbol becomes

$$\begin{Bmatrix} S_A & S_A & 1 \\ S_B & S_B & 1 \\ S' & S & 1 \end{Bmatrix} = \frac{S(S+1) - S'(S'+1)}{2[1 \cdot 2 \cdot 3 \cdot S_A(S_A+1)(2S_A+1)]^{1/2}} (-1)^{S'+S_B+1+S_A} \\ \times \begin{Bmatrix} S & S' & 1 \\ S_B & S_B & S_A \end{Bmatrix}$$

and consequently

$$\begin{aligned} \langle S_A S_B S' \| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \| S_A S_B S \rangle &= \langle S_A \| \vec{S}_A \| S_A \rangle \cdot \langle S_B \| \vec{S}_B \| S_B \rangle \\ &\times [(2S+1)(2S'+1)3]^{1/2} \frac{S(S+1) - S'(S'+1)}{2[6S_A(S_A+1)(2S_A+1)]^{1/2}} (-1)^{S'+S_B+1+S_A} \\ &\times \begin{Bmatrix} S & S' & 1 \\ S_B & S_B & S_A \end{Bmatrix} \end{aligned}$$

The triangular restriction for the $6j$ -symbol implies $S' = S \pm 1$. The $6j$ -symbol itself becomes expressed through a special formula

$$\begin{aligned} \begin{Bmatrix} S & (S+1) & 1 \\ S_B & S_B & S_A \end{Bmatrix} &= \begin{Bmatrix} S_A & S_B & S \\ 1 & (S+1) & S_B \end{Bmatrix} = \begin{Bmatrix} a & b & c \\ 1 & (c+1) & b \end{Bmatrix} \\ &= (-1)^{s+1} \frac{1}{2} \left[\frac{(s+2)(s-2c)(s-2b+1)(s-2a+1)}{b(2b+1)(b+1)(2c+1)(c+1)(2c+3)} \right]^{1/2} \end{aligned}$$

with

$$s = a + b + c$$

After substitution of the reduced matrix elements of the uncoupled spins we get

$$\begin{aligned} \langle S_A S_B, S+1 \| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \| S_A S_B S \rangle &= [S_A(S_A+1)(2S_A+1)]^{1/2} [S_B(S_B+1)(2S_B+1)]^{1/2} \\ &\times [(2S+1)(2S+3)3]^{1/2} \frac{S(S+1) - (S+1)(S+2)}{2[6S_A(S_A+1)(2S_A+1)]^{1/2}} \frac{1}{2} \\ &\times (-1)^{S+1+S_B+1+S_A} (-1)^{S_A+S_B+S+1} \\ &\times \left[\frac{(S_A+S_B+S+2)(S_A+S_B-S)(S_A-S_B+S+1)(-S_A+S_B+S+1)}{S_B(2S_B+1)(S_B+1)(2S+1)(S+1)(2S+3)} \right]^{1/2} \\ &\times [\hbar^2] \end{aligned}$$

which simplifies to

$$\begin{aligned} & \langle S_A S_B, S+1 \| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \| S_A S_B S \rangle \\ &= [(S+1)(S_A + S_B + S+2)(S_A + S_B - S) \\ & \quad \times (S_A - S_B + S+1)(-S_A + S_B + S+1)/8]^{1/2} [\hbar^2] \end{aligned}$$

Now the z -component ($q=0$) of the antisymmetric exchange becomes expressed

$$\begin{aligned} A_{S+1,M,S,M,z} &= A_{S+1,M,S,M,(0)} \\ &= (-i\sqrt{2})(-1)^{(S+1)-M} \begin{pmatrix} (S+1) & 1 & S \\ -M & 0 & M \end{pmatrix} \langle S+1 \| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \| S \rangle [\hbar^{-2}] \\ &= (-i\sqrt{2})(-1)^{(S+1)-M} (-1)^{M-S+1} \left[\frac{(S-M+1)(S+M+1)}{(2S+1)(S+1)(2S+3)} \right]^{1/2} \\ & \quad \times [(S+1)(S_A + S_B + S+2)(S_A + S_B - S)(S_A - S_B + S+1) \\ & \quad \times (-S_A + S_B + S+1)/8]^{1/2} \end{aligned}$$

which yields

$$\begin{aligned} A_{S+1,M,S,M,z} &= (-i) \frac{1}{2} \left[\frac{(S-M+1)(S+M+1)}{(2S+1)(2S+3)} \right]^{1/2} \\ & \quad \times [(S_A + S_B + S+2)(S_A + S_B - S) \\ & \quad \times (S_A - S_B + S+1)(-S_A + S_B + S+1)]^{1/2} \end{aligned}$$

The remaining spherical components are

$$\begin{aligned} A_{S+1,M\pm 1,S,M,(\pm 1)} &= (-i\sqrt{2})(-1)^{(S+1)-(M\pm 1)} \begin{pmatrix} (S+1) & 1 & S \\ -(M\pm 1) & \pm 1 & M \end{pmatrix} \\ & \quad \times \langle S+1 \| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \| S \rangle [\hbar^{-2}] \\ &= (-i\sqrt{2})(-1)^{(S+1)-(M\pm 1)} (-1)^{M-S} \left[\frac{(S\pm M+1)(S\pm M+2)}{2(S+1)(2S+1)(2S+3)} \right]^{1/2} \\ & \quad \times [(S+1)(S_A + S_B + S+2)(S_A + S_B - S) \\ & \quad \times (S_A - S_B + S+1)(-S_A + S_B + S+1)/8]^{1/2} \end{aligned}$$

and consequently the Cartesian components become

$$\begin{aligned}
 A_{S+1,M+1,S,M,x} &= \frac{1}{\sqrt{2}}(A_{S+1,M+1,S,M,(-1)} - A_{S+1,M+1,S,M,(+1)}) \\
 &= \left(-\frac{1}{\sqrt{2}}\right)A_{S+1,M+1,S,M,(+1)} \\
 &= \left(-\frac{1}{\sqrt{2}}\right)(-i\sqrt{2})\left[\frac{(S+M+1)(S+M+2)}{2(S+1)(2S+1)(2S+3)}\right]^{1/2} \\
 &\quad \times [(S+1)(S_A + S_B + S + 2)(S_A + S_B - S) \\
 &\quad \times (S_A - S_B + S + 1)(-S_A + S_B + S + 1)/8]^{1/2}
 \end{aligned}$$

and

$$\begin{aligned}
 A_{S+1,M+1,S,M,y} &= \left(\frac{i}{\sqrt{2}}\right)(A_{S+1,M+1,S,M,(-1)} + A_{S+1,M+1,S,M,(+1)}) \\
 &= \left(\frac{i}{\sqrt{2}}\right)A_{S+1,M+1,S,M,(+1)} \\
 &= \left(\frac{i}{\sqrt{2}}\right)(-i\sqrt{2})\left[\frac{(S+M+1)(S+M+2)}{2(S+1)(2S+1)(2S+3)}\right]^{1/2} \\
 &\quad \times [(S+1)(S_A + S_B + S + 2)(S_A + S_B - S) \\
 &\quad \times (S_A - S_B + S + 1)(-S_A + S_B + S + 1)/8]^{1/2}
 \end{aligned}$$

For $M' = M - 1$ we get

$$\begin{aligned}
 A_{S+1,M-1,S,M,x} &= \frac{1}{\sqrt{2}}(A_{S+1,M-1,S,M,(-1)} - A_{S+1,M-1,S,M,(+1)}) \\
 &= \left(\frac{1}{\sqrt{2}}\right)A_{S+1,M-1,S,M,(-1)} \\
 &= \left(\frac{1}{\sqrt{2}}\right)(-i\sqrt{2})\left[\frac{(S-M+1)(S-M+2)}{2(S+1)(2S+1)(2S+3)}\right]^{1/2} \\
 &\quad \times [(S+1)(S_A + S_B + S + 2)(S_A + S_B - S) \\
 &\quad \times (S_A - S_B + S + 1)(-S_A + S_B + S + 1)/8]^{1/2}
 \end{aligned}$$

These matrix elements are collected in Table 10.19. The interaction matrix follows the scheme

	M'	$M - 1$	M	$M + 1$	$M + 2$
$S' = S$	$M - 1$	0	0	0	0
	M	0	0	0	0
	$M + 1$	0	0	0	0
	$M + 2$	0	0	0	0
$S' = S + 1$	$M - 1$	a	c	0	0
	M	b	a	c	0
	$M + 1$	0	b	a	c
	$M + 2$	0	0	b	a

For the simplest system of $S_A = S_B = 1/2$ the antisymmetric exchange interaction matrix adopts the form of

$$\mathbf{H}^{\text{anti}} = \begin{pmatrix} 0 & (1/\sqrt{8})c^* & (-1/2)a^* & (1/\sqrt{8})b^* \\ (1/\sqrt{8})c & 0 & 0 & 0 \\ (-1/2)a & 0 & 0 & 0 \\ (1/\sqrt{8})b & 0 & 0 & 0 \end{pmatrix}$$

with general parameters

$$a \equiv id_z$$

$$b \equiv +id_x + d_y$$

$$c \equiv -id_x + d_y = b^*$$

For the system of $S_A = 1/2, S_B = 1$ the interaction matrix is

$$\mathbf{H}^{\text{anti}} = \begin{pmatrix} 0 & 0 & (\sqrt{3/8})c^* & (-1/\sqrt{2})a^* & (1/\sqrt{8})b^* & 0 \\ 0 & 0 & 0 & (1/\sqrt{8})c^* & (-1/\sqrt{2})a^* & (\sqrt{3/8})b^* \\ (\sqrt{3/8})c & 0 & 0 & 0 & 0 & 0 \\ (-1/\sqrt{2})a & (1/\sqrt{8})c & 0 & 0 & 0 & 0 \\ (1/\sqrt{8})b & (-1/\sqrt{2})a & 0 & 0 & 0 & 0 \\ 0 & (\sqrt{3/8})b & 0 & 0 & 0 & 0 \end{pmatrix}$$

For the system of $S_A = S_B = 1$ the interaction matrix becomes

$$\mathbf{H}^{\text{anti}} = \begin{pmatrix} 0 & (1/\sqrt{3})c^* & (-\sqrt{2/3})a^* & (1/\sqrt{3})b^* & 0 & 0 & 0 & 0 & 0 \\ (1/\sqrt{3})c & 0 & 0 & 0 & c^* & -a^* & (1/\sqrt{6})b^* & 0 & 0 \\ (-\sqrt{2/3})a & 0 & 0 & 0 & 0 & (1/\sqrt{2})c^* & (-2/\sqrt{3})a^* & (1/\sqrt{2})b^* & 0 \\ (1/\sqrt{3})b & 0 & 0 & 0 & 0 & 0 & (1/\sqrt{6})c^* & -a^* & b^* \\ 0 & c & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -a & (1/\sqrt{2})c & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & (1/\sqrt{6})b & (-2/\sqrt{3})a & (1/\sqrt{6})c & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & (1/\sqrt{2})b & -a & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & b & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

The generation of the interaction matrices for the other combinations of spins is straightforward: one needs only the formulae listed in Table 10.19.

The effect of antisymmetric exchange alone (in a hypothetical case when the asymmetric exchange vanishes) is a splitting of the energy levels in the absence of the magnetic field. This kind of zero-field splitting is due to the mixing of the energy levels for $\Delta S = \pm 1$.

Assuming that the conditions for the application of perturbation theory are obeyed, we arrive at the second-order correction to the eigenvalues

$$\varepsilon_i^{(2)} = \varepsilon_i^{(0)} + \sum_{j \neq i} \frac{H_{ij}H_{ji}}{\varepsilon_i^{(0)} - \varepsilon_j^{(0)}}$$

TABLE 10.19

Matrix elements for the antisymmetric exchange Hamiltonian^a

Type	Expression
$H_{S+1,M,S,M}^{\text{anti}}(\text{a})$	$-id_z \frac{1}{2} \left[\frac{(S-M+1)(S+M+1)}{(2S+1)(2S+3)} \right]^{1/2} \times [(S_A + S_B + S + 2)(S_A + S_B - S)(S_A - S_B + S + 1)(-S_A + S_B + S + 1)]^{1/2}$
$H_{S+1,M+1,S,M}^{\text{anti}}(\text{b})$	$(id_x + d_y) \frac{1}{4} \left[\frac{(S+M+1)(S+M+2)}{(2S+1)(2S+3)} \right]^{1/2} \times [(S_A + S_B + S + 2)(S_A + S_B - S)(S_A - S_B + S + 1)(-S_A + S_B + S + 1)]^{1/2}$
$H_{S+1,M-1,S,M}^{\text{anti}}(\text{c})$	$(-id_x + d_y) \frac{1}{4} \left[\frac{(S-M+1)(S-M+2)}{(2S+1)(2S+3)} \right]^{1/2} \times [(S_A + S_B + S + 2)(S_A + S_B - S)(S_A - S_B + S + 1)(-S_A + S_B + S + 1)]^{1/2}$

^aComponents d_x , d_y and d_z are in energy units.

For the system $S_A = S_B = 1/2$, one gets the eigenvalues $\varepsilon_{S,M}$ in the form

$$\varepsilon_{0,0} = 0 + \frac{d_x^2 + d_y^2 + d_z^2}{4J}$$

$$\varepsilon_{1,-1} = -J - \frac{d_x^2 + d_y^2}{8J}$$

$$\varepsilon_{1,0} = -J - \frac{2d_z^2}{8J}$$

$$\varepsilon_{1,+1} = -J - \frac{d_x^2 + d_y^2}{8J}$$

These energy levels are shown in Fig. 10.12. The zero-field splitting within the triplet state is given by

$$\Delta E = \varepsilon_{1,+1} - \varepsilon_{1,0} = \frac{2d_z^2 - d_x^2 - d_y^2}{8J} = D^{\text{anti}}$$

where we introduce the parameter D^{anti} adopting either positive or negative values.

The perturbed wave function includes a mixing of states of different spins, hence

$$|\Psi_i^{(2)}\rangle = |\Psi_i^{(0)}\rangle + \sum_{j \neq i} \frac{H_{ji}}{\varepsilon_i^{(0)} - \varepsilon_j^{(0)}} |\Psi_j^{(0)}\rangle$$

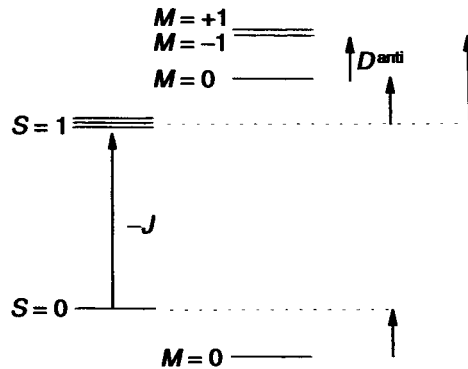


Fig. 10.12. Zero-field splitting of the energy levels due to antisymmetric exchange for an $S_A = S_B = 1/2$ system.

Thus the lowest singlet state contains an admixture of the triplet components

$$\left| \Psi_0^{(2)} \right\rangle = |0, 0\rangle + \frac{-id_x + d_y}{\sqrt{8}J} |1, -1\rangle + \frac{-id_z}{2J} |1, 0\rangle + \frac{id_x + d_y}{\sqrt{8}J} |1, +1\rangle$$

and it is no longer strictly diamagnetic. Although the average values of the spin operators are all zero

$$\left\langle \Psi_0 \left| \hat{S}_\alpha \right| \Psi_0 \right\rangle = 0$$

(for $\alpha = x, y, z$), the average value of the squared spin is non-zero

$$\left\langle \Psi_0 \left| \hat{S}^2 \right| \Psi_0 \right\rangle = \frac{d_x^2 + d_y^2 + d_z^2}{2J^2}$$

Consequently the averaged magnetic susceptibility to a low-temperature limit becomes

$$\chi(\text{LT}) = -N_A \mu_0 \mu_B^2 \frac{d_x^2 + d_y^2 + d_z^2}{3J^3}$$

For antiferromagnetic exchange ($J < 0$) the contribution to the powder magnetic susceptibility is positive and temperature-independent.

In extended lattices the antiferromagnetic exchange is at the origin of a weak ferromagnetism.

10.4 OTHER INTERACTIONS IN DINUCLEAR SYSTEMS

10.4.1 Biquadratic exchange

The operator of the biquadratic exchange for a dinuclear system is written as follows

$$\hat{H}^{\text{bq}} = -j(\vec{S}_A \cdot \vec{S}_B)^2 [\hbar^{-4}]$$

It can be rewritten by using the zero-order tensor product of two second-rank tensors as follows

$$\sqrt{5} \left\{ \hat{T}_0[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} = (\vec{S}_A \cdot \vec{S}_B)^2 - \frac{1}{3}(\vec{S}_A \cdot \vec{S}_A)(\vec{S}_B \cdot \vec{S}_B)$$

The left side is expanded using the general formula for the tensor product of the irreducible tensor operators

$$\left\{ \hat{T}_{K,q} [\hat{T}_{k,m}(\vec{S}_A) \otimes \hat{T}_{l,n}(\vec{S}_B)] \right\} = \sum_{m=-k}^{+k} \sum_{n=-l}^{+l} (2 \cdot K + 1)^{1/2} (-1)^{l-k-q} \\ \times \begin{pmatrix} k & l & K \\ m & n & -q \end{pmatrix} \hat{T}_{k,m}(\vec{S}_A) \hat{T}_{l,n}(\vec{S}_B)$$

Hence

$$\sqrt{5} \left\{ \hat{T}_0 [\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} = \sum_{m=-2}^{+2} (2 \cdot 0 + 1)^{1/2} (-1)^0 \\ \times \begin{pmatrix} 2 & 2 & 0 \\ m & -m & 0 \end{pmatrix} \hat{T}_{2,m}(\vec{S}_A) \hat{T}_{2,-m}(\vec{S}_B)$$

The special 3j-symbol can be evaluated through the formula

$$\begin{pmatrix} 2 & 2 & 0 \\ m & -m & 0 \end{pmatrix} = (-1)^{2-m} (2 \cdot 2 + 1)^{-1/2}$$

so that we get

$$\sqrt{5} \left\{ \hat{T}_0 [\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} \\ = \hat{T}_{2,+2}(\vec{S}_A) \hat{T}_{2,-2}(\vec{S}_B) - \hat{T}_{2,+1}(\vec{S}_A) \hat{T}_{2,-1}(\vec{S}_B) + \hat{T}_{2,0}(\vec{S}_A) \hat{T}_{2,0}(\vec{S}_B) \\ - \hat{T}_{2,-1}(\vec{S}_A) \hat{T}_{2,+1}(\vec{S}_B) + \hat{T}_{2,-2}(\vec{S}_A) \hat{T}_{2,+2}(\vec{S}_B)$$

The compound irreducible tensor operators of the second rank are constructed from the first-rank tensors (spherical vectors) as follows

$$\hat{T}_{2,+2}(\vec{S}_A) = \hat{T}_{1,+1}(\vec{S}_A) \hat{T}_{1,+1}(\vec{S}_A) \\ \hat{T}_{2,+1}(\vec{S}_A) = \frac{1}{\sqrt{2}} [\hat{T}_{1,+1}(\vec{S}_A) \hat{T}_{1,0}(\vec{S}_A) + \hat{T}_{1,0}(\vec{S}_A) \hat{T}_{1,+1}(\vec{S}_A)] \\ \hat{T}_{2,0}(\vec{S}_A) = \frac{2}{\sqrt{6}} \hat{T}_{1,0}(\vec{S}_A) \hat{T}_{1,0}(\vec{S}_A) \\ + \frac{1}{\sqrt{6}} [\hat{T}_{1,+1}(\vec{S}_A) \hat{T}_{1,-1}(\vec{S}_A) + \hat{T}_{1,-1}(\vec{S}_A) \hat{T}_{1,+1}(\vec{S}_A)]$$

$$\hat{T}_{2,-1}(\vec{S}_A) = \frac{1}{\sqrt{2}}[\hat{T}_{1,-1}(\vec{S}_A)\hat{T}_{1,0}(\vec{S}_A) + \hat{T}_{1,0}(\vec{S}_A)\hat{T}_{1,-1}(\vec{S}_A)]$$

$$\hat{T}_{2,-2}(\vec{S}_A) = \hat{T}_{1,-1}(\vec{S}_A)\hat{T}_{1,-1}(\vec{S}_A)$$

and analogously for the spin variable $\vec{S}_B$. Then one gets the left side in the form of

$$\begin{aligned} & \sqrt{5} \left\{ \hat{T}_0[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} \\ &= \{ 3[\hat{T}_{1,+1}(\vec{S}_A)]^2[\hat{T}_{1,-1}(\vec{S}_B)]^2 \\ &+ 2[\hat{T}_{1,-1}(\vec{S}_A)][\hat{T}_{1,+1}(\vec{S}_A)][\hat{T}_{1,-1}(\vec{S}_B)][\hat{T}_{1,+1}(\vec{S}_B)] \\ &+ 2[\hat{T}_{1,0}(\vec{S}_A)]^2[\hat{T}_{1,-1}(\vec{S}_B)][\hat{T}_{1,+1}(\vec{S}_B)] \\ &+ 3[\hat{T}_{1,-1}(\vec{S}_A)]^2[\hat{T}_{1,+1}(\vec{S}_B)]^2 \\ &- 6[\hat{T}_{1,+1}(\vec{S}_A)][\hat{T}_{1,0}(\vec{S}_A)][\hat{T}_{1,-1}(\vec{S}_B)][\hat{T}_{1,0}(\vec{S}_B)] \\ &- 6[\hat{T}_{1,-1}(\vec{S}_A)][\hat{T}_{1,0}(\vec{S}_A)][\hat{T}_{1,+1}(\vec{S}_B)][\hat{T}_{1,0}(\vec{S}_B)] \\ &+ 2[\hat{T}_{1,-1}(\vec{S}_A)][\hat{T}_{1,+1}(\vec{S}_A)][\hat{T}_{1,0}(\vec{S}_B)]^2 \\ &+ 2[\hat{T}_{1,0}(\vec{S}_A)]^2[\hat{T}_{1,0}(\vec{S}_B)]^2 \} / 3 \end{aligned}$$

In evaluating the right side, the scalar product of the first-rank tensors is

$$(\vec{S}_A \cdot \vec{S}_B) = -\sqrt{3} \left\{ \hat{T}_0(\vec{S}_A \otimes \vec{S}_B) \right\}$$

where

$$\begin{aligned} \left\{ \hat{T}_0(\vec{S}_A \otimes \vec{S}_B) \right\} &= \frac{1}{\sqrt{3}} \{ [\hat{T}_{1,+1}(\vec{S}_A)][\hat{T}_{1,-1}(\vec{S}_B)] - [\hat{T}_{1,0}(\vec{S}_A)][\hat{T}_{1,0}(\vec{S}_B)] \\ &+ [\hat{T}_{1,-1}(\vec{S}_A)][\hat{T}_{1,+1}(\vec{S}_B)] \} \end{aligned}$$

so that

$$\begin{aligned} (\vec{S}_A \cdot \vec{S}_B)^2 &= \{ -[\hat{T}_{1,+1}(\vec{S}_A)][\hat{T}_{1,-1}(\vec{S}_B)] + [\hat{T}_{1,0}(\vec{S}_A)][\hat{T}_{1,0}(\vec{S}_B)] \\ &- [\hat{T}_{1,-1}(\vec{S}_A)][\hat{T}_{1,+1}(\vec{S}_B)] \}^2 \end{aligned}$$

while

$$(\vec{S}_A \cdot \vec{S}_A) = -2[\hat{T}_{1,+1}(\vec{S}_A)][\hat{T}_{1,-1}(\vec{S}_A)] + [\hat{T}_{1,0}(\vec{S}_A)]^2$$

and

$$(\vec{S}_B \cdot \vec{S}_B) = -2[\hat{T}_{1,+1}(\vec{S}_B)][\hat{T}_{1,-1}(\vec{S}_B)] + [\hat{T}_{1,0}(\vec{S}_B)]^2$$

Therefore, after the insertion, the equality

$$\sqrt{5} \left\{ \hat{T}_0[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} = (\vec{S}_A \cdot \vec{S}_B)^2 - \frac{1}{3}(\vec{S}_A \cdot \vec{S}_A)(\vec{S}_B \cdot \vec{S}_B)$$

is proven.

The matrix elements of the first tensor product are evaluated by applying the Wigner–Eckart theorem

$$\begin{aligned} & \left\langle S' M' \left| \left\{ \hat{T}_{0,0}[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} \right| S M \right\rangle \\ &= (-1)^{S'-M'} \begin{pmatrix} S' & 0 & S \\ -M' & 0 & M \end{pmatrix} \left\langle S' \left\| \left\{ \hat{T}_0[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} \right\| S \right\rangle \end{aligned}$$

with the special $3j$ -symbol

$$\begin{pmatrix} S' & 0 & S \\ -M' & 0 & M \end{pmatrix} = (-1)^{S-M} (2S+1)^{-1/2} \delta_{S,S'} \delta_{M,M'}$$

The decoupling formula for the reduced matrix element yields

$$\begin{aligned} & \left\langle S' \left\| \left\{ \hat{T}_0[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} \right\| S \right\rangle \\ &= \delta_{S,S'} (2S+1)^{1/2} (2S+1)^{1/2} (2 \cdot 0 + 1)^{1/2} \left\langle S_A \left\| \vec{S}_A^2 \right\| S_A \right\rangle \left\langle S_B \left\| \vec{S}_B^2 \right\| S_B \right\rangle \\ & \quad \times \begin{Bmatrix} S_A & S_A & 2 \\ S_B & S_B & 2 \\ S & S & 0 \end{Bmatrix} \end{aligned}$$

The $9j$ -symbol collapses to the $6j$ -symbol

$$\begin{Bmatrix} S_A & S_A & 2 \\ S_B & S_B & 2 \\ S & S & 0 \end{Bmatrix} = (-1)^{S_A+S_B+2+S} [(2 \cdot 2 + 1)(2S+1)]^{-1/2} \begin{Bmatrix} S_A & S_A & 2 \\ S_B & S_B & S \end{Bmatrix}$$

which can be explicitly expressed as

$$\begin{Bmatrix} S_A & S_A & 2 \\ S_B & S_B & S \end{Bmatrix} = \begin{Bmatrix} S & S_A & S_B \\ 2 & S_B & S_A \end{Bmatrix} = (-1)^{S_A+S_B+S} \\ \times \frac{2[3X(X-1) - 4S_A(S_A+1)S_B(S_B+1)]}{[(2S_A-1)(2S_A)(2S_A+1)(2S_A+2)(2S_A+3)(2S_B-1)(2S_B)(2S_B+1)(2S_B+2)(2S_B+3)]^{1/2}}$$

with

$$X = S_A(S_A+1) + S_B(S_B+1) - S(S+1)$$

After substitution of the reduced matrix elements

$$\langle S_A \| \vec{S}_A^2 \| S_A \rangle = [S_A(S_A+1)(2S_A+1)(2S_A+3)(2S_A-1)/6]^{1/2} [\hbar^2]$$

$$\langle S_B \| \vec{S}_B^2 \| S_B \rangle = [S_B(S_B+1)(2S_B+1)(2S_B+3)(2S_B-1)/6]^{1/2} [\hbar^2]$$

one gets

$$\begin{aligned} & \langle SM | \sqrt{5} \{ \hat{T}_0[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \} | SM \rangle \\ &= \frac{1}{12} \{ 3[S_A(S_A+1) + S_B(S_B+1) - S(S+1)][S_A(S_A+1) + S_B(S_B+1) \\ & \quad - S(S+1) - 1] - 4S_A(S_A+1)S_B(S_B+1) \} [\hbar^2] \end{aligned}$$

The matrix elements of the operator of the biquadratic exchange are

$$\begin{aligned} \langle SM | (\vec{S}_A \cdot \vec{S}_B)^2 | SM \rangle &= \langle SM | \sqrt{5} \{ \hat{T}_0[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \} | SM \rangle \\ & \quad + \frac{1}{3} S_A(S_A+1)S_B(S_B+1) [\hbar^4] \end{aligned}$$

which finally yields

$$\begin{aligned} \langle SM | (\vec{S}_A \cdot \vec{S}_B)^2 | SM \rangle &= \left\langle \frac{1}{12} \{ 3[S_A(S_A+1) + S_B(S_B+1) \right. \\ & \quad - S(S+1)][S_A(S_A+1) + S_B(S_B+1) \\ & \quad - S(S+1) - 1] - 4S_A(S_A+1)S_B(S_B+1) \} \\ & \quad \left. + \frac{1}{3} S_A(S_A+1)S_B(S_B+1) \right\rangle [\hbar^4] \end{aligned}$$

Evidently, the matrix elements fill only the diagonal of the interaction matrix and consequently the biquadratic exchange is a kind of isotropic interaction.

The biquadratic exchange applies side by side with the bilinear exchange, hence

$$\langle SM | \hat{H} | SM \rangle = -J \langle SM | (\vec{S}_A \cdot \vec{S}_B) | SM \rangle [\hbar^{-2}] - j \langle SM | (\vec{S}_A \cdot \vec{S}_B)^2 | SM \rangle [\hbar^{-4}]$$

yielding the zero-field energy levels

$$\begin{aligned} \varepsilon(S, M) = & -J \frac{1}{2} [S(S+1) - S_A(S_A+1) - S_B(S_B+1)] \\ & - j \left\langle \frac{1}{12} [3[S_A(S_A+1) + S_B(S_B+1) - S(S+1)][S_A(S_A+1) \right. \\ & \quad \left. + S_B(S_B+1) - S(S+1) - 1] - 4S_A(S_A+1)S_B(S_B+1)] \right. \\ & \quad \left. + \frac{1}{3} S_A(S_A+1)S_B(S_B+1) \right\rangle \end{aligned}$$

The origin of the energy levels can be shifted by subtracting the constant factor depending only upon S_A and S_B , so that we get

$$\begin{aligned} \varepsilon(S, M) = & -J \frac{1}{2} [S(S+1)] - j \frac{1}{4} \{S(S+1)[S(S+1) + 1 - 2S_A(S_A+1) \\ & - 2S_B(S_B+1)]\} \end{aligned}$$

This form is equivalent to the expression

$$\begin{aligned} \varepsilon(S, M) = & -J' \frac{1}{2} [S(S+1)] - j \frac{1}{4} \{S(S+1)[S(S+1) - 2S_A(S_A+1) \\ & - 2S_B(S_B+1)]\} \end{aligned}$$

with the redefined bilinear exchange coupling constant accounting for the biquadratic exchange as

$$J' = J + \frac{j}{2}$$

The biquadratic exchange coupling constants adopt rather small values: the experimental data show that exchange coupling constants obey $|j/J| \approx 0.05$. The separation of the energy levels, however, alters significantly as the deviation from the Landé interval rule is dramatic for higher spin values [19]

$$\varepsilon(S) - \varepsilon(S-1) = -J'S - jS[S^2 - S_A(S_A+1) - S_B(S_B+1)]$$

Some illustrative examples are presented in Table 10.20.

TABLE 10.20
Zero-field energy levels for biquadratic exchange^a

S_A	S_B	S	$\varepsilon(S)$
1/2	1/2	1	$-J' + (1/2)j$
1	1	1	$-J' + 3j$
		2	$-3J' + 3j$
3/2	3/2	1	$-J' + (13/2)j$
		2	$-3J' + (27/2)j$
		3	$-6J' + 9j$
2	2	1	$-J' + 11j$
		2	$-3J' + 27j$
		3	$-6J' + 36j$
		4	$-10J' + 20j$
5/2	5/2	1	$-J' + (33/2)j$
		2	$-3J' + (87/2)j$
		3	$-6J' + 69j$
		4	$-10J' + 75j$
		5	$-15J' + (75/2)j$
3	3	1	$-J' + 23j$
		2	$-3J' + 63j$
		3	$-6J' + 108j$
		4	$-10J' + 140j$
		5	$-15J' + 135j$
		6	$-21J' + 63j$
7/2	7/2	1	$-J' + (61/2)j$
		2	$-3J' + (171/2)j$
		3	$-6J' + 153j$
		4	$-10J' + 215j$
		5	$-15J' + (495/2)j$
		6	$-21J' + (441/2)j$
		7	$-28J' + 98j$

^aThe lowest energy level lying at the origin is omitted.

For example, the mean magnetic susceptibility for the $S_A = S_B = 5/2$ dimer becomes

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{k} \frac{2g^2}{T} F(x, y)$$

with the characteristic function

$$F(x, y) = \{\exp[x + (33/2)y] + 5\exp[3x + (87/2)y] + 14\exp[6x + 69y] \\ + 30\exp[10x + 75y] + 55\exp[15x + (75/2)y] \\ / \{1 + 3\exp[x + (33/2)y] + 5\exp[3x + (87/2)y] + 7\exp[6x + 69y] \\ + 9\exp[10x + 75y] + 11\exp[15x + (75/2)y]\}$$

where

$$x = J'/kT$$

and

$$y = -j/kT$$

This function is plotted in Fig. 10.13.

10.4.2 Orbital angular momentum

The zero-field Hamiltonian in a dinuclear system that accounts for first-order (magnetic) angular momentum may be written in the form of

$$\hat{H}^Z = \hat{H}_A + \hat{H}_B + \hat{V}_A + \hat{V}_B + \hat{H}^{ss} + \hat{H}^{oo} + \hat{H}^{so}$$

The individual terms are:

- (a) the electronic Hamiltonians for the individual centres in high-symmetry (e.g. octahedral) configuration;
- (b) the distortion terms that account for the symmetry lowering along the z-axis

$$\hat{V}_A = \Delta\{\hat{L}_{A,z}^2[\hbar^{-2}] - \frac{1}{3}L_A(L_A + 1)\}$$

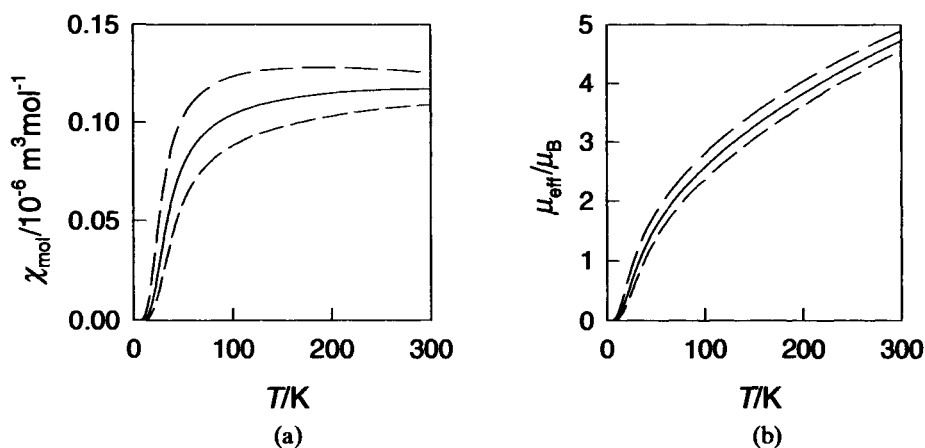


Fig. 10.13. Temperature variation of the magnetic susceptibility (a) and the effective magnetic moment (b) for the $S_A = S_B = 5/2$ dimer: solid—bilinear exchange with $J/hc = -100$ K; long dashed—biquadratic exchange with additional $j = -1$ K; medium dashed—biquadratic exchange with additional $j = +1$ K.

(c) the (isotropic) spin–spin coupling operator

$$\hat{H}^{ss} = -J(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}]$$

(d) the orbit–orbit coupling operator

$$\hat{H}^{oo} = -K(\vec{L}_A \cdot \vec{L}_B)[\hbar^{-2}]$$

(e) the spin–orbit coupling operator

$$\hat{H}^{so} = (\kappa_A v_A \vec{L}_A \cdot \vec{S}_A + \kappa_B v_B \vec{L}_B \cdot \vec{S}_B)[\hbar^{-2}]$$

where κ_A is the orbital reduction factor and v_A the spin–orbit equivalence parameter (accounting for the spin–orbit coupling constant and the T – P isomorphism—Table 8.37) for the given centre.

The basis set consists of the kets assigned to the uncoupled microstates; it transforms into the set of uncoupled atomic terms first, and then into the set of molecular eigenfunctions

$$\begin{aligned} |I\rangle &= |L_A, M_{LA}\rangle |S_A, M_{SA}\rangle |L_B, M_{LB}\rangle |S_B, M_{SB}\rangle \\ &\Rightarrow |\Gamma_A, \alpha_A, S_A, M_{SA}\rangle |\Gamma_B, \alpha_B, S_B, M_{SB}\rangle \Rightarrow |\Gamma_i, \alpha_i, S, M\rangle \end{aligned}$$

Each molecular eigenfunction transforms as an irreducible representation, Γ_i , which is contained in the direct product of the atomic terms

$$\Gamma_A \otimes \Gamma_B = \sum_i \Gamma_i$$

For example, the coupling of a pair of ${}^2T$ terms will produce $(3 \times 2)^2 = 36$ molecular states whereas the coupling of a pair of ${}^5T$ terms generates $(3 \times 5)^2 = 225$ states.

Using molecular eigenfunctions, the spin–spin coupling operator yields

$$\langle \Gamma, \alpha, S, M | J(\vec{S}_A \cdot \vec{S}_B) | \Gamma', \alpha', S', M' \rangle = J_\Gamma \delta_{\Gamma, \Gamma'} \delta_{\alpha, \alpha'} \langle S, M | (\vec{S}_A \cdot \vec{S}_B) | S', M' \rangle$$

with the orbital-dependent spin–spin coupling constant J_Γ . Analogously, the orbit–orbit operator gives

$$\begin{aligned} \langle \Gamma, \alpha, S, M | K(\vec{L}_A \cdot \vec{L}_B) | \Gamma', \alpha', S', M' \rangle &= K_{2S+1} \delta_{S, S'} \delta_{M, M'} \\ &\times \langle \Gamma, \alpha | (\vec{L}_A \cdot \vec{L}_B) | \Gamma', \alpha' \rangle \end{aligned}$$

with the spin-dependent orbit–orbit coupling constant K_{2S+1} .

The Zeeman term is to be added to the zero-field Hamiltonian; it becomes

$$\hat{H}^Z = \mu_B \vec{B} \cdot (\kappa_A \gamma_A \vec{L}_A + g_e \vec{S}_A) [\hbar^{-1}] + \mu_B \vec{B} \cdot (\kappa_B \gamma_B \vec{L}_B + g_e \vec{S}_B) [\hbar^{-1}]$$

where the equivalence coefficients γ_A depend upon the selection of which set of crystal field functions is actually used: the strong-field functions ($\gamma_A = -1$), the weak-field functions ($\gamma_A = -3/2$) or the intermediate-field functions ($-3/2 < \gamma_A < -1$).

In fact, the situation can be treated as if it were a pair-interaction coupling among four angular momenta ($\vec{J}_\alpha = \vec{L}_A, \vec{S}_A, \vec{L}_B, \vec{S}_B$). The pair interactions can be described by introducing a topologic function, $T_{\alpha\beta}$, the values of which are equal to the respective coupling constants

$$T_{12} = -\kappa_A \xi_{Ad}$$

$$T_{13} = -K_{AB}$$

$$T_{14} = 0$$

$$T_{23} = 0$$

$$T_{24} = -J_{AB}$$

$$T_{34} = -\kappa_B \xi_{Bd}$$

Then the matrix elements of the interaction Hamiltonian can be expressed through a weighted sum of pair-interaction operators

$$\langle I | \hat{H}^{\text{int}} | J \rangle = \sum_{\alpha=1}^4 \sum_{\beta>\alpha}^4 T_{\alpha\beta} \langle I | (\vec{J}_\alpha \cdot \vec{J}_\beta) | J \rangle [\hbar^{-2}]$$

Analogously, the matrix elements of the Zeeman term become expressed as

$$\langle I | \hat{H}^Z | J \rangle = \mu_B \vec{B} \cdot \sum_{\alpha=1}^4 g_\alpha \langle I | \vec{J}_\alpha | J \rangle [\hbar^{-1}]$$

with the magnetogyric factors

$$g_1 = \gamma_A \approx -1$$

$$g_2 = g_A \approx 2$$

$$g_3 = \gamma_B \approx -1$$

$$g_4 = g_B \approx 2$$

The magnetic energy levels are then obtained as the eigenvalues of the magnetic Hamiltonian

$$\langle I | \hat{H} | J \rangle = \langle I | \hat{V}_A + \hat{V}_B | J \rangle + \langle I | \hat{H}^{\text{int}} | J \rangle + \langle I | \hat{H}^Z | J \rangle$$

Owing to the complexity and high dimension of the interaction matrices an analytic expression for the magnetic susceptibility cannot be obtained. So a fully numerical approach can be applied: the magnetic energy levels are generated for several sets of magnetic fields and from their field dependence the first and second derivatives are evaluated; these are identified with the van Vleck coefficients entering the van Vleck formula. An example of the model calculation is presented in Fig. 10.14.

10.4.3 Spin delocalisation

Under spin delocalisation a situation is assumed when, in a magnetic system, an extra electron cannot be attributed to a single centre; it behaves as an itinerant. A prototype of this situation is represented by the homonuclear d^2-d^1 mixed-valence system (Fig. 10.15). Let the d^1-d^1 core of the system behave as high-spin. Then the extra electron can be added to either centre A or B and consequently the (determinantal) wave function of the dimer is degenerate

$$|A\rangle = |\phi_1^A \phi_2^A \phi_1^B|$$

$$|B\rangle = |\phi_1^A \phi_1^B \phi_2^B| = -|\phi_1^A \phi_2^B \phi_1^B|$$

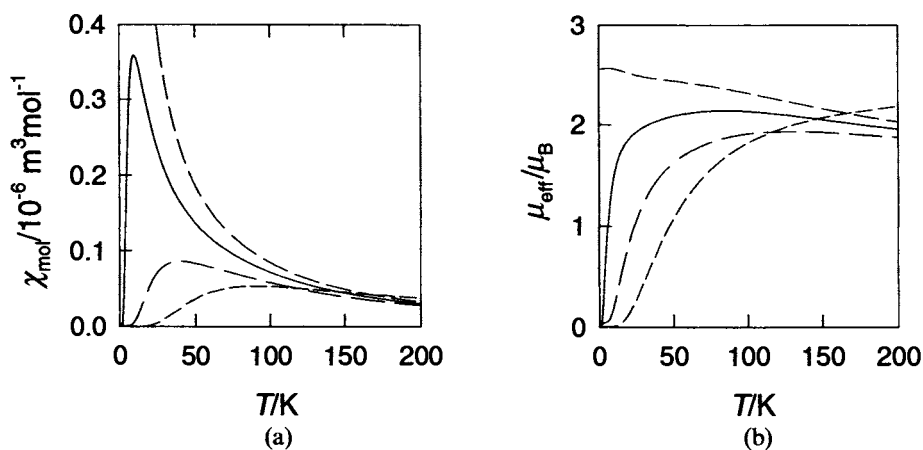


Fig. 10.14. Temperature dependence of the magnetic susceptibility (a) and the effective magnetic moment (b) for the $^2T-^2T$ dimer: $J/hc = -100 \text{ cm}^{-1}$, $g = 2$, $\gamma = -1$, $\kappa = 1$, $\xi/hc = 150 \text{ cm}^{-1}$; solid— $K = 0$; long dashed— $K/hc = -20 \text{ cm}^{-1}$; medium dashed— $K/hc = +20 \text{ cm}^{-1}$; short dashed—orbital contribution switched off (usual isotropic exchange for $S_A = S_B = 1/2$).

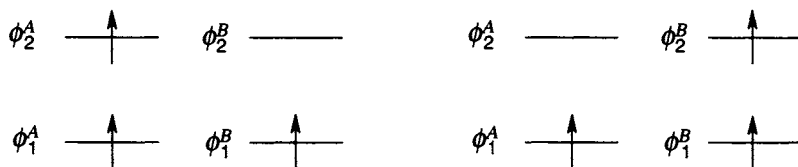


Fig. 10.15. Example of a spin delocalised system.

For the (orbitally) degenerate state a linear combination of two Slater determinants should be taken as the molecular wave function

$$|\Psi\rangle = C_A|A\rangle + C_B|B\rangle$$

and the variation method for the orthogonal states requires the solution of a secular equation

$$\det \begin{pmatrix} \langle A|\hat{H}|A\rangle - \varepsilon & \langle A|\hat{H}|B\rangle \\ \langle B|\hat{H}|A\rangle & \langle B|\hat{H}|B\rangle - \varepsilon \end{pmatrix} = 0$$

The diagonal matrix elements are equal to the relative energies depending on the total spin-spin state

$$\langle A|\hat{H}|A\rangle = \langle B|\hat{H}|B\rangle = E(S)$$

The off-diagonal ones

$$\langle A|\hat{H}|B\rangle = \langle B|\hat{H}|A\rangle$$

can be evaluated by taking into account the fact that the Slater determinants differ in one spin-orbital; then their matrix element involves only the one-electron integral, called the *transfer integral*

$$\langle A|\hat{H}|B\rangle = -\langle \phi_2^A|\hat{h}(1)|\phi_2^B\rangle \equiv -t$$

The secular equation

$$\det \begin{pmatrix} E(S) - \varepsilon & -t \\ -t & E(S) - \varepsilon \end{pmatrix} = 0$$

has the roots

$$\varepsilon_{\pm} = E(S) \pm |t|$$

The corresponding wave functions alter their parity: they are either of *g*- or *u*-type with respect to the centre of inversion.

A more complete solution of the spin delocalisation problem for homonuclear $d^{n+1} - d^n$ systems has been given by Anderson [20]. Denoting the total spins $S(d^n) = S_0$ and $S(d^{n+1}) = S_0 + 1/2$, the dimer involves $2S_0 + 1$ half-integer spin states, namely

$$S = 1/2, 3/2, \dots, (2S_0 + 1/2)$$

The off-diagonal matrix element becomes

$$\langle A | \hat{H} | B \rangle = \frac{t}{2} \frac{2S + 1}{2S_0 + 1}$$

and the energy levels are present in the form

$$\varepsilon(S) = -\frac{J}{2} S(S + 1) \pm \frac{t}{2} \frac{2S + 1}{2S_0 + 1}$$

In addition to the isotropic (bilinear) exchange the “*double exchange*” operates owing to the transfer integral. The energy levels split by the double exchange form a band of width $\Delta = 2t$; the levels of the *g*- and *u*-type alter systematically within the band. Due to the spin-dependence of double exchange splitting, the level with $S = S_{\max}$ becomes the ground state. Hence, in dimeric mixed-valence complexes, the double exchange always prefers the ferromagnetic ground state. The magnetic productivity of the final molecular state depends on the competition of the isotropic exchange (which can be of either antiferromagnetic or ferromagnetic nature) and the double exchange (which is always of ferromagnetic nature).

The energy levels for a mixed-valence Fe(II)–Fe(III) complex (the $d^6 - d^5$ system) with $S_0 = 2$ are

$$\varepsilon(1/2) = \pm(1/5)t$$

$$\varepsilon(3/2) = -(3/2)J \pm (2/5)t$$

$$\varepsilon(5/2) = -4J \pm (3/5)t$$

$$\varepsilon(7/2) = -(15/2)J \pm (4/5)t$$

$$\varepsilon(9/2) = -12J \pm t$$

The magnetic susceptibility is evaluated according to the formula derived in Section 10.2.3 as follows

$$\bar{\chi}_{\text{mol}} = \frac{C_0}{3T} \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} (2S+1)g_S^2 S(S+1) \exp[-\varepsilon(S)/kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} (2S+1) \exp[-\varepsilon(S)/kT]}$$

with the molecular-state g -factors

$$\bar{g}_S = \frac{1}{2}(\bar{g}_A + \bar{g}_B) + \frac{S_A(S_A+1) - S_B(S_B+1)}{S(S+1)} \frac{1}{2}(\bar{g}_A - \bar{g}_B)$$

The second-order van Vleck coefficients are omitted in the first approximation. The corresponding temperature behaviour is plotted in Fig. 10.16; it can be seen that the ground state alters, depending on the competition of the antiferromagnetic nature of the isotropic (bilinear) exchange and the ferromagnetic nature of the double exchange.

Some information about vibronic coupling in conjunction with spin localisation/delocalisation can be found elsewhere [21, 22].

10.4.4 Molecular field correction

The magnetic moment carrying entities in the solid state are distributed at definite distances and thus a weak intermolecular interaction exists between

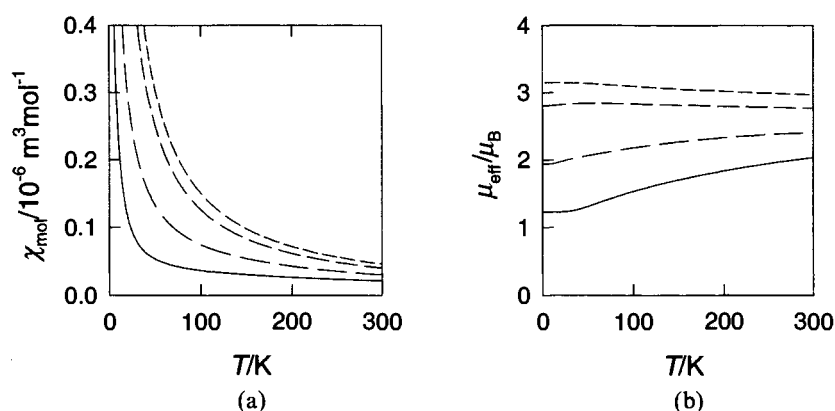


Fig. 10.16. Temperature dependence of the magnetic susceptibility (a) and the effective magnetic moment (b) for the mixed-valence d^6-d^5 dimer with $S_0 = 2$; $J/hc = -100 \text{ cm}^{-1}$, $g = 2$; solid— $t/hc = 0$ (no double exchange); long dashed— $t/hc = 1000 \text{ cm}^{-1}$; medium dashed— $t/hc = 2000 \text{ cm}^{-1}$; short dashed— $t/hc = 3000 \text{ cm}^{-1}$.

them. This is usually treated by means of the molecular field approximation. Let $\langle S_z \rangle$ denote the mean value of the z -component of the spin operator $\hat{S}_z$. Then the perturbation added to the Zeeman term becomes

$$\hat{H}' = -(zJ')\langle S_z \rangle \hat{S}_z [\hbar^{-1}]$$

Here, z is the number of nearest neighbours in the solid state and J' plays the role of the intercentre interaction parameter. It is assumed, however, that $|J| \gg |zJ'|$ is fulfilled in the exchange-coupled systems. Then the isotropic spin Hamiltonian, restricted to bilinear exchange, adopts the form of

$$\hat{H}^S = -J(\hat{S}_A \cdot \hat{S}_B)[\hbar^{-2}] + \mu_B g B \hat{S}_z [\hbar^{-1}] - (zJ')\langle S_z \rangle \hat{S}_z [\hbar^{-1}]$$

Its eigenvalues are simply

$$\varepsilon(S, M_S) = \varepsilon_0(S, M_S) + M_S [\mu_B g B - (zJ')\langle S_z \rangle]$$

where $\varepsilon_0(S, M_S)$ are the zero-field eigenvalues.

The mean value of the z -component of the spin operator is calculated as a Boltzmann average

$$\langle S_z \rangle = \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} M_S \exp[-\varepsilon(S, M_S)/kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} \exp[-\varepsilon(S, M_S)/kT]}$$

which can be approximated by expanding the exponentials as follows

$$\langle S_z \rangle = \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} M_S \exp[-\varepsilon_0(S, M_S)/kT] [1 - M_S(\mu_B g B - zJ'\langle S_z \rangle)/kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} \exp[-\varepsilon_0(S, M_S)/kT]}$$

The first-order term cancels exactly (since the quantum numbers $M_S = 0, \pm 1, \dots$; or $M_S = \pm 1/2, \pm 3/2, \dots$)

$$\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} M_S \exp[\varepsilon_0(S, M_S)/kT] = 0$$

and then

$$\langle S_z \rangle = [(\mu_B g B - zJ' \langle S_z \rangle) / kT] \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} (-1) M_S^2 \exp[-\varepsilon_0(S, M_S)/kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} \exp[-\varepsilon_0(S, M_S)/kT]}$$

After introducing the characteristic function

$$F(J, T) = \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} M_S^2 \exp[-\varepsilon_0(S, M_S)/kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} \exp[-\varepsilon_0(S, M_S)/kT]}$$

we get the mean value of the z-component of the spin operator in the form

$$\langle S_z \rangle = -\frac{\mu_B g B F(J, T)}{kT - zJ' F(J, T)}$$

Now the magnetisation is expressed as follows

$$M = -N_A \mu_B g \langle S_z \rangle$$

and finally the magnetic susceptibility becomes

$$\begin{aligned} \chi &= \mu_0 \frac{\partial M}{\partial B} = -N_A \mu_0 \mu_B g \frac{\partial}{\partial B} \langle S_z \rangle \\ &= N_A \mu_0 \mu_B^2 g^2 \frac{F(J, T)}{kT - zJ' F(J, T)} = C_0 g^2 \frac{F(J, T)}{T - (zJ'/k) F(J, T)} \end{aligned}$$

In the case of isotropic exchange the eigenvalues are

$$\varepsilon_0(S) = -\frac{S}{2}(S+1)J$$

and the characteristic function simplifies to

$$\begin{aligned}
 F(J, T) &= \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} M_S^2 \exp[JS(S+1)/2kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} \sum_{M_S=-S}^{+S} \exp[JS(S+1)/2kT]} \\
 &= \frac{\sum_{S=|S_A-S_B|}^{S_A+S_B} \frac{(2S+1)S(S+1)}{3} \exp[JS(S+1)/2kT]}{\sum_{S=|S_A-S_B|}^{S_A+S_B} (2S+1) \exp[JS(S+1)/2kT]}
 \end{aligned}$$

The effect of intermolecular interaction becomes important at low temperature when the ground state is magnetically productive. An example is given in Fig. 10.17 where a maximum on the product function (or the effective magnetic moment) replaces a plateau expected for pure ferromagnetic intercentre coupling.

The solid state rarely represents a perfect duplication of complex molecular entities. One should take into account that, along with the dominant portion of almost perfect dimeric units, a fraction of monomeric entities, at least concerning the magnetic properties, coexists. Such a paramagnetic impurity may have a considerable effect at low temperature when the ground state of the dinuclear complex is diamagnetic (i.e. for $J < 0$).

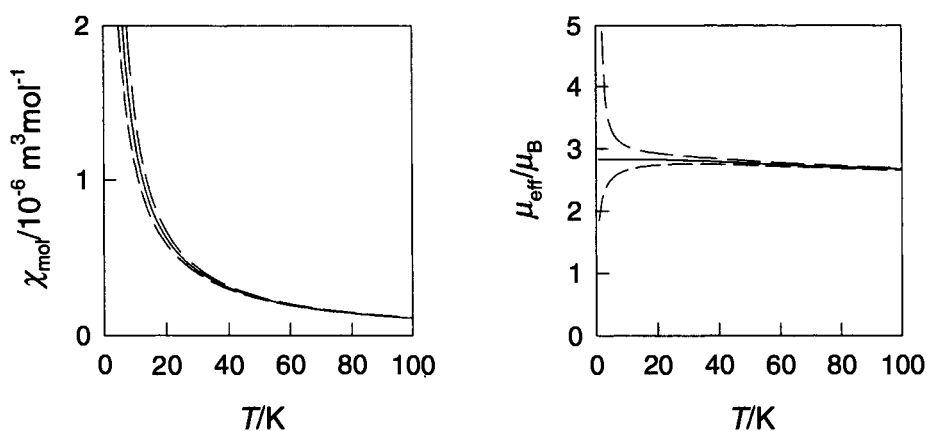


Fig. 10.17. Temperature behaviour of the $S_A = S_B = 1/2$ dimer in the presence of the weak intermolecular interactions: $g = 2$, $J/k = 100$ K; solid— $zJ'/k = 0$; long dashed— $zJ'/k = +2$ K; medium dashed— $zJ'/k = -2$ K.

In the presence of paramagnetic impurity the magnetic susceptibility is weighted by the corresponding mole fraction

$$\chi' = (1 - x_{\text{PI}})\chi_{\text{dim}} + x_{\text{PI}}\chi_{\text{PI}}$$

The susceptibility function of the paramagnetic impurity, to a good approximation, can be taken in the form of the Curie or Curie–Weiss law, hence

$$\chi_{\text{PI}} = C_0 \frac{S_{\text{PI}}(S_{\text{PI}} + 1)}{3} \frac{g_{\text{PI}}^2}{T - \Theta_{\text{PI}}}$$

The mole fraction of the paramagnetic impurity is unknown (and often dependent on the sample aging). It used to be determined as a result of the fitting procedure.

It is assumed that the measured magnetic susceptibility has already been corrected for the underlying diamagnetism (usually using the set of Pascal constants) and also for the temperature-independent paramagnetic (van Vleck) term (its mononuclear estimate being multiplied by the number of magnetic centres).

SUMMARY

1. Several kinds of exchange interactions, which couple the magnetic centres, are distinguished: the (bilinear) isotropic, asymmetric, antisymmetric, biquadratic and double exchange. Various fine-structure Hamiltonian terms enter the spin–spin coupling tensor $\overline{D}$; these were derived from the relativistic Dirac and Breit equation.
2. In analysing the exchange interaction the concept of magnetic orbitals is helpful. These cover either the natural magnetic orbitals or the orthogonalised magnetic orbitals. The limited valence bond method is superior to the simple molecular orbital method for analysing the nature of the singlet–triplet energy gap. The ferromagnetic portion of J (given mainly by the exchange integral) survives for the vanishing overlap integral of the magnetic orbitals. For large overlap integral, on the other hand, the antiferromagnetic term (given mainly by the resonance integral) dominates. The complete VB method is equivalent to the configuration interaction applied after the MO method.
3. The simple molecular orbital approach overestimates the role of the “ionic structures” which becomes well balanced when the configuration interaction is applied. A direct evaluation of the exchange coupling constant is based on the following steps: the MO calculation is done first;

then a transformation to orthogonalised magnetic orbitals is performed; finally a perturbative configuration interaction is applied. The two-orbital model yields the most important contributions: the potential exchange and the kinetic exchange. The involvement of the bridging ligand brings the ligand-to-metal charge transfer term which contributes to the superexchange. More occupied and vacant molecular orbitals bring the other interaction terms. In the framework of second-order perturbative CI these are: hole polarisation, particle polarisation, double spin polarisation, metal-to-ligand charge transfer and a simultaneous excitation + polarisation term.

4. A prototype for exchange coupling is represented by the $S_A = S_B = 1/2$ system. The temperature behaviour of the corresponding magnetic susceptibility is given by the Bleaney–Bowers equation which passes through a maximum when the exchange interaction is of the antiferromagnetic nature. Isotropic exchange in the other homospin dimers is described by analogous equations differing only in more terms involved in the numerator and the denominator. For a sufficiently low temperature the magnetisation versus magnetic field curve exhibits non-linear behaviour: for antiferromagnetic coupling the magnetisation displays some steps when the magnetically less productive ground state alters to the more productive one. Consequently the differential magnetic susceptibility is no longer a field-independent quantity: it varies with the magnetic field as a wave-type function.
5. Isotropic exchange in heterospin dinuclear complexes differs from the homospin case in that the second-order van Vleck coefficients are also non-zero. The final formula for the magnetic susceptibility resembles the case of the narrow multiplets for mononuclear systems; spin–orbit coupling can be formally substituted by spin–spin (exchange) coupling. However, the local atomic g -tensors should be properly combined into the molecular-state g -tensor.
6. Non-isotropic exchange interactions in dinuclear systems are represented by asymmetric exchange and antisymmetric exchange. In the first case the local atomic D -tensors and the pair-interaction D -tensor should be properly combined into the molecular-state D -tensor (all are symmetric and traceless). In the strong exchange limit the spin Hamiltonian, to a good approximation, adopts a block-diagonal form and the set of magnetic parameters reduces to D_S and E_S pairs. The situation resembles the case of isolated (wide) multiplets in mononuclear systems. In the weak exchange limit, on the other hand, the off-diagonal blocks for different spin states should be considered. Asymmetric exchange results in zero-field splitting: the magnetic levels for $S \geq 1$ are split in the absence of the magnetic field into a set of Kramers doublets and eventually single levels

- (for odd-multiplicity systems). For a ferromagnetically coupled system asymmetric exchange is the origin of magnetic anisotropy.
7. Antisymmetric exchange also results in zero-field splitting of energy levels. Its matrix elements, along with the d -vector components, fill the off-diagonal blocks of the interaction matrix. For antiferromagnetic coupling the contribution of the antisymmetric exchange to powder magnetic susceptibility is positive and temperature-independent.
 8. Biquadratic exchange is a kind of isotropic interaction. It alters the Landé interval rule, which is reflected in the temperature dependence of the magnetic susceptibility.
 9. The inclusion of orbital angular momentum along with the exchange interaction results in high-dimensional Hamiltonian matrices, and an analytic expression for the energy levels no longer exists. A fully numerical approach, however, can be applied: the magnetic energy levels result as the eigenvalues of the Hamiltonian matrix which can be generated for several values of the magnetic field.
 10. Spin delocalisation in mixed-valence dimers produces an additional splitting of the energy levels into a band. Due to the spin-dependence of the double exchange splitting, the level with the maximum spin becomes the ground state. The magnetic productivity of the final molecular state depends on the competition of the isotropic exchange and the ferromagnetic nature of the double exchange.

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Clusters

11.1 GENERAL STRATEGY

As in dinuclear systems, exchange interaction in clusters requires the evaluation of the following matrix elements:

- (a) bilinear isotropic exchange, $\hat{H}^{\text{iso}}$;
- (b) Zeeman perturbation, $\hat{H}^Z$;
- (c) asymmetric exchange, $\hat{H}^{\text{asym}}$;
- (d) antisymmetric exchange, $\hat{H}^{\text{anti}}$;
- (e) biquadratic exchange, $\hat{H}^{\text{bq}}$;
- (f) double exchange;
- (g) orbital angular momentum.

We have seen in the case of dinuclear complexes that there is no principal methodological difference between orbital and spin angular momentum; the orbital angular momentum can be included as if it were an extra spin angular momentum, taking into account the proper equivalence coefficients.

In principle, there are several computational strategies at our disposal which will be presented below.

11.1.1 Uncoupled basis set

As a first strategy, all matrix elements are evaluated in the basis set of uncoupled spin functions, i.e.

$$|I\rangle = |S_A, M_A\rangle |S_B, M_B\rangle \dots |S_N, M_N\rangle$$

The dimension of the basis set is

$$n = \prod_A^N (2S_A + 1)^4$$

In other words, the basis set is a direct product expansion of the local states.

The complete or truncated spin Hamiltonian matrix is then formed, e.g.

$$\mathbf{H}^S = \mathbf{H}^Z + \mathbf{H}^{\text{iso}} + \mathbf{H}^{\text{asym}} + \mathbf{H}^{\text{anti}} + \mathbf{H}^{\text{bq}}$$

and its eigenvalues are found by solving the secular equation. In fact the variation method is used. This approach is quite general, irrespective of the strong or weak exchange limit and the magnitude of the magnetic field. It has, however, one disadvantage: the matrices may adopt quite a large dimension and cannot be split into blocks of reduced dimension.

11.1.1.1 Isotropic exchange

As far as isotropic exchange is concerned the interaction matrix consists of all combinations of the pair-interaction matrices

$$\langle I | \hat{H}^{\text{iso}} | J \rangle = \sum_{A=1}^N \sum_{B>A}^N T_{AB} \langle I | (\vec{S}_A \cdot \vec{S}_B) | J \rangle [\hbar^{-2}]$$

weighted by a topologic function that includes a proper sign and magnitude of the coupling parameter

$$T_{AB} \approx J_{AB}$$

The scalar product in the isotropic exchange operator can be expressed by using the shift (step-up and step-down) operators

$$\begin{aligned} \vec{S}_A \cdot \vec{S}_B &= \hat{S}_{Ax} \hat{S}_{Bx} + \hat{S}_{Ay} \hat{S}_{By} + \hat{S}_{Az} \hat{S}_{Bz} \\ &= \frac{1}{2} (\hat{S}_{A,+} \hat{S}_{B,-} + \hat{S}_{A,-} \hat{S}_{B,+}) + \hat{S}_{Az} \hat{S}_{Bz} \end{aligned}$$

They operate on the uncoupled microstates as follows

$$\hat{S}_{A,+} |S_A, M_A\rangle = [(S_A + M_A + 1)(S_A - M_A)]^{1/2} |S_A, M_A + 1\rangle [\hbar]$$

$$\hat{S}_{A,-} |S_A, M_A\rangle = [(S_A - M_A + 1)(S_A + M_A)]^{1/2} |S_A, M_A - 1\rangle [\hbar]$$

$$\hat{S}_{A,z} |S_A, M_A\rangle = M_A |S_A, M_A\rangle [\hbar]$$

and analogously for the centre B . Then

$$\begin{aligned}
 & \hat{S}_{A,+} \hat{S}_{B,-} | \dots S_A, M_A, \dots S_B, M_B, \dots \rangle \\
 &= \hat{S}_{A,+} [(S_B - M_B + 1)(S_B + M_B)]^{1/2} | \dots S_A, M_A, \dots S_B, M_B - 1, \dots \rangle [\hbar] \\
 &= [(S_B - M_B + 1)(S_B + M_B)]^{1/2} \\
 &\quad \times [(S_A + M_A + 1)(S_A - M_A)]^{1/2} \\
 &\quad \times | \dots S_A, M_A + 1, \dots S_B, M_B - 1, \dots \rangle [\hbar^2]
 \end{aligned}$$

and

$$\begin{aligned}
 & \hat{S}_{A,-} \hat{S}_{B,+} | \dots S_A, M_A, \dots S_B, M_B, \dots \rangle \\
 &= \hat{S}_{A,-} [(S_B + M_B + 1)(S_B - M_B)]^{1/2} | \dots S_A, M_A, \dots S_B, M_B + 1, \dots \rangle [\hbar] \\
 &= [(S_B + M_B + 1)(S_B - M_B)]^{1/2} \\
 &\quad \times [(S_A - M_A + 1)(S_A + M_A)]^{1/2} \\
 &\quad \times | \dots S_A, M_A - 1, \dots S_B, M_B + 1, \dots \rangle [\hbar^2]
 \end{aligned}$$

and for the z -components

$$\begin{aligned}
 & \hat{S}_{A,z} \hat{S}_{B,z} | \dots S_A, M_A, \dots S_B, M_B, \dots \rangle \\
 &= M_A M_B | \dots S_A, M_A, \dots S_B, M_B, \dots \rangle [\hbar^2]
 \end{aligned}$$

Thus the diagonal of the interaction matrix is filled by the elements

$$\begin{aligned}
 & \langle \dots S_A, M_A, \dots S_B, M_B, \dots | \hat{S}_{A,z} \hat{S}_{B,z} | \dots S_A, M_A, \dots S_B, M_B, \dots \rangle \\
 &= M_{Az} M_{Bz} \langle \dots S_A, M_A, \dots S_B, M_B, \dots | \dots S_A, M_A, \dots S_B, M_B, \dots \rangle [\hbar^2] \\
 &= M_{Az} M_{Bz} [\hbar^2]
 \end{aligned}$$

whereas the non-zero off-diagonal elements are

$$\begin{aligned}
 & \langle \dots S_A, M'_A, \dots S_B, M'_B, \dots | \hat{S}_{A,+} \hat{S}_{B,-} | \dots S_A, M_A, \dots S_B, M_B, \dots \rangle \\
 &= [(S_B - M_B + 1)(S_B + M_B)]^{1/2} [(S_A + M_A + 1)(S_A - M_A)]^{1/2} \\
 &\quad \times \langle \dots S_A, M'_A, \dots S_B, M'_B, \dots | \dots S_A, M_A + 1, \dots S_B, M_B - 1, \dots \rangle [\hbar^2] \\
 &= [(S_B - M_B + 1)(S_B + M_B)]^{1/2} \\
 &\quad \times [(S_A + M_A + 1)(S_A - M_A)]^{1/2} \delta_{M'_A, M_A+1} \delta_{M'_B, M_B-1} [\hbar^2]
 \end{aligned}$$

and

$$\begin{aligned}
 & \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \hat{S}_{A,-} \hat{S}_{B,+} \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
 &= [(S_B + M_B + 1)(S_B - M_B)]^{1/2} [(S_A - M_A + 1)(S_A + M_A)]^{1/2} \\
 &\quad \times \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \dots S_A, M_A - 1, \dots S_B, M_B + 1, \dots \right\rangle [\hbar^2] \right\rangle \\
 &= [(S_B + M_B + 1)(S_B - M_B)]^{1/2} \\
 &\quad \times [(S_A - M_A + 1)(S_A + M_A)]^{1/2} \delta_{M'_A, M_A - 1} \delta_{M'_B, M_B + 1} [\hbar^2]
 \end{aligned}$$

In order to exemplify the above procedure let us consider the simplest case of the $S_A = S_B = 1/2$ system. Let the members of the basis set be ordered as follows

$$|(S_A, M_A); (S_B, M_B)\rangle = \begin{pmatrix} (1/2, -1/2); (1/2, -1/2) \\ (1/2, -1/2); (1/2, +1/2) \\ (1/2, +1/2); (1/2, -1/2) \\ (1/2, +1/2); (1/2, +1/2) \end{pmatrix}$$

Then the isotropic exchange interaction matrix is

$$\mathbf{H}_{AB}^{\text{iso}} = -J \begin{pmatrix} +1/4 & 0 & 0 & 0 \\ 0 & -1/4 & 1/2 & 0 \\ 0 & 1/2 & -1/4 & 0 \\ 0 & 0 & 0 & +1/4 \end{pmatrix}$$

Its eigenvalues are

$$\varepsilon_1 = +(3/4)J, \quad [\text{once}]$$

$$\varepsilon_{2,3,4} = -(1/4)J, \quad [\text{three times}]$$

Evidently the result is identical to the well-known coupling formula

$$\varepsilon(S) = -\frac{J}{2} [S(S+1) - S_A(S_A+1) - S_B(S_B+1)]$$

For the simplest cluster of $S_A = S_B = S_C = 1/2$ let the members of the basis set be ordered as follows

$$|(S_A, M_A); (S_B, M_B); (S_C, M_C)\rangle = \begin{vmatrix} (1/2, -1/2); (1/2, -1/2); (1/2, -1/2) \\ (1/2, -1/2); (1/2, -1/2); (1/2, +1/2) \\ (1/2, -1/2); (1/2, +1/2); (1/2, -1/2) \\ (1/2, -1/2); (1/2, +1/2); (1/2, +1/2) \\ (1/2, +1/2); (1/2, -1/2); (1/2, -1/2) \\ (1/2, +1/2); (1/2, -1/2); (1/2, +1/2) \\ (1/2, +1/2); (1/2, +1/2); (1/2, -1/2) \\ (1/2, +1/2); (1/2, +1/2); (1/2, +1/2) \end{vmatrix}$$

Then the pair-interaction matrices become (only the upper triangle is displayed because the matrices are symmetric)

$$\mathbf{H}_{AB}^{\text{iso}} = -J_{AB} \begin{pmatrix} +1/4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ & +1/4 & 0 & 0 & 0 & 0 & 0 & 0 \\ & & -1/4 & 0 & 1/2 & 0 & 0 & 0 \\ & & & -1/4 & 0 & 1/2 & 0 & 0 \\ & & & & -1/4 & 0 & 0 & 0 \\ & & & & & -1/4 & 0 & 0 \\ & & & & & & +1/4 & 0 \\ & & & & & & & +1/4 \end{pmatrix}$$

$$\mathbf{H}_{AC}^{\text{iso}} = -J_{AC} \begin{pmatrix} +1/4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ & -1/4 & 0 & 0 & 1/2 & 0 & 0 & 0 \\ & & +1/4 & 0 & 0 & 0 & 0 & 0 \\ & & & -1/4 & 0 & 0 & 1/2 & 0 \\ & & & & -1/4 & 0 & 0 & 0 \\ & & & & & +1/4 & 0 & 0 \\ & & & & & & -1/4 & 0 \\ & & & & & & & +1/4 \end{pmatrix}$$

$$\mathbf{H}_{BC}^{\text{iso}} = -J_{BC} \begin{pmatrix} +1/4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ & -1/4 & 1/2 & 0 & 0 & 0 & 0 & 0 \\ & & -1/4 & 0 & 0 & 0 & 0 & 0 \\ & & & +1/4 & 0 & 0 & 0 & 0 \\ & & & & +1/4 & 0 & 0 & 0 \\ & & & & & -1/4 & 1/2 & 0 \\ & & & & & & -1/4 & 0 \\ & & & & & & & +1/4 \end{pmatrix}$$

The final interaction matrix depends upon the coupling topology:

(a) regular triangle

$$\mathbf{H}^{\text{iso}} = -J(\mathbf{H}_{AB}^{\text{iso}} + \mathbf{H}_{AC}^{\text{iso}} + \mathbf{H}_{BC}^{\text{iso}})$$

(b) equilateral triangle

$$\mathbf{H}^{\text{iso}} = -J'\mathbf{H}_{AC}^{\text{iso}} - J(\mathbf{H}_{AB}^{\text{iso}} + \mathbf{H}_{BC}^{\text{iso}})$$

(c) general triangle

$$\mathbf{H}^{\text{iso}} = -J_{AB}\mathbf{H}_{AB}^{\text{iso}} - J_{AC}\mathbf{H}_{AC}^{\text{iso}} - J_{BC}\mathbf{H}_{BC}^{\text{iso}}$$

(d) a chain A–B–C

$$\mathbf{H}^{\text{iso}} = -J(\mathbf{H}_{AB}^{\text{iso}} + \mathbf{H}_{BC}^{\text{iso}})$$

11.1.1.2 The Zeeman term

The matrix elements of the Zeeman term become expressed as

$$\langle I | \hat{H}^Z | J \rangle = \mu_B \vec{B} \cdot \sum_{A=1}^N g_A \langle I | \vec{S}_A | J \rangle [\hbar^{-1}]$$

where only the local atomic g -tensors occur. Then the following identity is helpful

$$\vec{B} \cdot \vec{S}_A = B_x \hat{S}_{Ax} + B_y \hat{S}_{Ay} + B_z \hat{S}_{Az} = \frac{1}{2} (B_+ \hat{S}_{A,-} + B_- \hat{S}_{A,+}) + B_z \hat{S}_{Az}$$

with the field-shift values

$$B_+ = B_x + iB_y$$

$$B_- = B_x - iB_y$$

Then the spin operators yield

$$\begin{aligned} & \vec{B} \cdot \vec{S}_A | \dots S_A, M_A, \dots \rangle \\ &= \frac{1}{2} B_+ [(S_A - M_A + 1)(S_A + M_A)]^{1/2} | \dots S_A, M_A - 1, \dots \rangle [\hbar] \\ &+ \frac{1}{2} B_- [(S_A + M_A + 1)(S_A - M_A)]^{1/2} | \dots S_A, M_A + 1, \dots \rangle [\hbar] \\ &+ B_z M_A | \dots S_A, M_A, \dots \rangle [\hbar] \end{aligned}$$

and consequently

$$\begin{aligned}
 & \left\langle \dots S_A, M'_A, \dots \left| \vec{B} \cdot \vec{S}_A \right| \dots S_A, M_A, \dots \right\rangle \\
 &= \frac{1}{2} B_+ [(S_A - M_A + 1)(S_A + M_A)]^{1/2} \delta_{M'_A, M_A - 1} [\hbar] \\
 &+ \frac{1}{2} B_- [(S_A + M_A + 1)(S_A - M_A)]^{1/2} \delta_{M'_A, M_A + 1} [\hbar] \\
 &+ B_z M_A \delta_{M'_A, M_A} [\hbar]
 \end{aligned}$$

The overall Zeeman term adopts the form of

$$\begin{aligned}
 \langle I | \hat{H}^Z | J \rangle &= \mu_B \sum_{A=1}^N g_A \left\langle \dots S_A, M'_A, \dots \left| \vec{B} \cdot \vec{S}_A \right| \dots S_A, M_A, \dots \right\rangle [\hbar^{-1}] \\
 &= \mu_B \sum_{A=1}^N g_A \left\{ \frac{1}{2} B_+ [(S_A - M_A + 1)(S_A + M_A)]^{1/2} \delta_{M'_A, M_A - 1} \right. \\
 &\quad + \frac{1}{2} B_- [(S_A + M_A + 1)(S_A - M_A)]^{1/2} \delta_{M'_A, M_A + 1} \\
 &\quad \left. + B_z M_A \delta_{M'_A, M_A} \right\}
 \end{aligned}$$

When the g -tensor components are distinguished, one can use the fact that the scalar product of two vectors can be written in terms of the spherical tensor components, hence

$$\vec{G} \cdot \vec{A} = -\hat{G}_{1,+1} \hat{A}_{1,-1} + \hat{G}_{1,0} \hat{A}_{1,0} - \hat{G}_{1,-1} \hat{A}_{1,+1}$$

Let the vector $\vec{G}$ be defined through

$$\vec{G} = \vec{B} \cdot \vec{g}_A$$

which for the diagonal g -tensor yields

$$\vec{G} = (B_x g_{Ax}; B_y g_{Ay}; B_z g_{Az})$$

Its spherical components are

$$\hat{G}_{1,+1} = -\frac{1}{\sqrt{2}} (B_x g_{Ax} + i B_y g_{Ay})$$

$$\hat{G}_{1,-1} = \frac{1}{\sqrt{2}} (B_x g_{Ax} - i B_y g_{Ay})$$

$$\hat{G}_{1,0} = B_z g_{Az}$$

and thus

$$\begin{aligned}\vec{G} \cdot \vec{S}_A &= \frac{1}{\sqrt{2}}(B_x g_{Ax} + iB_y g_{Ay})\hat{S}_{A1,-1} + B_z g_{Az}\hat{S}_{A1,0} \\ &\quad - \frac{1}{\sqrt{2}}(B_x g_{Ax} - iB_y g_{Ay})\hat{S}_{A1,+1}\end{aligned}$$

Now the Wigner–Eckart theorem, applied to the spherical tensor operators, implies

$$\begin{aligned}&\langle \dots S_A, M'_A, \dots | \vec{G} \cdot \vec{S}_A | \dots S_A, M_A, \dots \rangle \\ &= \frac{1}{\sqrt{2}}(B_x g_{Ax} + iB_y g_{Ay})(-1)^{S_A-M'_A} \begin{pmatrix} S_A & 1 & S_A \\ -M'_A & -1 & M_A \end{pmatrix} \langle S_A \| \vec{S}_A \| S_A \rangle \\ &\quad + B_z g_{Az}(-1)^{S_A-M'_A} \begin{pmatrix} S_A & 1 & S_A \\ -M'_A & 0 & M_A \end{pmatrix} \langle S_A \| \vec{S}_A \| S_A \rangle \\ &\quad - \frac{1}{\sqrt{2}}(B_x g_{Ax} - iB_y g_{Ay})(-1)^{S_A-M'_A} \begin{pmatrix} S_A & 1 & S_A \\ -M'_A & +1 & M_A \end{pmatrix} \langle S_A \| \vec{S}_A \| S_A \rangle\end{aligned}$$

The reduced matrix element is simply

$$\langle S_A \| \vec{S}_A \| S_A \rangle = [S_A(S_A + 1)(2S_A + 1)]^{1/2}[\hbar]$$

and the 3j-symbols are expressed according to the special formulae

$$\begin{aligned}\begin{pmatrix} S_A & 1 & S_A \\ -(M_A - 1) & -1 & M_A \end{pmatrix} &= (-1)^{M_A - S_A + 1} \left[\frac{(S_A - M_A + 1)(S_A + M_A)}{2S_A(S_A + 1)(2S_A + 1)} \right]^{1/2} \\ \begin{pmatrix} S_A & 1 & S_A \\ -M_A & 0 & M_A \end{pmatrix} &= (-1)^{M_A - S_A} M_A \left[\frac{1}{S_A(S_A + 1)(2S_A + 1)} \right]^{1/2} \\ \begin{pmatrix} S_A & 1 & S_A \\ -(M_A + 1) & +1 & M_A \end{pmatrix} &= (-1)^{M_A - S_A} \left[\frac{(S_A + M_A + 1)(S_A - M_A)}{2S_A(S_A + 1)(2S_A + 1)} \right]^{1/2}\end{aligned}$$

Finally one gets the result

$$\begin{aligned}&\langle \dots S_A, M'_A, \dots | \vec{B} \cdot \vec{g}_A \cdot \vec{S}_A | \dots S_A, M_A, \dots \rangle \\ &= \frac{1}{2}(B_x g_{Ax} + iB_y g_{Ay})[(S_A - M_A + 1)(S_A + M_A)]^{1/2} \delta_{M'_A, M_A - 1}[\hbar] \\ &\quad + B_z g_{Az} M_A \delta_{M'_A, M_A}[\hbar] \\ &\quad + \frac{1}{2}(B_x g_{Ax} - iB_y g_{Ay})[(S_A + M_A + 1)(S_A - M_A)]^{1/2} \delta_{M'_A, M_A + 1}[\hbar]\end{aligned}$$

For the $S_A = S_B = 1/2$ dimer the Zeeman matrix in the basis set of local (uncoupled) functions is

$$\mathbf{H}^Z/\mu_B = \begin{pmatrix} (-g_{Az} - g_{Bz})B_z/2 & (g_{Bx}B_x + ig_{By}B_y)/2 & (g_{Ax}B_x + ig_{Ay}B_y)/2 & 0 \\ & (-g_{Az} + g_{Bz})B_z/2 & 0 & (g_{Ax}B_x + ig_{Ay}B_y)/2 \\ & & (g_{Az} - g_{Bz})B_z/2 & (g_{Bx}B_x + ig_{By}B_y)/2 \\ & & & (g_{Az} + g_{Bz})B_z/2 \end{pmatrix}$$

where only the upper triangle of the Hermitian matrix is displayed.

For the simplest cluster of $S_A = S_B = S_C = 1/2$ the above procedure yields

$$\mathbf{H}^Z/\mu_B = \begin{pmatrix} (-g_{Az} - g_{Bz} - g_{Cz})B_z/2 & C & B & 0 \\ c & (-g_{Az} - g_{Bz} + g_{Cz})B_z/2 & 0 & B \\ b & 0 & (-g_{Az} + g_{Bz} - g_{Cz})B_z/2 & C \\ 0 & b & c & (-g_{Az} + g_{Bz} + g_{Cz})B_z/2 \\ a & 0 & 0 & 0 \\ 0 & a & 0 & 0 \\ 0 & 0 & a & 0 \\ 0 & 0 & 0 & a \\ A & 0 & 0 & 0 \\ 0 & A & 0 & 0 \\ 0 & 0 & A & 0 \\ 0 & 0 & 0 & A \\ (g_{Az} - g_{Bz} - g_{Cz})B_z/2 & C & B & 0 \\ c & (g_{Az} - g_{Bz} + g_{Cz})B_z/2 & 0 & B \\ b & 0 & (g_{Az} + g_{Bz} - g_{Cz})B_z/2 & C \\ 0 & b & c & (g_{Az} + g_{Bz} + g_{Cz})B_z/2 \end{pmatrix}$$

where the following substitutions have been used

$$A = (g_{Ax}B_x + ig_{Ay}B_y)/2$$

$$B = (g_{Bx}B_x + ig_{By}B_y)/2$$

$$C = (g_{Cx}B_x + ig_{Cy}B_y)/2$$

$$a = (g_{Ax}B_x - ig_{Ay}B_y)/2$$

$$b = (g_{Bx}B_x - ig_{By}B_y)/2$$

$$c = (g_{Cx}B_x - ig_{Cy}B_y)/2$$

In the case of isotropic exchange one can handle only the z-component of the Zeeman term; the corresponding matrix is diagonal.

The coupling of the local microstates into the proper molecular states is provided by the diagonalisation of the spin Hamiltonian matrix. For the zero-field case the diagonalisation matrix represents an orthogonal transformation and its matrix elements relate to the combination of the Clebsch–Gordan coefficients.

11.1.1.3 Asymmetric exchange

Assuming a diagonal and traceless form of the D -tensors, the scalar product is expanded as follows (see Section 10.3.1)

$$\vec{S}_A \cdot \vec{D}_{AB} \cdot \vec{S}_B = \frac{D}{3}(3\hat{S}_{Az}\hat{S}_{Bz} - \vec{S}_A \cdot \vec{S}_B) + E(\hat{S}_{Ax}\hat{S}_{Bx} - \hat{S}_{Ay}\hat{S}_{By})$$

The compound spherical tensors are constituted in the following way (Table 1.14)

$$\begin{aligned} 3\hat{S}_{Az}\hat{S}_{Bz} - \vec{S}_A \cdot \vec{S}_B &= 3\hat{S}_{A1,0}\hat{S}_{B1,0} - (\vec{S}_A \cdot \vec{S}_B) \\ \hat{S}_{Ax}\hat{S}_{Bx} - \hat{S}_{Ay}\hat{S}_{By} &= \hat{S}_{A1,-1}\hat{S}_{B1,-1} + \hat{S}_{A1,+1}\hat{S}_{B1,+1} \end{aligned}$$

The scalar product is given through the spherical components as

$$\vec{S}_A \cdot \vec{S}_B = -\hat{S}_{A1,+1}\hat{S}_{B1,-1} + \hat{S}_{A1,0}\hat{S}_{B1,0} - \hat{S}_{A1,-1}\hat{S}_{B1,+1}$$

and it has the following matrix elements

$$\begin{aligned} &\left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \vec{S}_A \cdot \vec{S}_B \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\ &= -\left\langle S_A, M'_A \left| \hat{S}_{A1,+1} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,-1} \right| S_B, M_B \right\rangle \\ &\quad + \left\langle S_A, M'_A \left| \hat{S}_{A1,0} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,0} \right| S_B, M_B \right\rangle \\ &\quad - \left\langle S_A, M'_A \left| \hat{S}_{A1,-1} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,+1} \right| S_B, M_B \right\rangle \end{aligned}$$

Using the Wigner–Eckart theorem, we get

$$\begin{aligned} &\left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \vec{S}_A \cdot \vec{S}_B \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\ &= -\left[(-1)^{S_A-M'_A} \begin{pmatrix} S_A & 1 & S_A \\ M'_A & +1 & M_A \end{pmatrix} \left\langle S_A \left\| \vec{S}_A \right\| S_A \right\rangle \right] \\ &\quad \left[(-1)^{S_B-M'_B} \begin{pmatrix} S_B & 1 & S_B \\ M'_B & -1 & M_B \end{pmatrix} \left\langle S_B \left\| \vec{S}_B \right\| S_B \right\rangle \right] \end{aligned}$$

$$\begin{aligned}
& + \left[(-1)^{S_A - M'_A} \begin{pmatrix} S_A & 1 & S_A \\ M'_A & 0 & M_A \end{pmatrix} \langle S_A \| \vec{S}_A \| S_A \rangle \right] \\
& \left[(-1)^{S_B - M'_B} \begin{pmatrix} S_B & 1 & S_B \\ M'_B & 0 & M_B \end{pmatrix} \langle S_B \| \vec{S}_B \| S_B \rangle \right] \\
& - \left[(-1)^{S_A - M'_A} \begin{pmatrix} S_A & 1 & S_A \\ M'_A & -1 & M_A \end{pmatrix} \langle S_A \| \vec{S}_A \| S_A \rangle \right] \\
& \left[(-1)^{S_B - M'_B} \begin{pmatrix} S_B & 1 & S_B \\ M'_B & +1 & M_B \end{pmatrix} \langle S_B \| \vec{S}_B \| S_B \rangle \right]
\end{aligned}$$

and with the special formulae for $3j$ -symbols and the expressions for reduced matrix elements one gets

$$\begin{aligned}
& \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \vec{S}_A \cdot \vec{S}_B \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
& = \delta_{M'_A, M_A + 1} \sqrt{\frac{(S_A + M_A + 1)(S_A - M_A)}{2}} \\
& \quad \times \delta_{M'_B, M_B - 1} \sqrt{\frac{(S_B - M_B + 1)(S_B + M_B)}{2}} [\hbar^2] + \delta_{M'_A, M_A} \delta_{M'_B, M_B} M_A M_B [\hbar^2] \\
& \quad + \delta_{M'_A, M_A - 1} \sqrt{\frac{(S_A - M_A + 1)(S_A + M_A)}{2}} \\
& \quad \times \delta_{M'_B, M_B + 1} \sqrt{\frac{(S_B + M_B + 1)(S_B - M_B)}{2}} [\hbar^2]
\end{aligned}$$

which is a result identical to that obtained for isotropic exchange. Now the matrix elements of the axial zero-field splitting become

$$\begin{aligned}
& \frac{D}{3} \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| 3\hat{S}_{A1,0}\hat{S}_{B1,0} - (\vec{S}_A \cdot \vec{S}_B) \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle [\hbar^{-2}] = \frac{D}{3} [\delta_{M'_A, M_A} \delta_{M'_B, M_B} 2M_A M_B \\
& - \delta_{M'_A, M_A + 1} \delta_{M'_B, M_B - 1} \frac{1}{2} \sqrt{(S_A + M_A + 1)(S_A - M_A)} \\
& \quad \times \sqrt{(S_B - M_B + 1)(S_B + M_B)} - \delta_{M'_A, M_A - 1} \delta_{M'_B, M_B + 1} \frac{1}{2} \\
& \quad \times \sqrt{(S_A - M_A + 1)(S_A + M_A)} \sqrt{(S_B + M_B + 1)(S_B - M_B)}]
\end{aligned}$$

The matrix elements of the second term become

$$\begin{aligned}
 & \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \hat{S}_{A1,-1} \hat{S}_{B1,-1} + \hat{S}_{A1,+1} \hat{S}_{B1,+1} \right| \right. \\
 & \quad \left. \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
 &= \left\langle S_A, M'_A \left| \hat{S}_{A1,-1} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,-1} \right| S_B, M_B \right\rangle \\
 & \quad + \left\langle S_A, M'_A \left| \hat{S}_{A1,+1} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,+1} \right| S_B, M_B \right\rangle
 \end{aligned}$$

and then

$$\begin{aligned}
 & \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \hat{S}_{A1,-1} \hat{S}_{B1,-1} + \hat{S}_{A1,+1} \hat{S}_{B1,+1} \right| \right. \\
 & \quad \left. \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
 &= \left[(-1)^{S_A - M'_A} \begin{pmatrix} S_A & 1 & S_A \\ M'_A & -1 & M_A \end{pmatrix} \langle S_A \| \vec{S}_A \| S_A \rangle \right] \\
 & \quad \left[(-1)^{S_B - M'_B} \begin{pmatrix} S_B & 1 & S_B \\ M'_B & -1 & M_B \end{pmatrix} \langle S_B \| \vec{S}_B \| S_B \rangle \right] \\
 & \quad + \left[(-1)^{S_A - M'_A} \begin{pmatrix} S_A & 1 & S_A \\ M'_A & +1 & M_A \end{pmatrix} \langle S_A \| \vec{S}_A \| S_A \rangle \right] \\
 & \quad \left[(-1)^{S_B - M'_B} \begin{pmatrix} S_B & 1 & S_B \\ M'_B & +1 & M_B \end{pmatrix} \langle S_B \| \vec{S}_B \| S_B \rangle \right]
 \end{aligned}$$

yielding finally the rhombic zero-field splitting elements

$$\begin{aligned}
 & E \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \hat{S}_{A1,-1} \hat{S}_{B1,-1} + \hat{S}_{A1,+1} \hat{S}_{B1,+1} \right| \right. \\
 & \quad \left. \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle [\hbar^{-2}] = E[\delta_{M'_A, M_A-1} \delta_{M'_B, M_B-1}] \frac{1}{2} \\
 & \quad \times \sqrt{(S_A - M_A + 1)(S_A + M_A)} \sqrt{(S_B - M_B + 1)(S_B + M_B)} \\
 & \quad + \delta_{M'_A, M_A+1} \delta_{M'_B, M_B+1} \frac{1}{2} \sqrt{(S_A + M_A + 1)(S_A - M_A)} \\
 & \quad \times \sqrt{(S_B + M_B + 1)(S_B - M_B)}
 \end{aligned}$$

The expressions for the matrix elements of the exchange interaction operators in the uncoupled basis set are collected in Table 11.1.

For the $S_A = S_B = 1/2$ dimer the matrix elements of the asymmetric exchange are

$$\mathbf{H}_{AB}^{\text{asym}} = \begin{pmatrix} (+1/2)(D/3) & 0 & 0 & (+1/2)E \\ 0 & (-1/2)(D/3) & (+1/2)(D/3) & 0 \\ 0 & (+1/2)(D/3) & (-1/2)(D/3) & 0 \\ (+1/2)E & 0 & 0 & (+1/2)(D/3) \end{pmatrix}$$

where the axial and the rhombic zero-field splitting parameters relate to the pair-interaction D -tensor

$$D = \frac{3}{2}(D_{AB})_{zz}$$

$$E = \frac{1}{2}[(D_{AB})_{xx} - (D_{AB})_{yy}]$$

since the local D -tensors, $\bar{D}_A$ and $\bar{D}_B$, vanish for the $S_A = S_B = 1/2$ system.

11.1.1.4 Antisymmetric exchange

The operator of the antisymmetric exchange

$$\hat{H}^{\text{anti}} = \vec{d}_{AB} \cdot \vec{A}$$

with

$$\vec{A} = (\vec{S}_A \times \vec{S}_B)[\hbar^{-2}]$$

can be written over the spherical components as

$$\hat{H}^{\text{anti}} = -d_{(AB)1,+1}\hat{A}_{1,-1} + d_{(AB)1,0}\hat{A}_{1,0} - d_{(AB)1,-1}\hat{A}_{1,+1}$$

Here the spherical components are expressed through the Cartesian ones

$$d_{(AB)1,+1} = -\frac{1}{\sqrt{2}}(d_{(AB)x} + id_{(AB)y})$$

$$d_{(AB)1,-1} = \frac{1}{\sqrt{2}}(d_{(AB)x} - id_{(AB)y})$$

$$d_{(AB)1,0} = d_{(AB)z}$$

TABLE 11.1
Matrix elements in the local basis set

Operator	$\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \hat{O} \dots S_A, M_A, \dots S_B, M_B, \dots \rangle$
$-J_{AB}(\vec{S}_A \cdot \vec{S}_B)[\hbar^{-2}]$	$ \begin{aligned} & -J_{AB}\{\delta_{M'_A, M_A}\delta_{M'_B, M_B}M_AM_B \\ & + \delta_{M'_A, M_A+1}\delta_{M'_B, M_B-1}\frac{1}{2}\sqrt{(S_A+M_A+1)(S_A-M_A)}\sqrt{(S_B-M_B+1)(S_B+M_B)} \\ & + \delta_{M'_A, M_A-1}\delta_{M'_B, M_B+1}\frac{1}{2}\sqrt{(S_A-M_A+1)(S_A+M_A)}\sqrt{(S_B+M_B+1)(S_B-M_B)}\} \end{aligned} $
$(D_{AB}/3)[3\hat{S}_{A1,0}\hat{S}_{B1,0} - (\vec{S}_A \cdot \vec{S}_B)][\hbar^{-2}]$	$ \begin{aligned} & (D_{AB}/3)\{\delta_{M'_A, M_A}\delta_{M'_B, M_B}2M_AM_B \\ & - \delta_{M'_A, M_A+1}\delta_{M'_B, M_B-1}\frac{1}{2}\sqrt{(S_A+M_A+1)(S_A-M_A)}\sqrt{(S_B-M_B+1)(S_B+M_B)} \\ & - \delta_{M'_A, M_A-1}\delta_{M'_B, M_B+1}\frac{1}{2}\sqrt{(S_A-M_A+1)(S_A+M_A)}\sqrt{(S_B+M_B+1)(S_B-M_B)}\} \end{aligned} $
$E_{AB}(\hat{S}_{A1,-1}\hat{S}_{B1,-1} + \hat{S}_{A1,+1}\hat{S}_{B1,+1})[\hbar^{-2}]$	$ \begin{aligned} & E_{AB}\{\delta_{M'_A, M_A-1}\delta_{M'_B, M_B-1}\frac{1}{2}\sqrt{(S_A-M_A+1)(S_A+M_A)}\sqrt{(S_B-M_B+1)(S_B+M_B)} \\ & + \delta_{M'_A, M_A+1}\delta_{M'_B, M_B+1}\frac{1}{2}\sqrt{(S_A+M_A+1)(S_A-M_A)}\sqrt{(S_B+M_B+1)(S_B-M_B)}\} \end{aligned} $
$\mu_B(\vec{B} \cdot \vec{g}_A \cdot \vec{S}_A)[\hbar^{-1}]$	$ \begin{aligned} & \mu_B\{\delta_{M'_A, M_A}B_zg_{Az}M_A \\ & + \delta_{M'_A, M_A-1}\frac{1}{2}(B_xg_{Ax} + iB_yg_{Ay})\sqrt{(S_A-M_A+1)(S_A+M_A)} \\ & + \delta_{M'_A, M_A+1}\frac{1}{2}(B_xg_{Ax} - iB_yg_{Ay})\sqrt{(S_A+M_A+1)(S_A-M_A)}\} \end{aligned} $

$$\vec{d}_{AB} \cdot (\vec{S}_A \times \vec{S}_B) [\hbar^{-2}]$$

$$\begin{aligned} & -i\frac{1}{2}\{[(d_{(AB)x} + id_{(AB)y})][\delta_{M'_A, M_A} \delta_{M'_B, M_B-1} M_A \sqrt{(S_B - M_B + 1)(S_B + M_B)} \\ & - \delta_{M'_A, M_A-1} \delta_{M'_B, M_B} \sqrt{(S_A - M_A + 1)(S_A + M_A) M_B}] \\ & + d_{(AB)z} [\delta_{M'_A, M_A+1} \delta_{M'_B, M_B-1} \sqrt{(S_A + M_A + 1)(S_A - M_A)} \sqrt{(S_B - M_B + 1)(S_B + M_B)} \\ & - \delta_{M'_A, M_A-1} \delta_{M'_B, M_B+1} \sqrt{(S_A - M_A + 1)(S_A + M_A)} \sqrt{(S_B + M_B + 1)(S_B - M_B)}] \\ & - (d_{(AB)x} - id_{(AB)y}) [\delta_{M'_A, M_A+1} \delta_{M'_B, M_B} \sqrt{(S_A + M_A + 1)(S_A - M_A) M_B} \\ & - \delta_{M'_A, M_A} \delta_{M'_B, M_B+1} M_A \sqrt{(S_B + M_B + 1)(S_B - M_B)}]\} \end{aligned}$$

$$-j_{AB} (\vec{S}_A \cdot \vec{S}_B)^2 [\hbar^{-4}]$$

$$\begin{aligned} & -j_{AB} \{ \delta_{M'_A, M_A+2} \delta_{M'_B, M_B-2} \frac{1}{4} [(S_A + M_A + 1)(S_A + M_A + 2)(S_A - M_A - 1)(S_A - M_A) \\ & \times (S_B - M_B + 1)(S_B - M_B + 2)(S_B + M_B - 1)(S_B + M_B)]^{1/2} \\ & - \delta_{M'_A, M_A+1} \delta_{M'_B, M_B-1} \frac{1}{4} (1 + 2M_A)(1 - 2M_B) \\ & \times [(S_A + M_A + 1)(S_A - M_A)(S_B - M_B + 1)(S_B + M_B)]^{1/2} \\ & + \delta_{M'_A, M_A} \delta_{M'_B, M_B} \frac{1}{6} [3M_A^2 - S_A(S_A + 1)][3M_B^2 - S_B(S_B + 1)] \\ & - \delta_{M'_A, M_A-1} \delta_{M'_B, M_B+1} \frac{1}{4} (1 - 2M_A)(1 + 2M_B) \\ & \times [(S_A - M_A + 1)(S_A + M_A)(S_B + M_B + 1)(S_B - M_B)]^{1/2} \\ & + \delta_{M'_A, M_A-2} \delta_{M'_B, M_B+2} \\ & \times \frac{1}{4} [(S_A - M_A + 1)(S_A - M_A + 2)(S_A + M_A - 1)(S_A + M_A) \\ & \times (S_B + M_B + 1)(S_B + M_B + 2)(S_B - M_B - 1)(S_B - M_B)]^{1/2} \\ & + \delta_{M_A, M'_A} \delta_{M_B, M'_B} \frac{1}{3} S_A(S_A + 1) S_B(S_B + 1) \} \end{aligned}$$

The cross-product can be expressed with the help of the first-order tensor product

$$\hat{A}_{1,q} = (\vec{S}_A \times \vec{S}_B)_q [\hbar^{-2}] = -i\sqrt{2} \left\{ \hat{T}_{1,q} (\vec{S}_A \otimes \vec{S}_B) \right\} [\hbar^{-2}]$$

for $q = 0, \pm 1$ and the compound tensor operator is formed from the spin operators as follows

$$\left\{ \hat{T}_{1,-1} (\vec{S}_A \otimes \vec{S}_B) \right\} = \frac{1}{\sqrt{2}} (\hat{S}_{A1,0} \hat{S}_{B1,-1} - \hat{S}_{A1,-1} \hat{S}_{B1,0})$$

$$\left\{ \hat{T}_{1,0} (\vec{S}_A \otimes \vec{S}_B) \right\} = \frac{1}{\sqrt{2}} (\hat{S}_{A1,+1} \hat{S}_{B1,-1} - \hat{S}_{A1,-1} \hat{S}_{B1,+1})$$

$$\left\{ \hat{T}_{1,+1} (\vec{S}_A \otimes \vec{S}_B) \right\} = \frac{1}{\sqrt{2}} (\hat{S}_{A1,+1} \hat{S}_{B1,0} - \hat{S}_{A1,0} \hat{S}_{B1,+1})$$

Therefore the following identity is fulfilled

$$\begin{aligned} \hat{H}^{\text{anti}} &= \left[\frac{1}{\sqrt{2}} (d_{(AB)x} + i d_{(AB)y}) \right] \hat{A}_{1,-1} + d_{(AB)z} \hat{A}_{1,0} \\ &\quad - \left[\frac{1}{\sqrt{2}} (d_{(AB)x} - i d_{(AB)y}) \right] \hat{A}_{1,+1} \\ &= -i\sqrt{2} \left\{ \left[\frac{1}{\sqrt{2}} (d_{(AB)x} + i d_{(AB)y}) \right] \left[\frac{1}{\sqrt{2}} (\hat{S}_{A1,0} \hat{S}_{B1,-1} - \hat{S}_{A1,-1} \hat{S}_{B1,0}) \right] \right. \\ &\quad \left. + d_{(AB)z} \left[\frac{1}{\sqrt{2}} (\hat{S}_{A1,+1} \hat{S}_{B1,-1} - \hat{S}_{A1,-1} \hat{S}_{B1,+1}) \right] \right. \\ &\quad \left. - \left[\frac{1}{\sqrt{2}} (d_{(AB)x} - i d_{(AB)y}) \right] \left[\frac{1}{\sqrt{2}} (\hat{S}_{A1,+1} \hat{S}_{B1,0} - \hat{S}_{A1,0} \hat{S}_{B1,+1}) \right] \right\} [\hbar^{-2}] \end{aligned}$$

and the matrix elements of the antisymmetric exchange operator become

$$\begin{aligned}
& \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \hat{H}^{\text{anti}} \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
&= -i \left\{ \frac{1}{\sqrt{2}} (d_{(AB)x} + i d_{(AB)y}) \left[\left\langle S_A, M'_A \left| \hat{S}_{A1,0} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,-1} \right| S_B, M_B \right\rangle \right. \right. \\
&\quad \left. \left. - \left\langle S_A, M'_A \left| \hat{S}_{A1,-1} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,0} \right| S_B, M_B \right\rangle \right] \right. \\
&\quad + d_{(AB)z} \left[\left\langle S_A, M'_A \left| \hat{S}_{A1,+1} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,-1} \right| S_B, M_B \right\rangle \right. \\
&\quad \left. \left. - \left\langle S_A, M'_A \left| \hat{S}_{A1,-1} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,+1} \right| S_B, M_B \right\rangle \right] \\
&\quad \left. - \frac{1}{\sqrt{2}} (d_{(AB)x} - i d_{(AB)y}) \left[\left\langle S_A, M'_A \left| \hat{S}_{A1,+1} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,0} \right| S_B, M_B \right\rangle \right. \right. \\
&\quad \left. \left. - \left\langle S_A, M'_A \left| \hat{S}_{A1,0} \right| S_A, M_A \right\rangle \left\langle S_B, M'_B \left| \hat{S}_{B1,+1} \right| S_B, M_B \right\rangle \right] \right\} [\hbar^{-2}]
\end{aligned}$$

Now, the application of the Wigner–Eckart theorem, special formulae for the $3j$ -symbols and the formulae for the reduced matrix elements finally yields

$$\begin{aligned}
& \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \hat{H}^{\text{anti}} \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
&= -i \frac{1}{2} \left\{ (d_{(AB)x} + i d_{(AB)y}) [\delta_{M'_A, M_A} \delta_{M'_B, M_B-1} M_A \sqrt{(S_B - M_B + 1)(S_B + M_B)} \right. \\
&\quad \left. - \delta_{M'_A, M_A-1} \delta_{M'_B, M_B} \sqrt{(S_A - M_A + 1)(S_A + M_A) M_B}] \right. \\
&\quad + d_{(AB)z} [\delta_{M'_A, M_A+1} \delta_{M'_B, M_B-1} \sqrt{(S_A + M_A + 1)(S_A - M_A)} \\
&\quad \times \sqrt{(S_B - M_B + 1)(S_B + M_B)} - \delta_{M'_A, M_A-1} \delta_{M'_B, M_B+1} \\
&\quad \times \sqrt{(S_A - M_A + 1)(S_A + M_A)} \sqrt{(S_B + M_B + 1)(S_B - M_B)}] \\
&\quad \left. - (d_{(AB)x} - i d_{(AB)y}) [\delta_{M'_A, M_A+1} \delta_{M'_B, M_B} \sqrt{(S_A + M_A + 1)(S_A - M_A) M_B} \right. \\
&\quad \left. - \delta_{M'_A, M_A} \delta_{M'_B, M_B+1} M_A \sqrt{(S_B + M_B + 1)(S_B - M_B)}] \right\}
\end{aligned}$$

11.1.1.5 Biquadratic exchange

The operator of the biquadratic exchange contains the scalar product

$$\hat{H}^{\text{bq}} = -j(\vec{S}_A \cdot \vec{S}_B)^2 [\hbar^{-4}]$$

which can be expanded over the spherical tensor components as follows

$$\begin{aligned}
(\vec{S}_A \cdot \vec{S}_B)^2 &= (-\hat{S}_{A1,+1}\hat{S}_{B1,-1} + \hat{S}_{A1,0}\hat{S}_{B1,0} - \hat{S}_{A1,-1}\hat{S}_{B1,+1}) \\
&\quad (-\hat{S}_{A1,+1}\hat{S}_{B1,-1} + \hat{S}_{A1,0}\hat{S}_{B1,0} - \hat{S}_{A1,-1}\hat{S}_{B1,+1}) \\
&= \hat{S}_{A1,+1}\hat{S}_{B1,-1}\hat{S}_{A1,+1}\hat{S}_{B1,-1} - \hat{S}_{A1,0}\hat{S}_{B1,0}\hat{S}_{A1,+1}\hat{S}_{B1,-1} \\
&\quad + \hat{S}_{A1,-1}\hat{S}_{B1,+1}\hat{S}_{A1,+1}\hat{S}_{B1,-1} - \hat{S}_{A1,+1}\hat{S}_{B1,-1}\hat{S}_{A1,0}\hat{S}_{B1,0} \\
&\quad + \hat{S}_{A1,0}\hat{S}_{B1,0}\hat{S}_{A1,0}\hat{S}_{B1,0} - \hat{S}_{A1,-1}\hat{S}_{B1,+1}\hat{S}_{A1,0}\hat{S}_{B1,0} \\
&\quad + \hat{S}_{A1,+1}\hat{S}_{B1,-1}\hat{S}_{A1,-1}\hat{S}_{B1,+1} - \hat{S}_{A1,0}\hat{S}_{B1,0}\hat{S}_{A1,-1}\hat{S}_{B1,+1} \\
&\quad + \hat{S}_{A1,-1}\hat{S}_{B1,+1}\hat{S}_{A1,-1}\hat{S}_{B1,+1}
\end{aligned}$$

We have seen in Section 10.4.1 that the equivalent form is

$$\begin{aligned}
(\vec{S}_A \cdot \vec{S}_B)^2 &= \sqrt{5} \left\{ \hat{T}_0[\hat{T}_2(\vec{S}_A) \otimes \hat{T}_2(\vec{S}_B)] \right\} + \frac{1}{3}(\vec{S}_A \cdot \vec{S}_A)(\vec{S}_B \cdot \vec{S}_B) \\
&= \hat{T}_{2,+2}(\vec{S}_A)\hat{T}_{2,-2}(\vec{S}_B) - \hat{T}_{2,+1}(\vec{S}_A)\hat{T}_{2,-1}(\vec{S}_B) \\
&\quad + \hat{T}_{2,0}(\vec{S}_A)\hat{T}_{2,0}(\vec{S}_B) - \hat{T}_{2,-1}(\vec{S}_A)\hat{T}_{2,+1}(\vec{S}_B) \\
&\quad + \hat{T}_{2,-2}(\vec{S}_A)\hat{T}_{2,+2}(\vec{S}_B) + \frac{1}{3}(\vec{S}_A \cdot \vec{S}_A)(\vec{S}_B \cdot \vec{S}_B) \\
&= T_{AB} + \frac{1}{3}(\vec{S}_A \cdot \vec{S}_A)(\vec{S}_B \cdot \vec{S}_B)
\end{aligned}$$

The first term has the following matrix elements

$$\begin{aligned}
T_{AB} &= \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \begin{array}{c} \hat{T}_{2,+2}(\vec{S}_A)\hat{T}_{2,-2}(\vec{S}_B) \\ -\hat{T}_{2,+1}(\vec{S}_A)\hat{T}_{2,-1}(\vec{S}_B) \\ +\hat{T}_{2,0}(\vec{S}_A)\hat{T}_{2,0}(\vec{S}_B) \\ -\hat{T}_{2,-1}(\vec{S}_A)\hat{T}_{2,+1}(\vec{S}_B) \\ +\hat{T}_{2,-2}(\vec{S}_A)\hat{T}_{2,+2}(\vec{S}_B) \end{array} \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
&= \left\langle S_A \parallel \vec{S}_A^2 \parallel S_A \right\rangle \left\langle S_B \parallel \vec{S}_B^2 \parallel S_B \right\rangle \\
&\quad \times \left[(-1)^{S_A-M'_A} \begin{pmatrix} S_A & 2 & S_A \\ M'_A & +2 & M_A \end{pmatrix} (-1)^{S_B-M'_B} \begin{pmatrix} S_B & 2 & S_B \\ M'_B & -2 & M_B \end{pmatrix} \right. \\
&\quad - (-1)^{S_A-M'_A} \begin{pmatrix} S_A & 2 & S_A \\ M'_A & +1 & M_A \end{pmatrix} (-1)^{S_B-M'_B} \begin{pmatrix} S_B & 2 & S_B \\ M'_B & -1 & M_B \end{pmatrix} \\
&\quad + (-1)^{S_A-M'_A} \begin{pmatrix} S_A & 2 & S_A \\ M'_A & 0 & M_A \end{pmatrix} (-1)^{S_B-M'_B} \begin{pmatrix} S_B & 2 & S_B \\ M'_B & 0 & M_B \end{pmatrix} \\
&\quad - (-1)^{S_A-M'_A} \begin{pmatrix} S_A & 2 & S_A \\ M'_A & -1 & M_A \end{pmatrix} (-1)^{S_B-M'_B} \begin{pmatrix} S_B & 2 & S_B \\ M'_B & +1 & M_B \end{pmatrix} \\
&\quad \left. + (-1)^{S_A-M'_A} \begin{pmatrix} S_A & 2 & S_A \\ M'_A & -2 & M_A \end{pmatrix} (-1)^{S_B-M'_B} \begin{pmatrix} S_B & 2 & S_B \\ M'_B & +2 & M_B \end{pmatrix} \right]
\end{aligned}$$

Now, the special formulae for the $3j$ -symbols and the reduced matrix elements yield

$$\begin{aligned} \langle S \| \tilde{S}^2 \| S \rangle \begin{pmatrix} S & 2 & S \\ -(M-2) & -2 & M \end{pmatrix} \\ = (-1)^{S-M} \frac{1}{2} [(S-M+1)(S-M+2)(S+M-1)(S+M)]^{1/2} [\hbar^2] \end{aligned}$$

$$\begin{aligned} \langle S \| \tilde{S}^2 \| S \rangle \begin{pmatrix} S & 2 & S \\ -(M+2) & +2 & M \end{pmatrix} \\ = (-1)^{S-M} \frac{1}{2} [(S+M+1)(S+M+2)(S-M-1)(S-M)]^{1/2} [\hbar^2] \end{aligned}$$

$$\begin{aligned} \langle S \| \tilde{S}^2 \| S \rangle \begin{pmatrix} S & 2 & S \\ -(M-1) & -1 & M \end{pmatrix} \\ = (-1)^{S-M} \frac{1}{2} (1-2M) [(S-M+1)(S+M)]^{1/2} [\hbar^2] \end{aligned}$$

$$\begin{aligned} \langle S \| \tilde{S}^2 \| S \rangle \begin{pmatrix} S & 2 & S \\ -(M+1) & +1 & M \end{pmatrix} \\ = (-1)^{S-M} \frac{1}{2} (1+2M) [(S+M+1)(S-M)]^{1/2} [\hbar^2] \end{aligned}$$

$$\langle S \| \tilde{S}^2 \| S \rangle \begin{pmatrix} S & 2 & S \\ -(M) & 0 & M \end{pmatrix} = (-1)^{S-M} \frac{1}{\sqrt{6}} [3M^2 - S(S+1)] \hbar^2$$

Then

$$\begin{aligned} T_{AB} = & \{ \delta_{M'_A, M_A+2} \delta_{M'_B, M_B-2} \\ & \times \frac{1}{4} [(S_A + M_A + 1)(S_A + M_A + 2)(S_A - M_A - 1)(S_A - M_A) \\ & \times (S_B - M_B + 1)(S_B - M_B + 2)(S_B + M_B - 1)(S_B + M_B)]^{1/2} \\ & - \delta_{M'_A, M_A+1} \delta_{M'_B, M_B-1} \frac{1}{4} (1 + 2M_A)(1 - 2M_B) \\ & \times [(S_A + M_A + 1)(S_A - M_A)(S_B - M_B + 1)(S_B + M_B)]^{1/2} \\ & + \delta_{M'_A, M_A} \delta_{M'_B, M_B} \frac{1}{6} [3M_A^2 - S_A(S_A + 1)][3M_B^2 - S_B(S_B + 1)] \} \end{aligned}$$

$$\begin{aligned}
& -\delta_{M'_A, M_A-1} \delta_{M'_B, M_B+1} \frac{1}{4} (1-2M_A)(1+2M_B) \\
& \times [(S_A - M_A + 1)(S_A + M_A)(S_B + M_B + 1)(S_B - M_B)]^{1/2} \\
& + \delta_{M'_A, M_A-2} \delta_{M'_B, M_B+2} \frac{1}{4} [(S_A - M_A + 1)(S_A - M_A + 2) \\
& (S_A + M_A - 1)(S_A + M_A) \\
& \times (S_B + M_B + 1)(S_B + M_B + 2)(S_B - M_B - 1)(S_B - M_B)]^{1/2} [\hbar^4]
\end{aligned}$$

The second term is simply

$$\begin{aligned}
& \frac{1}{3} \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \hat{S}_A^2 \hat{S}_B^2 \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
& = \delta_{M'_A, M_A} \delta_{M'_B, M_B} \frac{1}{3} S_A(S_A + 1) S_B(S_B + 1)
\end{aligned}$$

and hence

$$\begin{aligned}
& \left\langle \dots S_A, M'_A, \dots S_B, M'_B, \dots \left| \hat{H}^{\text{bq}} \right| \dots S_A, M_A, \dots S_B, M_B, \dots \right\rangle \\
& = -j\{T_{AB}[\hbar^{-4}] + \delta_{M'_A, M_A} \delta_{M'_B, M_B} \frac{1}{3} S_A(S_A + 1) S_B(S_B + 1)\}
\end{aligned}$$

11.1.2. Coupled basis set

The basis set of the uncoupled microstates $\{|S_A, M_A\rangle\}$ and that of the molecular states $\{|S, M\rangle\}$ are related through an orthogonal transformation

$$\{|S, M\rangle\} = \mathbf{U} \{|S_A, M_A\rangle\}$$

where $\mathbf{U}$ is an orthogonal matrix

$$\mathbf{U}\mathbf{U}^T = \mathbf{I}$$

We have seen in Section 1.4.10 that such a matrix can be generated via an iterative procedure during which the next-generation coupling coefficients are created from the previous-generation coefficients and a new set of Clebsch-Gordan coefficients. The coupling coefficient matrix has the following properties:

- (a) a sign alteration of any row is possible;
- (b) the actual form may depend upon the coupling sequence.

With the coupling matrix determined, all the interaction matrices can be transformed from the local basis set into the molecular-state basis, hence

$$\mathbf{H}_{\text{mol}}^{\text{iso}} = \mathbf{U} \mathbf{H}_{\text{loc}}^{\text{iso}} \mathbf{U}^T$$

$$\mathbf{H}_{\text{mol}}^Z = \mathbf{U} \mathbf{H}_{\text{loc}}^Z \mathbf{U}^T$$

$$\mathbf{H}_{\text{mol}}^{\text{asym}} = \mathbf{U} \mathbf{H}_{\text{loc}}^{\text{asym}} \mathbf{U}^T$$

$$\mathbf{H}_{\text{mol}}^{\text{anti}} = \mathbf{U} \mathbf{H}_{\text{loc}}^{\text{anti}} \mathbf{U}^T$$

$$\mathbf{H}_{\text{mol}}^{\text{bq}} = \mathbf{U} \mathbf{H}_{\text{loc}}^{\text{bq}} \mathbf{U}^T$$

Such a transformation may have some advantages. The isotropic (bilinear) exchange matrix in the molecular-state basis adopts a block-diagonal form: only the matrix elements corresponding to the same spin are non-zero

$$(\mathbf{H}_{\text{mol}}^{\text{iso}})_{S', M', S, M} = \langle S', M' | \hat{H}^{\text{iso}} | S, M \rangle \delta_{S, S'}$$

For example, for the $S_A = S_B = S_C = 1/2$ cluster the structure of the isotropic exchange matrix is

$$\mathbf{H}_{\text{mol}}^{\text{iso}} = \left(\begin{array}{c|c|c} S = 1/2 & & 0 \\ \hline & S = 1/2 & 0 \\ \hline 0 & 0 & S = 3/2 \end{array} \right)$$

The z-component of the Zeeman matrix appeared only at the diagonal of the local matrix $\mathbf{H}_{\text{loc}}^Z$. However, after the transformation into the molecular-state basis the off-diagonal elements become non-zero. For small magnetic fields the Zeeman term can be treated as a perturbation and then second-order perturbation theory can be applied in order to determine the magnetic energy levels

$$\varepsilon_i(S, M; B) = \varepsilon_{0i}(S, M) + \sum_{j \neq i} \frac{H_{ij}^Z H_{ji}^Z}{\varepsilon_{0i} - \varepsilon_{0j}}$$

where the summation (j) runs over a row of the interaction matrix. There is no need to diagonalise the high-dimensional matrices and an identification of the van Vleck coefficients is an easy task.

For high-dimensional matrices the time required to transform the interaction matrices from the local into the molecular-state basis set may increase considerably and the procedure loses its battle. Either the direct diagonalisation of the spin Hamiltonian in the local basis set or the irreducible tensor method may be much faster.

11.1.3 Irreducible tensor method

The principal feature of this method lies in the fact that a direct evaluation of an arbitrary matrix element is possible without knowing the explicit form of the wave function. In other words, we no longer need the coupling coefficient matrix. Only the expressions for the reduced matrix elements, the $9j$ -, $6j$ - and $3j$ -symbols are required. The procedure is a generalisation of the method outlined for dinuclear systems [1,2] and will be described in detail for trinuclear and tetranuclear clusters.

11.1.4 Vector addition model

In a certain fortunate case the molecular-state zero-field Hamiltonian adopts a diagonal form. Then a vector addition model assumes the validity.

We have already seen that in a dinuclear system the addition of the spin angular momenta

$$\vec{S}^2 = (\vec{S}_1 + \vec{S}_2)^2 = \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2$$

can be utilised to express the exchange coupling diad

$$\vec{S}_1 \cdot \vec{S}_2 = \frac{1}{2}(\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2)$$

Then the energy levels are the eigenvalues of the spin Hamiltonian

$$\hat{H} = -J(\vec{S}_1 \cdot \vec{S}_2)[\hbar^{-2}] = -J\frac{1}{2}(\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2)[\hbar^{-2}]$$

and when the eigenkets are labelled as $|S_1 S_2 SM\rangle$ then

$$\varepsilon = -\frac{J}{2}[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]$$

An analogous procedure is possible for a trinuclear system

$$\vec{S}^2 = (\vec{S}_1 + \vec{S}_2 + \vec{S}_3)^2 = \vec{S}_1^2 + \vec{S}_2^2 + \vec{S}_3^2 + 2\vec{S}_1 \cdot \vec{S}_2 + 2\vec{S}_1 \cdot \vec{S}_3 + 2\vec{S}_2 \cdot \vec{S}_3$$

When all diads are equivalent (a symmetric triad) then

$$\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3 = \frac{1}{2}(\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2 - \vec{S}_3^2)$$

yielding the eigenvalues of the spin Hamiltonian

$$\hat{H} = -J(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3)[\hbar^{-2}] = -J\frac{1}{2}(\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2 - \vec{S}_3^2)[\hbar^{-2}]$$

in the form of

$$\varepsilon = -\frac{J}{2}[S(S+1) - S_1(S_1+1) - S_2(S_2+1) - S_3(S_3+1)]$$

When only two diads are equivalent (an equilateral triangle) then the spin Hamiltonian is

$$\begin{aligned}\hat{H} &= [-J_a(\vec{S}_1 \cdot \vec{S}_2) - J_b(\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3)][\hbar^{-2}] \\ &= [-(J_a - J_b)(\vec{S}_1 \cdot \vec{S}_2) - J_b(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3)][\hbar^{-2}] \\ &= [-(J_a - J_b)\frac{1}{2}(\vec{S}_{12}^2 - \vec{S}_1^2 - \vec{S}_2^2) - J_b\frac{1}{2}(\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2 - \vec{S}_3^2)][\hbar^{-2}]\end{aligned}$$

and its eigenvalues, with the eigenkets $|S_1 S_2 S_{12} S_3 S M\rangle$, are

$$\begin{aligned}\varepsilon &= -\frac{J_a - J_b}{2}[S_{12}(S_{12}+1) - S_1(S_1+1) - S_2(S_2+1)] \\ &\quad -\frac{J_b}{2}[S(S+1) - S_1(S_1+1) - S_2(S_2+1) - S_3(S_3+1)]\end{aligned}$$

The constant factor can be omitted for relative energies

$$\varepsilon = -\frac{J_a - J_b}{2}[S_{12}(S_{12}+1)] - \frac{J_b}{2}[S(S+1)]$$

Simple expressions exist also for some tetranuclear systems. For example, a magnetic atom surrounded by three other atoms forming a symmetric triangle corresponds to the spin Hamiltonian

$$\hat{H} = -J(\vec{S}_1 \cdot \vec{S}_4 + \vec{S}_2 \cdot \vec{S}_4 + \vec{S}_3 \cdot \vec{S}_4)[\hbar^{-2}] = -J\frac{1}{2}(\vec{S}^2 - \vec{S}_{123}^2 - \vec{S}_4^2)[\hbar^{-2}]$$

with

$$\vec{S}_{123} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3$$

and

$$\vec{S} = \vec{S}_{123} + \vec{S}_4$$

Then the relative energies are

$$\varepsilon = -\frac{J}{2}[S(S+1) - S_{123}(S_{123}+1)]$$

11.2 TRINUCLEAR CLUSTERS

11.2.1 Isotropic exchange

The spin Hamiltonian of bilinear isotropic exchange for a trinuclear cluster adopts the form of

$$\hat{H}^{\text{iso}} = [-J_{12}(\vec{S}_1 \cdot \vec{S}_2) - J_{13}(\vec{S}_1 \cdot \vec{S}_3) - J_{23}(\vec{S}_2 \cdot \vec{S}_3)][\hbar^{-2}]$$

where we have used one of the possible numerical factors in front of the exchange coupling constants (i.e., -1). The coupling scheme applied hereafter is

$$S_1 + S_2 = S_{12}$$

$$S_{12} + S_3 = S$$

and it should be used consistently. Then the kets are labelled as follows

$$|I\rangle = |S_1 S_2 S_{12} S_3 S M\rangle$$

For the next consideration we need:

- the expression of the matrix elements of the spin Hamiltonian in the form of the spherical irreducible tensor operator $\hat{X}_{kq}$;
- application of the Wigner–Eckart theorem for such a matrix element

$$\begin{aligned} & \langle S_1 S_2 S'_{12} S_3 S' M' | \hat{X}_{kq} | S_1 S_2 S_{12} S_3 S M \rangle \\ &= (-1)^{S'-M'} \begin{pmatrix} S' & k & S \\ -M' & q & M \end{pmatrix} \langle S_1 S_2 S'_{12} S_3 S' || \hat{X}_k || S_1 S_2 S_{12} S_3 S \rangle \end{aligned}$$

- (c) expression of the reduced matrix element of the compound tensor operator through uncoupled spin operators

$$\begin{aligned}
 \langle S_1 S_2 S'_{12} S_3 S' \| \hat{X}_k \| S_1 S_2 S_{12} S_3 S \rangle &= \langle S_1 S_2 S'_{12} \| \hat{T}_{k12}(\vec{S}_{12}) \| S_1 S_2 S_{12} \rangle \\
 &\times [(2S' + 1)(2S + 1)(2k + 1)]^{1/2} \left\{ \begin{matrix} S'_{12} & S_{12} & k_{12} \\ S_3 & S_3 & k_3 \\ S' & S & k \end{matrix} \right\} \langle S_3 \| \hat{T}_{k3}(\vec{S}_3) \| S_3 \rangle \\
 &= [(2S'_{12} + 1)(2S_{12} + 1)(2k_{12} + 1)]^{1/2} \left\{ \begin{matrix} S_1 & S_1 & k_1 \\ S_2 & S_2 & k_2 \\ S'_{12} & S_{12} & k_{12} \end{matrix} \right\} \\
 &\times \langle S_1 \| \hat{T}_{k1}(\vec{S}_1) \| S_1 \rangle \langle S_2 \| \hat{T}_{k2}(\vec{S}_2) \| S_2 \rangle \\
 &\times [(2S' + 1)(2S + 1)(2k + 1)]^{1/2} \left\{ \begin{matrix} S'_{12} & S_{12} & k_{12} \\ S_3 & S_3 & k_3 \\ S' & S & k \end{matrix} \right\} \langle S_3 \| \hat{T}_{k3}(\vec{S}_3) \| S_3 \rangle
 \end{aligned}$$

The scalar product of the spin operators can be rewritten using the spherical irreducible tensor as follows

$$\vec{S}_i \cdot \vec{S}_j = -\sqrt{3} \left\{ \hat{T}_1(\vec{S}_i) \otimes \hat{T}_1(\vec{S}_j) \right\}_{0,0}$$

Then the application of the Wigner–Eckart theorem yields

$$\begin{aligned}
 \langle S_1 S_2 S'_{12} S_3 S' M' | \vec{S}_i \cdot \vec{S}_j | S_1 S_2 S_{12} S_3 S M \rangle \\
 = -\sqrt{3} (-1)^{S'-M'} \begin{pmatrix} S' & k & S \\ -M' & q & M \end{pmatrix} \\
 \times \langle S_1 S_2 S'_{12} S_3 S' \| \left\{ \hat{T}_1(\vec{S}_i) \otimes \hat{T}_1(\vec{S}_j) \right\}_0 \| S_1 S_2 S_{12} S_3 S \rangle
 \end{aligned}$$

where the $3j$ -symbol of the special form occurs

$$\begin{pmatrix} S' & 0 & S \\ -M' & 0 & M \end{pmatrix} = (-1)^{S-M} (2S + 1)^{-1/2} \delta_{S,S'} \delta_{M,M'}$$

The reduced matrix elements are evaluated for the tensor ranks according to the scheme

	k_1	k_2	k_{12}	k_3	k
$\vec{S}_1 \cdot \vec{S}_2$	1	1	0	0	0
$\vec{S}_1 \cdot \vec{S}_3$	1	0	1	1	0
$\vec{S}_2 \cdot \vec{S}_3$	0	1	1	1	0

Just this coupling scheme determines the $9j$ -symbols which all collapse into $6j$ -symbols owing to the presence of one zero element (Table 11.2).

The reduced matrix elements of the constituent spin operators are

$$\langle S_i \| \hat{T}_0(\vec{S}_i) \| S'_i \rangle = \delta_{S_i, S'_i} [2S_i + 1]^{1/2}$$

$$\langle S_i \| \hat{T}_1(\vec{S}_i) \| S'_i \rangle = \delta_{S_i, S'_i} [S_i(S_i + 1)(2S_i + 1)]^{1/2} [\hbar]$$

and are limited to only the diagonal elements.

Returning to the reduced matrix elements of the compound operators, these become:

(1) the first type

TABLE 11.2
Selected expressions for $9j$ -symbols

$$\begin{Bmatrix} a & a' & 0 \\ b & b' & 0 \\ c & c' & 0 \end{Bmatrix} = \delta_{a,a'} \delta_{b,b'} \delta_{c,c'} [(2a+1)(2b+1)(2c+1)]^{-1/2}$$

$$\begin{Bmatrix} a & a' & 1 \\ b & b' & 1 \\ c & c' & 0 \end{Bmatrix} = \delta_{c,c'} (-1)^{a'+1+b+c} [3(2c+1)]^{-1/2} \begin{Bmatrix} a & a' & 1 \\ b' & b & c \end{Bmatrix}$$

$$\begin{Bmatrix} a & a' & 1 \\ b & b' & 0 \\ c & c' & 1 \end{Bmatrix} = \delta_{b,b'} (-1)^{a+1+b+c'} [3(2b+1)]^{-1/2} \begin{Bmatrix} a' & a & 1 \\ c & c' & b \end{Bmatrix}$$

$$\begin{Bmatrix} a & a' & 0 \\ b & b' & 1 \\ c & c' & 1 \end{Bmatrix} = \delta_{a,a'} (-1)^{a+1+b'+c} [3(2a+1)]^{-1/2} \begin{Bmatrix} c' & c & 1 \\ b & b' & a \end{Bmatrix}$$

$$\begin{aligned}
R_{12} &= \left\langle S_1 S_2 S'_{12} S_3 S' \right\| \left\{ \hat{T}_1(\vec{S}_1) \otimes \hat{T}_1(\vec{S}_2) \right\}_0 \left\| S_1 S_2 S_{12} S_3 S \right\rangle \\
&= [(2S' + 1)(2S + 1)]^{1/2} [(2S'_{12} + 1)(2S_{12} + 1)]^{1/2} \\
&\quad \times \begin{Bmatrix} S'_{12} & S_{12} & 0 \\ S_3 & S_3 & 0 \\ S' & S & 0 \end{Bmatrix} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 1 \\ S'_{12} & S_{12} & 0 \end{Bmatrix} \\
&\quad \times \left\langle S_1 \left\| \hat{T}_1(\vec{S}_1) \right\| S_1 \right\rangle \left\langle S_2 \left\| \hat{T}_1(\vec{S}_2) \right\| S_2 \right\rangle \left\langle S_3 \left\| \hat{T}_0(\vec{S}_3) \right\| S_3 \right\rangle \\
&= [(2S' + 1)(2S + 1)]^{1/2} [(2S'_{12} + 1)(2S_{12} + 1)]^{1/2} \\
&\quad \times \delta_{S,S'} \delta_{S_{12},S'_{12}} [(2S_{12} + 1)(2S_3 + 1)(2S + 1)]^{-1/2} \\
&\quad \times \delta_{S_{12},S'_{12}} (-1)^{S_1+1+S_2+S_{12}} [3(2S_{12} + 1)]^{-1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & S_{12} \end{Bmatrix} \\
&\quad \times [S_1(S_1 + 1)(2S_1 + 1)]^{1/2} [S_2(S_2 + 1)(2S_2 + 1)]^{1/2} [2S_3 + 1]^{1/2} [\hbar^2] \\
&= -\delta_{S,S'} \delta_{S_{12},S'_{12}} \sqrt{\frac{2S+1}{3}} \frac{1}{2} [S_{12}(S_{12} + 1) - S_1(S_1 + 1) - S_2(S_2 + 1)] [\hbar^2]
\end{aligned}$$

(2) the second type

$$\begin{aligned}
R_{13} &= \left\langle S_1 S_2 S'_{12} S_3 S' \right\| \left\{ \hat{T}_1(\vec{S}_1) \otimes \hat{T}_1(\vec{S}_3) \right\}_0 \left\| S_1 S_2 S_{12} S_3 S \right\rangle \\
&= [(2S' + 1)(2S + 1)]^{1/2} [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \\
&\quad \times \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 1 \\ S' & S & 0 \end{Bmatrix} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\
&\quad \times \left\langle S_1 \left\| \hat{T}_1(\vec{S}_1) \right\| S_1 \right\rangle \left\langle S_2 \left\| \hat{T}_0(\vec{S}_2) \right\| S_2 \right\rangle \left\langle S_3 \left\| \hat{T}_1(\vec{S}_3) \right\| S_3 \right\rangle \\
&= [(2S' + 1)(2S + 1)]^{1/2} [(2S'_{12} + 1)(2S_{12} + 1)3]^{1/2} \\
&\quad \times \delta_{S,S'} (-1)^{S_{12}+S_3+S+1} [3(2S + 1)]^{-1/2} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & S \end{Bmatrix} \\
&\quad \times (-1)^{S_1+1+S_2+S_{12}} [3(2S_2 + 1)]^{-1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S'_{12} & S_{12} & S_2 \end{Bmatrix} \\
&\quad \times [S_1(S_1 + 1)(2S_1 + 1)]^{1/2} [2S_2 + 1]^{1/2} [S_3(S_3 + 1)(2S_3 + 1)]^{1/2} [\hbar^2] \\
&= [(2S + 1)/3]^{1/2} [(2S'_{12} + 1)(2S_{12} + 1)]^{1/2} \delta_{S,S'} (-1)^{S_1+S_2+S_3+S+2S_{12}} \\
&\quad \times [S_3(S_3 + 1)(2S_3 + 1)]^{1/2} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & S \end{Bmatrix} \\
&\quad \times [S_1(S_1 + 1)(2S_1 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S'_{12} & S_{12} & S_2 \end{Bmatrix} [\hbar^2]
\end{aligned}$$

(3) the third type

$$\begin{aligned}
 R_{23} &= \left\langle S_1 S_2 S'_{12} S_3 S' \left\| \left\{ \hat{T}_1(\vec{S}_2) \otimes \hat{T}_1(\vec{S}_3) \right\}_0 \right\| S_1 S_2 S_{12} S_3 S \right\rangle \\
 &= [(2S' + 1)(2S + 1)]^{1/2} [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \\
 &\quad \times \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 1 \\ S' & S & 0 \end{Bmatrix} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 1 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\
 &\quad \times \left\langle S_1 \left\| \hat{T}_0(\vec{S}_1) \right\| S_1 \right\rangle \left\langle S_2 \left\| \hat{T}_1(\vec{S}_2) \right\| S_2 \right\rangle \left\langle S_3 \left\| \hat{T}_1(\vec{S}_3) \right\| S_3 \right\rangle \\
 &= [(2S' + 1)(2S + 1)]^{1/2} [(2S'_{12} + 1)(2S_{12} + 1)3]^{1/2} \\
 &\quad \times \delta_{S,S'} (-1)^{S_{12}+S_3+S+1} [3(2S + 1)]^{-1/2} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & S \end{Bmatrix} \\
 &\quad \times (-1)^{S_1+1+S_2+S'_{12}} [3(2S_1 + 1)]^{-1/2} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} \\
 &\quad \times [2S_1 + 1]^{1/2} [S_2(S_2 + 1)(2S_2 + 1)]^{1/2} [S_3(S_3 + 1)(2S_3 + 1)]^{1/2} [\hbar^2] \\
 &= [(2S + 1)/3]^{1/2} [(2S'_{12} + 1)(2S_{12} + 1)]^{1/2} \delta_{S,S'} (-1)^{S_1+S_2+S_3+S+S_{12}+S'_{12}} \\
 &\quad \times [S_3(S_3 + 1)(2S_3 + 1)]^{1/2} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & S \end{Bmatrix} \\
 &\quad \times [S_2(S_2 + 1)(2S_2 + 1)]^{1/2} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} [\hbar^2]
 \end{aligned}$$

A further simplification follows from the triangular conditions which should be fulfilled for the $6j$ -symbols, i.e.

(a) when $S'_{12} = S_{12}$ then

$$\begin{aligned}
 &\begin{Bmatrix} S_{12} & S_{12} & 1 \\ S_3 & S_3 & S \end{Bmatrix} \\
 &= (-1)^{-S_{12}-S_3-S} \frac{1}{2} \frac{S(S + 1) - S_{12}(S_{12} + 1) - S_3(S_3 + 1)}{[S_{12}(S_{12} + 1)(2S_{12} + 1)S_3(S_3 + 1)(2S_3 + 1)]^{1/2}}
 \end{aligned}$$

(b) when $S'_{12} = S_{12} - 1$ then

$$\begin{aligned}
 &\begin{Bmatrix} S_{12} & (S_{12} - 1) & 1 \\ S_3 & S_3 & S \end{Bmatrix} = (-1)^{-S_{12}-S_3-S} \\
 &\quad \times \frac{1}{2} \frac{[(S + S_{12} - S_3)(-S + S_{12} + S_3)(1 + S - S_{12} + S_3)(1 + S + S_{12} + S_3)]^{1/2}}{[S_{12}(2S_{12} - 1)(2S_{12} + 1)S_3(S_3 + 1)(2S_3 + 1)]^{1/2}}
 \end{aligned}$$

Therefore, for $S'_{12} = S_{12}$ one gets the diagonal reduced matrix elements in the form

$$R_{13}(a) = \delta_{S,S'} \sqrt{\frac{2S+1}{3}} \times \frac{1}{4} \frac{[S(S+1) - S_{12}(S_{12}+1) - S_3(S_3+1)][S_2(S_2+1) - S_{12}(S_{12}+1) - S_1(S_1+1)]}{S_{12}(S_{12}+1)} [\hbar^2]$$

$$R_{23}(a) = \delta_{S,S'} \sqrt{\frac{2S+1}{3}} \times \frac{1}{4} \frac{[S(S+1) - S_{12}(S_{12}+1) - S_3(S_3+1)][S_1(S_1+1) - S_{12}(S_{12}+1) - S_2(S_2+1)]}{S_{12}(S_{12}+1)} [\hbar^2]$$

Using these expressions, the isotropic exchange Hamiltonian of a trinuclear system has the following diagonal elements

$$\begin{aligned} H_{II}^{\text{iso}}(a) &\equiv H_{S_{12}SM, S_{12}SM}^{\text{iso}} = \langle S_1 S_2 S_{12} S_3 SM | \hat{H}^{\text{iso}} | S_1 S_2 S_{12} S_3 SM \rangle \\ &= -\sqrt{3/(2S+1)} [-J_{12}R_{12}(a) - J_{13}R_{13}(a) - J_{23}R_{23}(a)] [\hbar^{-2}] \end{aligned}$$

or

$$\begin{aligned} H_{II}^{\text{iso}}(a) &= -J_{12} \frac{1}{2} [S_{12}(S_{12}+1) - S_1(S_1+1) - S_2(S_2+1)] \\ &\quad + \left[-(J_{13} + J_{23}) - (J_{13} - J_{23}) \frac{S_1(S_1+1) - S_2(S_2+1)}{S_{12}(S_{12}+1)} \right] \\ &\quad \times \frac{1}{4} [S(S+1) - S_{12}(S_{12}+1) - S_3(S_3+1)] \end{aligned}$$

and it can be rewritten in the form

$$H_{II}^{\text{iso}}(a) = -J_{12}X_1 - (J_{13} + J_{23})X_2 - (J_{13} - J_{23})X_3$$

where the coefficients X_1 , X_2 and X_3 are tabulated (Table 11.3) [1].

The off-diagonal reduced matrix elements for $S'_{12} = S_{12} - 1$ are evaluated as follows

$$\begin{aligned} R_{13}(b) = -R_{23}(b) &= \delta_{S,S'} \sqrt{\frac{2S+1}{3}} \frac{1}{4S_{12}[(2S_{12}-1)(2S_{12}+1)]^{1/2}} \\ &\quad \times [(S + S_{12} - S_3)(-S + S_{12} + S_3)(1 + S - S_{12} + S_3) \\ &\quad \times (1 + S + S_{12} + S_3)]^{1/2} \\ &\quad \times [(S_2 + S_{12} - S_1)(-S_2 + S_{12} + S_1)(1 + S_2 - S_{12} + S_1) \\ &\quad \times (1 + S_2 + S_{12} + S_1)]^{1/2} [\hbar^2] \end{aligned}$$

TABLE 11.3

Coefficients of the non-zero matrix elements of the isotropic exchange Hamiltonian for general triads of $S_1 = S_2 = S_3$

S_1	S_{12}	S'_{12}	S	X_1	X_2	X_3
1/2	1	1	3/2	1/4	1/4	0
	1	1	1/2	1/4	-1/2	0
	0	0	1/2	-3/4	0	0
	1	0	1/2	0	0	$\sqrt{3}/4$
1	2	2	3	1	1	0
	2	2	2	1	-1/2	0
	1	1	2	-1	1/2	0
	2	1	2	0	0	$\sqrt{3}/2$
	2	2	1	1	-3/2	0
	1	1	1	-1	-1/2	0
	0	0	1	-2	0	0
	2	1	1	0	0	$\sqrt{5/12}$
	1	0	1	0	0	$2/\sqrt{3}$
	1	1	0	-1	-1	0
3/2	3	3	9/2	9/4	9/4	0
	3	3	7/2	9/4	0	0
	2	2	7/2	-3/4	3/2	0
	3	2	7/2	0	0	$3\sqrt{3}/4$
	3	3	5/2	9/4	-7/4	0
	2	2	5/2	-3/4	-1/4	0
	1	1	5/2	-11/4	3/4	0
	3	2	5/2	0	0	$2\sqrt{2/5}$
	2	1	5/2	0	0	$3\sqrt{7/20}$
	3	3	3/2	9/4	-3	0
	2	2	3/2	-3/4	-3/2	0
	1	1	3/2	-11/4	-1/2	0
	0	0	3/2	-15/4	0	0
	3	2	3/2	0	0	$3\sqrt{7/80}$
	2	1	3/2	0	0	$2\sqrt{3/5}$
	1	0	3/2	0	0	$5\sqrt{3}/4$
	2	2	1/2	-3/4	-9/4	0
	1	1	1/2	-11/4	-5/4	0
	2	1	1/2	0	0	$\sqrt{3}/2$
2	4	4	6	4	4	0
	4	4	5	4	1	0
	3	3	5	0	3	0
	4	3	5	0	0	$\sqrt{3}$
	4	4	4	4	-3/2	0
	3	3	4	0	1/2	0
	2	2	4	-3	2	0
	4	3	4	0	0	$3\sqrt{11/28}$
	3	2	4	0	0	$2\sqrt{10/7}$
	4	4	3	4	-7/2	0
	3	3	3	0	-3/2	0
	2	2	3	-3	0	0

TABLE 11.3

Coefficients of the non-zero matrix elements of the isotropic exchange Hamiltonian for general triads of $S_1 = S_2 = S_3$ (contd.)

S_1	S_{12}	S'_{12}	S	X_1	X_2	X_3
5/2	1	1	3	-5	1	0
	4	3	3	0	0	$5\sqrt{3/28}$
	3	2	3	0	0	$6\sqrt{6/35}$
	2	1	3	0	0	$\sqrt{42/5}$
	4	4	2	4	-5	0
	3	3	2	0	-3	0
	2	2	2	-3	-3/2	0
	1	1	2	-5	-1/2	0
	0	0	2	-6	0	0
	4	3	2	0	0	$3/\sqrt{7}$
	3	2	2	0	0	$12/\sqrt{35}$
	2	1	2	0	0	$21/\sqrt{60}$
	1	0	2	0	0	$2\sqrt{3}$
	3	3	1	0	-4	0
	2	2	1	-3	-5/2	0
	1	1	1	-5	-3/2	0
	3	2	1	0	0	$2\sqrt{2/5}$
	2	1	1	0	0	$3\sqrt{7/20}$
	5	5	15/2	25/4	25/4	0
	5	5	13/2	25/4	5/2	0
	4	4	13/2	5/4	5	0
	5	4	13/2	0	0	$5\sqrt{3}/4$
	5	5	11/2	25/4	-3/4	0
	4	4	11/2	5/4	7/4	0
	3	3	11/2	-11/4	15/4	0
	5	4	11/2	0	0	$\sqrt{56}/3$
	4	3	11/2	0	0	$5\sqrt{13}/6$
	5	5	9/2	25/4	-7/2	0
	4	4	9/2	5/4	-1	0
	3	3	9/2	-11/4	1	0
	2	2	9/2	-23/4	5/2	0
	5	4	9/2	0	0	$\sqrt{91}/4$
	4	3	9/2	0	0	$4\sqrt{57}$
	3	2	9/2	0	0	$3\sqrt{165/112}$
	5	5	7/2	25/4	-23/4	0
	4	4	7/2	5/4	-13/4	0
	3	3	7/2	-11/4	-5/4	0
	2	2	7/2	-23/4	1/4	0
	1	1	7/2	-31/4	5/4	0
	5	4	7/2	0	0	2
	4	3	7/2	0	0	$5\sqrt{11/28}$
	3	2	7/2	0	0	$6\sqrt{3/7}$
	2	1	7/2	0	0	$3\sqrt{2}$
	5	5	5/2	25/4	-15/2	0
	4	4	5/2	5/4	-5	0

(contd.)

TABLE 11.3

Coefficients of the non-zero matrix elements of the isotropic exchange Hamiltonian for general triads of $S_1 = S_2 = S_3$ (contd.)

S_1	S_{12}	S'_{12}	S	X_1	X_2	X_3
5/2	3	3	5/2	-11/4	-3	0
	2	2	5/2	-23/4	-3/2	0
	1	1	5/2	-31/4	-1/2	0
	0	0	5/2	-35/4	0	0
	5	4	5/2	0	0	$5\sqrt{11}/12$
	4	3	5/2	0	0	$20/\sqrt{63}$
	3	2	5/2	0	0	$81/\sqrt{560}$
	2	1	5/2	0	0	$16/\sqrt{15}$
	1	0	5/2	0	0	$35/\sqrt{48}$
	4	4	3/2	5/4	-25/4	0
	3	3	3/2	-11/4	-17/4	0
	2	2	3/2	-23/4	-11/4	0
	1	1	3/2	-31/4	-7/4	0
	4	3	3/2	0	0	$5\sqrt{3}/28$
	3	2	3/2	0	0	$6\sqrt{6}/35$
	2	1	3/2	0	0	$\sqrt{42}/5$
	3	3	1/2	-11/4	-5	0
	2	2	1/2	-23/4	-7/2	0
	3	2	1/2	0	0	$3\sqrt{3}/4$

and they yield the following matrix elements of the isotropic exchange Hamiltonian

$$H_{IJ}^{\text{iso}}(\mathbf{b}) \equiv H_{S'_{12}SM, S_{12}SM}^{\text{iso}} = \langle S_1 S_2 S'_{12} S_3 SM | \hat{H}^{\text{iso}} | S_1 S_2 S_{12} S_3 SM \rangle$$

$$= -\sqrt{3/(2S+1)}[-J_{13}R_{13}(\mathbf{b}) - J_{23}R_{23}(\mathbf{b})][\hbar^{-2}]$$

or

$$H_{IJ}^{\text{iso}}(\mathbf{b}) = -(J_{23} - J_{13}) \frac{1}{4S_{12}[(2S_{12}-1)(2S_{12}+1)]^{1/2}}$$

$$\times [(S+S_{12}-S_3)(-S+S_{12}+S_3)(1+S-S_{12}+S_3)$$

$$\times (1+S+S_{12}+S_3)]^{1/2} [(S_2+S_{12}-S_1)(-S_2+S_{12}+S_1)$$

$$\times (1+S_2-S_{12}+S_1)(1+S_2+S_{12}+S_1)]^{1/2}$$

Again, the coefficients X_3 of the expression

$$H_{IJ}^{\text{iso}}(\mathbf{b}) = -(J_{23} - J_{13})X_3$$

are tabulated (Table 11.3).

The zero-field exchange Hamiltonian takes the form of

Total spin	Intermediate spin	Matrix elements	
$S' = S$	$S'_{12} = S_{12}$	a	b
	$S'_{12} = S_{12} - 1$	b	a

In order to exemplify the construction of the zero-field exchange Hamiltonian matrix let us consider the simplest case of $S_1 = S_2 = S_3 = 1/2$. Then the structure of the isotropic exchange matrix is

$$H^{\text{iso}} = \left(\begin{array}{cccc|cccc} a & 0 & 0 & 0 & & & & \\ 0 & a & 0 & 0 & & & & \\ 0 & 0 & a & 0 & & & & \\ 0 & 0 & 0 & a & & & & \\ \hline & & & & a & 0 & b & 0 \\ & & & & 0 & a & 0 & b \\ \hline & & & & b & 0 & a & 0 \\ & & & & 0 & b & 0 & a \end{array} \right)$$

for

$$\left[\begin{array}{lll} S_{12} = 1 & S = 3/2 & M = -3/2 \\ & & M = -1/2 \\ & & M = +1/2 \\ & & M = +3/2 \\ \hline S_{12} = 1 & S = 1/2 & M = -1/2 \\ & & M = +1/2 \\ \hline S_{12} = 0 & S = 1/2 & M = -1/2 \\ & & M = +1/2 \end{array} \right]$$

with

$$H_{S_{12}, S; S_{12}, S}^{\text{iso}}(a) = -J_{12}X_1(a) - (J_{13} + J_{23})X_2(a) - (J_{13} - J_{23})X_3(a)$$

and

$$H_{S_{12}-1, S; S_{12}, S}^{\text{iso}}(b) = -(J_{23} - J_{13})X_3(b)$$

It is obvious that the isotropic exchange Hamiltonian is diagonal (for the symmetric triad, regular triad, symmetric linear triad) unless $J_{23} \neq J_{13}$ (a general triad). The number of combinations for $S_1 \neq S_2 \neq S_3$ becomes

high and the tabulation of the Hamiltonian coefficients is rather impractical so that one should return to the analytical formulae given in Table 11.4.

Notice that the matrix elements for the isotropic exchange do not depend upon the magnetic quantum numbers.

The zero-field energies of a cluster are obtained by constructing the spin Hamiltonian matrix, which should be diagonalised when non-zero off-diagonal matrix elements occur.

With increasing spin numbers the number of zero-field energy levels becomes high; however, they are distributed within a definite energy interval. Therefore it is possible to generate a density of state (DOS) function, defined as

$$N(\varepsilon) = \frac{1}{\sqrt{2\pi}\sigma} \sum_{i=1}^n \exp[(\varepsilon - \varepsilon_i)^2 / 2\sigma^2]$$

Here the Gaussian broadening parameter σ (a small number) secures that the DOS function is continuous; the height of the DOS function is proportional to the spin multiplicity of the given state times its accidental degeneracy.

Using the DOS function each cluster has its characteristic spectrum of the zero-field (or magnetic) energy levels. Some examples are shown in Figs. 11.1 and 11.2.

11.2.2 Zeeman interaction

The Zeeman operator for a trinuclear cluster is written as

$$\hat{H}^Z = \mu_B \vec{B} \cdot (\vec{g}_1 \cdot \vec{S}_1 + \vec{g}_2 \cdot \vec{S}_2 + \vec{g}_3 \cdot \vec{S}_3) [\hbar^{-1}]$$

TABLE 11.4

Matrix elements of the isotropic exchange for a general triad

$$\begin{aligned}
 H_{S_{12}, S, S_{12}, S}^{\text{iso}}(a) &= -J_{12} \frac{1}{2} [S_{12}(S_{12} + 1) - S_1(S_1 + 1) - S_2(S_2 + 1)] \\
 &+ \left[-(J_{13} + J_{23}) - (J_{13} - J_{23}) \frac{S_1(S_1 + 1) - S_2(S_2 + 1)}{S_{12}(S_{12} + 1)} \right] \frac{1}{4} [S(S + 1) - S_{12}(S_{12} + 1) - S_3(S_3 + 1)] \\
 H_{S_{12}-1, S, S_{12}, S}^{\text{iso}}(b) &= -(J_{23} - J_{13}) \frac{1}{4S_{12}[(2S_{12} - 1)(2S_{12} + 1)]^{1/2}} \\
 &\times [(S + S_{12} - S_3)(-S + S_{12} + S_3)(1 + S - S_{12} + S_3)(1 + S + S_{12} + S_3)]^{1/2} \\
 &\times [(S_2 + S_{12} - S_1)(-S_2 + S_{12} + S_1)(1 + S_2 - S_{12} + S_1)(1 + S_2 + S_{12} + S_1)]^{1/2}
 \end{aligned}$$

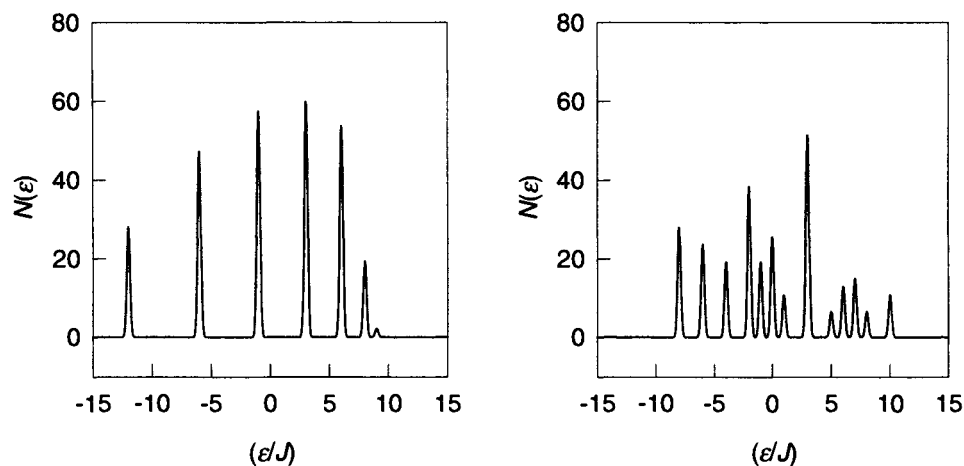


Fig. 11.1. Density of state function for an $S_1 = S_2 = S_3 = 2$ triad; left—an isosceles triangle ($J_{12} = J_{23} = J_{13} = J$); right—a linear cluster ($J_{12} = J_{23} = J$, $J_{13} = 0$).

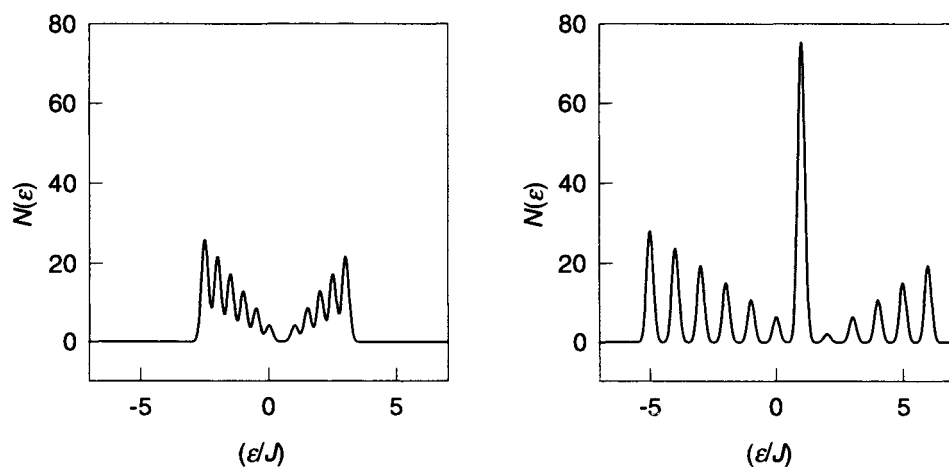


Fig. 11.2. Density of state function for linear clusters ($J_{12} = J_{23} = J$, $J_{13} = 0$): left— $S_1 = S_3 = 5/2$ and $S_2 = 1/2$; right— $S_1 = S_3 = 5/2$ and $S_2 = 1$.

The tensor ranks entering the decoupling formula for the evaluation of the reduced matrix elements are assigned as follows

	k_1	k_2	k_{12}	k_3	k
S_1	1	0	1	0	1
S_2	0	1	1	0	1
S_3	0	0	0	1	1

The reduced matrix elements of the constituent spins are expressed as follows

$$\begin{aligned}
 R_1 &\equiv \langle S_1 S_2 S'_{12} S_3 S' | \hat{T}_1(\vec{S}_1) | S_1 S_2 S_{12} S_3 S \rangle \\
 &= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\
 &\quad \times \langle S_1 | \hat{T}_1(\vec{S}_1) | S_1 \rangle \langle S_2 | \hat{T}_0(\vec{S}_2) | S_2 \rangle \\
 &\quad \times [(2S' + 1)(2S + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 0 \\ S' & S & 1 \end{Bmatrix} \langle S_3 | \hat{T}_0(\vec{S}_3) | S_3 \rangle \\
 R_2 &\equiv \langle S_1 S_2 S'_{12} S_3 S' | \hat{T}_1(\vec{S}_2) | S_1 S_2 S_{12} S_3 S \rangle \\
 &= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 1 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\
 &\quad \times \langle S_1 | \hat{T}_0(\vec{S}_1) | S_1 \rangle \langle S_2 | \hat{T}_1(\vec{S}_2) | S_2 \rangle \\
 &\quad \times [(2S' + 1)(2S + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 0 \\ S' & S & 1 \end{Bmatrix} \langle S_3 | \hat{T}_0(\vec{S}_3) | S_3 \rangle \\
 R_3 &\equiv \langle S_1 S_2 S'_{12} S_3 S' | \hat{T}_1(\vec{S}_3) | S_1 S_2 S_{12} S_3 S \rangle \\
 &= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 0 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 0 \end{Bmatrix} \\
 &\quad \times \langle S_1 | \hat{T}_0(\vec{S}_1) | S_1 \rangle \langle S_2 | \hat{T}_0(\vec{S}_2) | S_2 \rangle \\
 &\quad \times [(2S' + 1)(2S + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S'_{12} & S_{12} & 0 \\ S_3 & S_3 & 1 \\ S' & S & 1 \end{Bmatrix} \langle S_3 | \hat{T}_1(\vec{S}_3) | S_3 \rangle
 \end{aligned}$$

The $9j$ -symbols containing one zero or three zero collapse into $6j$ -symbols (Table 11.2), hence

$$R_1 = [(2S'_{12} + 1)(2S_{12} + 1)]^{1/2} [(2S' + 1)(2S + 1)]^{1/2} \\ \times [S_1(S_1 + 1)(2S_1 + 1)]^{1/2} (-1)^{S_1+1+S_2+S_{12}} \\ \times \left\{ \begin{matrix} S_1 & S_1 & 1 \\ S'_{12} & S_{12} & S_2 \end{matrix} \right\} (-1)^{S'_{12}+1+S_3+S} \left\{ \begin{matrix} S_{12} & S'_{12} & 1 \\ S' & S & S_3 \end{matrix} \right\} [\hbar]$$

$$R_2 = [(2S'_{12} + 1)(2S_{12} + 1)]^{1/2} [(2S' + 1)(2S + 1)]^{1/2} \\ \times [S_2(S_2 + 1)(2S_2 + 1)]^{1/2} (-1)^{S_1+1+S_2+S'_{12}} \\ \times \left\{ \begin{matrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{matrix} \right\} (-1)^{S'_{12}+1+S_3+S} \left\{ \begin{matrix} S_{12} & S'_{12} & 1 \\ S' & S & S_3 \end{matrix} \right\} [\hbar]$$

$$R_3 = \delta_{S_{12}, S'_{12}} [(2S' + 1)(2S + 1)]^{1/2} [S_3(S_3 + 1)(2S_3 + 1)]^{1/2} \\ \times (-1)^{S'_{12}+1+S_3+S'} \left\{ \begin{matrix} S & S' & 1 \\ S_3 & S_3 & S'_{12} \end{matrix} \right\} [\hbar]$$

The triangular restrictions for the $6j$ -symbols imply that $S' = S, S \pm 1$ and $S'_{12} = S_{12}, S_{12} \pm 1$. Therefore the reduced matrix elements fill the places according to the recipe

Total spin	Intermediate spin	Reduced matrix elements	
$S' = S$	$S'_{12} = S_{12}$	a	b
	$S'_{12} = S_{12} - 1$	b	a
$S' = S - 1$	$S'_{12} = S_{12}$	c	d
	$S'_{12} = S_{12} - 1$	d	c

There are four possibilities for the reduced matrix elements $R_{i(S'_{12}, S'; S_{12}, S)}$:

(1) for $S' = S$ and $S'_{12} = S_{12}$

$$R_1(a) = F_1 \left\{ \begin{matrix} S_1 & S_1 & 1 \\ S_{12} & S_{12} & S_2 \end{matrix} \right\} \cdot \left\{ \begin{matrix} S_{12} & S_{12} & 1 \\ S & S' & S_3 \end{matrix} \right\}$$

$$R_2(a) = F_2 \left\{ \begin{matrix} S_2 & S_2 & 1 \\ S_{12} & S_{12} & S_1 \end{matrix} \right\} \cdot \left\{ \begin{matrix} S_{12} & S_{12} & 1 \\ S & S & S_3 \end{matrix} \right\}$$

$$R_3(a) = F_3 \left\{ \begin{matrix} S & S & 1 \\ S_3 & S_3 & S_{12} \end{matrix} \right\}$$

(2) for $S' = S$ and $S'_{12} = S_{12} \pm 1$

$$R_1(b) = F_1 \begin{Bmatrix} S_1 & S_1 & 1 \\ (S_{12} \pm 1) & S_{12} & S_2 \end{Bmatrix} \cdot \begin{Bmatrix} S_{12} & (S_{12} \pm 1) & 1 \\ S & S & S_3 \end{Bmatrix}$$

$$R_2(b) = F_2 \begin{Bmatrix} S_{12} & (S_{12} \pm 1) & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} \cdot \begin{Bmatrix} S_{12} & (S_{12} \pm 1) & 1 \\ S & S & S_3 \end{Bmatrix}$$

$$R_3(b) = 0$$

(3) for $S' = S \pm 1$ and $S'_{12} = S_{12}$

$$R_1(c) = F_1 \begin{Bmatrix} S_1 & S_1 & 1 \\ S_{12} & S_{12} & S_2 \end{Bmatrix} \cdot \begin{Bmatrix} S_{12} & S_{12} & 1 \\ (S \pm 1) & S & S_3 \end{Bmatrix}$$

$$R_2(c) = F_2 \begin{Bmatrix} S_{12} & S_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} \cdot \begin{Bmatrix} S_{12} & S_{12} & 1 \\ (S \pm 1) & S & S_3 \end{Bmatrix}$$

$$R_3(c) = F_3 \begin{Bmatrix} S & (S \pm 1) & 1 \\ S_3 & S_3 & S_{12} \end{Bmatrix}$$

(4) for $S' = S \pm 1$ and $S'_{12} = S_{12} \pm 1$

$$R_1(d) = F_1 \begin{Bmatrix} S_1 & S_1 & 1 \\ (S_{12} \pm 1) & S_{12} & S_2 \end{Bmatrix} \cdot \begin{Bmatrix} S_{12} & (S_{12} \pm 1) & 1 \\ (S \pm 1) & S & S_3 \end{Bmatrix}$$

$$R_2(d) = F_2 \begin{Bmatrix} S_{12} & (S_{12} \pm 1) & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} \cdot \begin{Bmatrix} S_{12} & (S_{12} \pm 1) & 1 \\ (S \pm 1) & S & S_3 \end{Bmatrix}$$

$$R_3(d) = 0$$

where F_i are the corresponding scalar factors. The $6j$ -symbols can be expressed through special formulae (Appendix 3), yielding the final formulae for the reduced matrix elements (Table 11.5).

The Zeeman operator can be written as the sum of the contributions over individual centres

$$\hat{H}^Z = \mu_B [\hbar^{-1}] \sum_{i=1}^3 \vec{B} \cdot \vec{g}_i \cdot \vec{S}_i = \mu_B [\hbar^{-1}] \sum_{i=1}^3 \vec{\gamma}_i \cdot \vec{S}_i$$

where we have introduced magnetogyric vectors

$$\vec{\gamma}_i = \vec{B} \cdot \vec{g}_i$$

TABLE 11.5

Reduced matrix elements of the Zeeman operator for a general triad

Spins	$R_{\ell(S'_{12}, S'; S_{12}, S)}$
$S' = S$ $S'_{12} = S_{12}$	$R_1(a) = \frac{2S+1}{[S(S+1)(2S+1)]^{1/2}} \frac{1}{4S_{12}(S_{12}+1)}$ $\times [S_3(S_3+1) - S_{12}(S_{12}+1) - S(S+1)]$ $\times [S_2(S_2+1) - S_{12}(S_{12}+1) - S_1(S_1+1)][\hbar]$ $R_2(a) = \frac{2S+1}{[S(S+1)(2S+1)]^{1/2}} \frac{1}{4S_{12}(S_{12}+1)}$ $\times [S_3(S_3+1) - S_{12}(S_{12}+1) - S(S+1)]$ $\times [S_1(S_1+1) - S_{12}(S_{12}+1) - S_2(S_2+1)][\hbar]$ $R_3(a) = \frac{2S+1}{2[S(S+1)(2S+1)]^{1/2}} [S_3(S_3+1) - S_{12}(S_{12}+1) + S(S+1)][\hbar]$
$S' = S$ $S'_{12} = S_{12} - 1$	$R_1(b) = \frac{-(2S+1)}{[S(S+1)(2S+1)]^{1/2}} \frac{1}{4S_{12}[(2S_{12}-1)(2S_{12}+1)]^{1/2}}$ $\times [(1+S_2+S_1-S_{12})(S_2-S_1+S_{12})(-S_2+S_1+S_{12})(1+S_2+S_1+S_{12})]^{1/2}$ $\times [(1+S_3+S-S_{12})(S_3-S+S_{12})(-S_3+S+S_{12})(1+S_3+S+S_{12})]^{1/2}[\hbar]$ $R_2(b) = -R_1(b); R_3(b) = 0$
$S' = S - 1$ $S'_{12} = S_{12}$	$R_1(c) = \frac{S_2(S_2+1) - S_1(S_1+1) - S_{12}(S_{12}+1)}{4S_{12}(S_{12}+1)(S)^{1/2}}$ $\times [(S+S_{12}-S_3)(S-S_{12}+S_3)(1-S+S_{12}+S_3)(1+S+S_{12}+S_3)]^{1/2}[\hbar]$ $R_2(c) = \frac{S_1(S_1+1) - S_2(S_2+1) - S_{12}(S_{12}+1)}{4S_{12}(S_{12}+1)(S)^{1/2}}$ $\times [(S+S_{12}-S_3)(S-S_{12}+S_3)(1-S+S_{12}+S_3)(1+S+S_{12}+S_3)]^{1/2}[\hbar]$ $R_3(c) = \frac{1}{2(S)^{1/2}}$ $\times [(1+S_{12}+S_3-S)(S_{12}-S_3+S)(-S_{12}+S_3+S)(1+S_{12}+S_3+S)]^{1/2}[\hbar]$
$S' = S - 1$ $S'_{12} = S_{12} - 1$	$R_1(d) = \frac{-1}{4S_{12}[S(2S_{12}+1)(2S_{12}-1)]^{1/2}}$ $\times [(S_1+S_{12}-S_2)(1+S_1-S_{12}+S_2)(-S_1+S_{12}+S_2)(1+S_1+S_{12}+S_2)]^{1/2}$ $\times [(S+S_{12}-S_3)(-1+S+S_{12}-S_3)(S+S_{12}+S_3)(1+S+S_{12}+S_3)]^{1/2}[\hbar]$ $R_2(d) = -R_1(d); R_3(d) = 0$

Assuming that the g_i -tensors are diagonal, with components $g_{i,x}$, $g_{i,y}$ and $g_{i,z}$, then the spherical transforms are easily obtained, hence

$$\gamma_{i,1,+1} = -\frac{1}{\sqrt{2}}(B_x g_{i,x} + iB_y g_{i,y})$$

$$\gamma_{i,1,-1} = \frac{1}{\sqrt{2}}(B_x g_{i,x} - iB_y g_{i,y})$$

$$\gamma_{i,1,0} = B_z g_{i,z}$$

(For non-diagonal g_i -tensors the expressions for $\vec{\gamma}_i = \vec{B} \cdot \vec{g}_i$ would be more complex.) In terms of the spherical components the Zeeman operator becomes

$$\begin{aligned} \hat{H}^Z &= \mu_B [\hbar^{-1}] \sum_{i=1}^3 \vec{\gamma}_i \cdot \vec{S}_i \\ &= \mu_B [\hbar^{-1}] \sum_{i=1}^3 (-\gamma_{i,1,+1} \hat{S}_{i,1,-1} + \gamma_{i,1,0} \hat{S}_{i,1,0} - \gamma_{i,1,-1} \hat{S}_{i,1,+1}) \\ &= \mu_B [\hbar^{-1}] \sum_{i=1}^3 \sum_{q=-1}^{+1} (-1)^q \gamma_{i,1,-q} \hat{S}_{i,1,q} \end{aligned}$$

Its matrix elements take the form

$$\begin{aligned} H_{IJ}^Z &\equiv H_{S_{12}S_{M'}, S_{12}SM}^Z = \langle S_1 S_2 S'_{12} S_3 S'_{M'} | \hat{H}^Z | S_1 S_2 S_{12} S_3 SM \rangle \\ &= \mu_B [\hbar^{-1}] \sum_{i=1}^3 \sum_{q=-1}^{+1} (-1)^q \gamma_{i,1,-q} \langle S_1 S_2 S'_{12} S_3 S'_{M'} | \hat{S}_{i,1,q} | S_1 S_2 S_{12} S_3 SM \rangle \end{aligned}$$

Now the application of the Wigner–Eckert theorem yields

$$\begin{aligned} H_{IJ}^Z &= \mu_B [\hbar^{-1}] \sum_{i=1}^3 \sum_{q=-1}^{+1} (-1)^q \gamma_{i,1,-q} \langle S_1 S_2 S'_{12} S_3 S'_{M'} | \hat{S}_{i,1,q} | S_1 S_2 S_{12} S_3 SM \rangle \\ &= \mu_B [\hbar^{-1}] \sum_{i=1}^3 \sum_{q=-1}^{+1} (-1)^q \gamma_{i,1,-q} (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} \\ &\quad \times \langle S_1 S_2 S'_{12} S_3 S' || \vec{S}_i || S_1 S_2 S_{12} S_3 S \rangle \end{aligned}$$

or

$$\begin{aligned}
 H_{IJ}^Z = \mu_B [\hbar^{-1}] \sum_{i=1}^3 R_{i,(S'_{12}, S', S_{12}, S)} & \left[(-1)^{\gamma_{i,1,+1}} (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & -1 & M \end{pmatrix} \right. \\
 & + \gamma_{i,1,0} (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & 0 & M \end{pmatrix} \\
 & \left. + (-1)^{\gamma_{i,1,-1}} (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & +1 & M \end{pmatrix} \right]
 \end{aligned}$$

The back transformation into the Cartesian representation is

$$\begin{aligned}
 H_{IJ}^Z = \mu_B [\hbar^{-1}] \sum_{i=1}^3 R_{i,(S'_{12}, S', S_{12}, S)} & \left[\frac{1}{\sqrt{2}} (B_x g_{i,x} + i B_y g_{i,y}) (-1)^{S'-M'} \right. \\
 & \times \begin{pmatrix} S' & 1 & S \\ -M' & -1 & M \end{pmatrix} + B_z g_{i,z} (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & 0 & M \end{pmatrix} \\
 & \left. - \frac{1}{\sqrt{2}} (B_x g_{i,x} - i B_y g_{i,y}) (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & +1 & M \end{pmatrix} \right]
 \end{aligned}$$

The triangular condition for the non-zero $3j$ -symbols implies $M' = M, M \pm 1$ while only one of the three terms can contribute. The required $3j$ -symbols are (Appendix 3)

$$\begin{aligned}
 \begin{pmatrix} S & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} &= (-1)^{-M+S+1} \frac{[(S+M)(S-M+1)]^{1/2}}{[2S(S+1)(2S+1)]^{1/2}} \\
 \begin{pmatrix} S & 1 & S \\ -M & 0 & M \end{pmatrix} &= (-1)^{M-S} \frac{M}{[S(S+1)(2S+1)]^{1/2}} \\
 \begin{pmatrix} S & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} &= (-1)^{M-S} \frac{[(S-M)(S+M+1)]^{1/2}}{[2S(S+1)(2S+1)]^{1/2}} \\
 \begin{pmatrix} (S-1) & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} &= (-1)^{S-M} \left[\frac{(S-M)(S-1-M)}{2S(2S+1)(2S-1)} \right]^{1/2} \\
 \begin{pmatrix} (S-1) & 1 & S \\ -M & 0 & M \end{pmatrix} &= (-1)^{S-M} \left[\frac{(S-M)(S+M)}{S(2S+1)(2S-1)} \right]^{1/2} \\
 \begin{pmatrix} (S-1) & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} &= (-1)^{S-M} \left[\frac{(S+M)(S-1+M)}{2S(2S+1)(2S-1)} \right]^{1/2}
 \end{aligned}$$

The structure of the Zeeman matrix (which is Hermitean) is exemplified for the case of $S_1 = S_2 = S_3 = 1/2$ as follows

$$\mathbf{H}^Z = \left(\begin{array}{cccc|cccc} a_0 & a_+^* & 0 & 0 & c_+^* & 0 & d_+^* & 0 \\ a_+ & a_0 & a_+^* & 0 & c_0 & c_+^* & d_0 & d_+^* \\ 0 & a_+ & a_0 & a_+^* & c_-^* & c_0 & d_-^* & d_0 \\ 0 & 0 & a_+ & a_0 & 0 & c_-^* & 0 & d_-^* \\ \hline c_+ & c_0 & c_- & 0 & a_0 & a_+^* & b_0 & b_+^* \\ 0 & c_+ & c_0 & c_- & a_+ & a_0 & b_-^* & b_0 \\ \hline d_+ & d_0 & d_- & 0 & b_0 & b_-^* & a_0 & a_+^* \\ 0 & d_+ & d_0 & d_- & b_+ & b_0 & a_+ & a_0 \end{array} \right)$$

for

$$\left[\begin{array}{l} S_{12} = 1 \quad S = 3/2 \quad M = -3/2 \\ \quad \quad \quad M = -1/2 \\ \quad \quad \quad M = +1/2 \\ \quad \quad \quad M = +3/2 \\ \hline S_{12} = 1 \quad S = 1/2 \quad M = -1/2 \\ \quad \quad \quad M = +1/2 \\ \hline S_{12} = 0 \quad S = 1/2 \quad M = -1/2 \\ \quad \quad \quad M = +1/2 \end{array} \right]$$

Here the letters indicate a type of reduced matrix element (common within a block); the lower indices indicate different angular parts (different $3j$ -symbols) determined by the application of the Wigner-Eckart theorem.

The above formula for the matrix elements of the Zeeman operator has a general validity irrespective of strong or weak exchange limits. Of frequent interest is the case of the strong exchange limit when the total spin S becomes a proper quantum number.

The Zeeman operator can be transformed to the form

$$\hat{H}^Z = \mu_B \vec{B} \cdot \vec{g}_S \cdot \vec{S} [\hbar^{-1}]$$

with the molecular-state g -tensor defined as

$$\vec{g}_S = c_1 \vec{g}_1 + c_2 \vec{g}_2 + c_3 \vec{g}_3$$

The combination coefficients can be expressed with the use of the replacement theorem as follows

$$c_i = \frac{\langle S_1 S_2 S'_1 S'_2 S'_3 S' | \hat{T}_1(\vec{S}_i) | S_1 S_2 S_1 S_2 S_3 S \rangle}{\langle S_1 S_2 S'_1 S'_2 S'_3 S' | \hat{T}_1(\vec{S}) | S_1 S_2 S_1 S_2 S_3 S \rangle} = \frac{R_i}{R}, \quad [\text{for } i = 1, 2, 3]$$

This formula is applicable only for $S' = S$ since the reduced matrix element of the total spin is diagonal

$$R \equiv \left\langle \dots S' \left\| \hat{T}_1(\vec{S}) \right\| \dots S \right\rangle = \delta_{S,S'} [S(S+1)(2S+1)]^{1/2} [\hbar]$$

and thus

$$c_i = \frac{R_i}{[S(S+1)(2S+1)]^{1/2} [\hbar]} \delta_{S,S'}$$

The expressions for R_i were collected in Table 11.5 (for $S' \neq S$ a different treatment will be used). Some numerical examples are included in Table 11.6. As the individual spins are added to yield the total spin

$$\hat{T}_1(\vec{S}_1) + \hat{T}_1(\vec{S}_2) + \hat{T}_1(\vec{S}_3) = \hat{T}_1(\vec{S})$$

then the combination coefficients obey the relationship

$$c_1 + c_2 + c_3 = 1$$

A more convenient way of evaluating the combination coefficients is the recursion scheme: two spins are added first

$$\bar{\bar{g}}_{12} = c_1(S_1 S_2 S_{12}) \bar{\bar{g}}_1 + c_2(S_1 S_2 S_{12}) \bar{\bar{g}}_2$$

and then the next spin is added

$$\begin{aligned} \bar{\bar{g}}_S &= c_1(S_{12} S_3 S) \bar{\bar{g}}_{12} + c_2(S_{12} S_3 S) \bar{\bar{g}}_3 \\ &= c_1(S_{12} S_3 S) [c_1(S_1 S_2 S_{12}) \bar{\bar{g}}_1 + c_2(S_1 S_2 S_{12}) \bar{\bar{g}}_2] + c_2(S_{12} S_3 S) \bar{\bar{g}}_3 \\ &= c_1(S_1 S_2 S_{12} S_3 S) \bar{\bar{g}}_1 + c_2(S_1 S_2 S_{12} S_3 S) \bar{\bar{g}}_2 + c_3(S_1 S_2 S_{12} S_3 S) \bar{\bar{g}}_3 \end{aligned}$$

so that one gets the combination coefficients of a triple as a product of the pair-interaction combination coefficients

$$c_1(S_1 S_2 S_{12} S_3 S) = c_1(S_{12} S_3 S) \cdot c_1(S_1 S_2 S_{12})$$

$$c_2(S_1 S_2 S_{12} S_3 S) = c_1(S_{12} S_3 S) \cdot c_2(S_1 S_2 S_{12})$$

$$c_3(S_1 S_2 S_{12} S_3 S) = c_2(S_{12} S_3 S)$$

TABLE 11.6

Combination coefficients of the a-type for the molecular-state g -tensor and D -tensor for selected triads [1,3]

S_1	S_2	S_3	S_{12}	S	c_1	c_2	c_3	C_1	C_2	C_3	C_{12}	C_{13}	C_{23}
1/2	1/2	1/2	1	3/2	1/3	1/3	1/3	0	0	0	1/6	1/6	1/6
				1/2	2/3	2/3	-1/3	0	0	0	0	0	0
				1/2	0	0	1	0	0	0	0	0	0
1/2	1/2	1	1	2	1/4	1/4	1/2	0	0	1/6	1/12	1/6	1/6
				1	1/4	1/4	1/2	0	0	-1/2	-1/4	1/2	1/2
				0	0	0	0	0	0	0	0	0	0
				1	0	0	1	0	0	1	0	0	0
1/2	1/2	3/2	1	5/2	1/5	1/5	3/5	0	0	3/10	1/20	3/20	3/20
				3/2	2/15	2/15	11/15	0	0	1/5	-2/15	4/15	4/15
				1/2	-1/3	-1/3	5/3	0	0	0	0	0	0
				3/2	0	0	1	0	0	1	0	0	0
1/2	1/2	2	1	3	1/6	1/6	2/3	0	0	2/5	1/30	2/15	2/15
				2	1/12	1/12	10/12	0	0	1/2	-1/12	1/6	1/6
				1	-1/4	-1/4	3/2	0	0	21/10	1/20	-3/10	-3/10
				2	0	0	1	0	0	1	0	0	0
1/2	1/2	5/2	1	7/2	1/7	1/7	5/7	0	0	10/21	1/42	5/42	5/42
				5/2	2/35	2/35	31/35	0	0	23/35	-2/35	4/35	4/35
				3/2	-1/5	-1/5	7/5	0	0	28/15	1/30	-7/30	-7/30
				5/2	0	0	1	0	0	1	0	0	0
1	1	1	2	3	1/3	1/3	1/3	1/15	1/15	1/15	2/15	2/15	2/15
				2	5/12	5/12	1/6	1/12	1/12	-1/6	1/6	1/6	1/6
				1	3/4	3/4	-1/2	7/20	7/20	1/10	7/10	-3/10	-3/10
			1	2	1/4	1/4	1/2	-1/12	-1/12	1/6	1/6	1/6	1/6
				1	1/4	1/4	1/2	1/4	1/4	-1/2	-1/2	1/2	1/2
				0	0	0	0	0	0	0	0	0	0
			0	1	0	0	1	0	0	1	0	0	0

This result can be proven analytically: the triad coefficient is defined through

$$c_1(S_1 S_2 S_{12} S_3 S) = [S(S+1)(2S+1)]^{-1/2} \\ \times [(2S_{12}+1)(2S_{12}+1)]^{1/2} [(2S+1)(2S+1)]^{1/2} [S_1(S_1+1)(2S_1+1)]^{1/2} \\ \times (-1)^{S_1+1+S_2+S_{12}} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_{12} & S_{12} & S_2 \end{Bmatrix} (-1)^{S_{12}+1+S_3+S} \begin{Bmatrix} S_{12} & S_{12} & 1 \\ S & S & S_3 \end{Bmatrix}$$

whereas the pair-interaction coefficients are expressed as follows

$$c_1(S_1 S_2 S_{12}) = \frac{\langle S_1 S_2 S_{12} \| \vec{S}_1 \| S_1 S_2 S_{12} \rangle}{\langle S_1 S_2 S_{12} \| \vec{S}_{12} \| S_1 S_2 S_{12} \rangle} \\ = \frac{[S_1(S_1+1)(2S_1+1)]^{1/2}}{[S_{12}(S_{12}+1)(2S_{12}+1)]^{1/2}} (2S_{12}+1)(-1)^{S_1+S_2+S_{12}+1} \\ \times \begin{Bmatrix} S_1 & S_1 & 1 \\ S_{12} & S_{12} & S_2 \end{Bmatrix} \\ = \frac{S_{12}(S_{12}+1) + S_1(S_1+1) - S_2(S_2+1)}{2S_{12}(S_{12}+1)}$$

and

$$c_1(S_{12} S_3 S) = \frac{\langle S_{12} S_3 S \| \vec{S}_{12} \| S_{12} S_3 S \rangle}{\langle S_{12} S_3 S \| \vec{S} \| S_{12} S_3 S \rangle} \\ = \frac{[S_{12}(S_{12}+1)(2S_{12}+1)]^{1/2}}{[S(S+1)(2S+1)]^{1/2}} (2S+1)(-1)^{S_{12}+S_3+S+1} \\ \times \begin{Bmatrix} S_{12} & S_{12} & 1 \\ S & S & S_3 \end{Bmatrix} \\ = \frac{S(S+1) + S_{12}(S_{12}+1) - S_3(S_3+1)}{2S(S+1)}$$

An analogous expression holds true for the second triad coefficient $c_2(S_1 S_2 S_{12} S_3 S)$. For example, for $S_1 = S_2 = S_3 = 1$, $S_{12} = 2$ and $S = 2$, with the help of Table 10.12, we get the result

$$c_1(1, 1, 2, 1, 2) = c_1(2, 1, 2) \cdot c_1(1, 1, 2) = (5/6) \cdot (1/2) = 5/12$$

$$c_2(1, 1, 2, 1, 2) = c_1(2, 1, 2) \cdot c_2(1, 1, 2) = (5/6) \cdot [1 - (1/2)] = 5/12$$

$$c_3(1, 1, 2, 1, 2) = c_2(2, 1, 2) = [1 - (5/6)] = 1/6$$

which is contained in Table 11.6.

The matrix elements of the Zeeman operator take the form

$$\begin{aligned}
 H_{IJ}^Z(a; b) &\equiv H_{S'_{12}SM', S_{12}SM}^Z \\
 &= \left\langle S_1 S_2 S'_{12} S_3 SM' \left| \mu_B \vec{B} \cdot \vec{g}_S \cdot \vec{S} [\hbar^{-1}] \right| S_1 S_2 S_{12} S_3 SM \right\rangle \\
 &= \mu_B [\hbar^{-1}] \vec{B} \cdot \vec{g}_S \cdot \left\langle S_1 S_2 S'_{12} S_3 SM' \left| \vec{S} \right| S_1 S_2 S_{12} S_3 SM \right\rangle
 \end{aligned}$$

Prior to the application of the Wigner–Eckart theorem the Zeeman operator should be transformed into spherical components. Assuming that the g_S -tensor is diagonal, with components $g_{S,x}$, $g_{S,y}$ and $g_{S,z}$, then the scalar product is expanded

$$\begin{aligned}
 (\vec{B} \cdot \vec{g}_S) \cdot \vec{S} &= \vec{G} \cdot \vec{S} = -G_{1,+1} \hat{S}_{1,-1} + G_{1,0} \hat{S}_{1,0} - G_{1,-1} \hat{S}_{1,+1} \\
 &= \sum_{q=-1}^{+1} (-1)^q G_{1,-q} \hat{S}_{1,q}
 \end{aligned}$$

with the spherical transform

$$\begin{aligned}
 G_{1,+1} &= -\frac{1}{\sqrt{2}} (B_x g_{S,x} + i B_y g_{S,y}) \\
 G_{1,-1} &= \frac{1}{\sqrt{2}} (B_x g_{S,x} - i B_y g_{S,y}) \\
 G_{1,0} &= B_z g_{S,z}
 \end{aligned}$$

Then the matrix elements of the Zeeman operator for $S' = S$ become

$$H_{IJ}^Z(a; b) = \mu_B [\hbar^{-1}] \sum_{q=-1}^{+1} (-1)^q G_{1,-q} \left\langle S_1 S_2 S'_{12} S_3 SM' \left| \hat{S}_q \right| S_1 S_2 S_{12} S_3 SM \right\rangle$$

and when the Wigner–Eckart theorem is applied

$$\begin{aligned}
 H_{IJ}^Z(a; b) &= \mu_B [\hbar^{-1}] \left\langle S_1 S_2 S'_{12} S_3 S \left\| \vec{S} \right\| S_1 S_2 S_{12} S_3 S \right\rangle \left[(-1) G_{1,+1} (-1)^{S-M'} \right. \\
 &\quad \times \begin{pmatrix} S & 1 & S \\ -M' & -1 & M \end{pmatrix} \\
 &\quad + G_{1,0} (-1)^{S-M'} \begin{pmatrix} S & 1 & S \\ -M' & 0 & M \end{pmatrix} + (-1) G_{1,-1} (-1)^{S-M'} \\
 &\quad \left. \times \begin{pmatrix} S & 1 & S \\ -M' & +1 & M \end{pmatrix} \right]
 \end{aligned}$$

In terms of Cartesian components they are

$$\begin{aligned}
 H_{IJ}^Z(a; b) = & \mu_B [S(S+1)(2S+1)]^{1/2} \\
 & \times \left[\frac{1}{\sqrt{2}} (B_x g_{S,x} + i B_y g_{S,y}) (-1)^{S-M'} \begin{pmatrix} S & 1 & S \\ -M' & -1 & M \end{pmatrix} \right. \\
 & + B_z g_{S,z} (-1)^{S-M'} \begin{pmatrix} S & 1 & S \\ -M' & 0 & M \end{pmatrix} \\
 & \left. - \frac{1}{\sqrt{2}} (B_x g_{S,x} - i B_y g_{S,y}) (-1)^{S-M'} \begin{pmatrix} S & 1 & S \\ -M' & +1 & M \end{pmatrix} \right]
 \end{aligned}$$

The triangular condition for the non-zero $3j$ -symbols implies $M' = M, M \pm 1$. Thus the matrix elements fill the places at the diagonal ($g_{S,z}$ -component, $q = 0, M' = M$) and adjacent to the diagonal ($g_{S,x}$ - and $g_{S,y}$ -components, $q = \pm 1, M' = \pm 1$) for each block of $S' = S$.

For the case of $S' = S - 1$ a different treatment is necessary. Analogously to the case of binuclear systems, the Zeeman operator couples states of different spin. The product, involving the molecular-state g -tensor, can be rewritten as follows

$$\begin{aligned}
 \bar{g}_S \cdot \vec{S} = & \bar{g}_3 \cdot (\vec{S}_1 + \vec{S}_2 + \vec{S}_3) + (\bar{g}_2 - \bar{g}_3) \cdot (\vec{S}_1 + \vec{S}_2) + (\bar{g}_1 - \bar{g}_2) \cdot \vec{S}_1 \\
 = & \bar{g}_3 \cdot \vec{S} + (\bar{g}_2 - \bar{g}_3) \cdot \vec{S}_{12} + (\bar{g}_1 - \bar{g}_2) \cdot \vec{S}_1
 \end{aligned}$$

Then its matrix elements become

$$\begin{aligned}
 \bar{g}_S \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \right| \vec{S} \left| S_1 S_2 S_{12} S_3 S M \right\rangle \\
 = \bar{g}_3 \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \right| \vec{S} \left| S_1 S_2 S_{12} S_3 S M \right\rangle \\
 + (\bar{g}_2 - \bar{g}_3) \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \right| \vec{S}_{12} \left| S_1 S_2 S_{12} S_3 S M \right\rangle \\
 + (\bar{g}_1 - \bar{g}_2) \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \right| \vec{S}_1 \left| S_1 S_2 S_{12} S_3 S M \right\rangle
 \end{aligned}$$

and the Zeeman term can be written as

$$\begin{aligned}
 H_{IJ}^Z(c; d) \equiv & H_{S'_{12} S' M', S_{12} S M}^Z \\
 = & \mu_B \vec{B} \cdot \bar{g}_S \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \right| \vec{S} \left| S_1 S_2 S_{12} S_3 S M \right\rangle [\hbar^{-1}] \\
 = & \mu_B \vec{B} \cdot \left[\bar{g}_3 \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \right| \vec{S} \left| S_1 S_2 S_{12} S_3 S M \right\rangle \right. \\
 & + (\bar{g}_2 - \bar{g}_3) \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \right| \vec{S}_{12} \left| S_1 S_2 S_{12} S_3 S M \right\rangle \\
 & \left. + (\bar{g}_1 - \bar{g}_2) \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \right| \vec{S}_1 \left| S_1 S_2 S_{12} S_3 S M \right\rangle \right] [\hbar^{-1}]
 \end{aligned}$$

The first term vanishes exactly for the off-diagonal matrix elements ($S' \neq S$) so that

$$H_{IJ}^Z(c; d) = \mu_B \vec{B} \cdot \left[(\bar{g}_2 - \bar{g}_3) \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \left| \vec{S}_{12} \right| S_1 S_2 S_{12} S_3 S M \right\rangle \right. \\ \left. + (\bar{g}_1 - \bar{g}_2) \cdot \left\langle S_1 S_2 S'_{12} S_3 S' M' \left| \vec{S}_1 \right| S_1 S_2 S_{12} S_3 S M \right\rangle \right] [\hbar^{-1}]$$

The transformation into spherical coordinates will need an introduction of two g -tensors, hence

$$g' = \bar{g}_1 - \bar{g}_2 \\ g'' = \bar{g}_2 - \bar{g}_3$$

so that two spherical vectors appear

$$G'_{1,+1} = -\frac{1}{\sqrt{2}}(B_x g'_x + i B_y g'_y) \\ G'_{1,-1} = \frac{1}{\sqrt{2}}(B_x g'_x - i B_y g'_y) \\ G'_{1,0} = B_z g'_z$$

and

$$G''_{1,+1} = -\frac{1}{\sqrt{2}}(B_x g''_x + i B_y g''_y) \\ G''_{1,-1} = \frac{1}{\sqrt{2}}(B_x g''_x - i B_y g''_y) \\ G''_{1,0} = B_z g''_z$$

yielding the off-diagonal Zeeman term in the form

$$H_{IJ}^Z(c; d) = \mu_B [\hbar^{-1}] \sum_{q=-1}^{+1} \left[(-1)^q G''_{1,-q} \right. \\ \times \left\langle S_1 S_2 S'_{12} S_3 S' M' \left| \hat{S}_{12,q} \right| S_1 S_2 S_{12} S_3 S M \right\rangle \\ \left. + (-1)^q G'_{1,-q} \left\langle S_1 S_2 S'_{12} S_3 S' M' \left| \hat{S}_{1,q} \right| S_1 S_2 S_{12} S_3 S M \right\rangle \right]$$

After the application of the Wigner–Eckart theorem one gets

$$H_{IJ}^Z(c; d) = \mu_B [\hbar^{-1}] \sum_{q=-1}^{+1} (-1)^q (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} \\ \times \left[G''_{1,-q} \langle S_1 S_2 S'_{12} S_3 S' \| \vec{S}_{12} \| S_1 S_2 S_{12} S_3 S \rangle \right. \\ \left. + G'_{1,-q} \langle S_1 S_2 S'_{12} S_3 S' \| \vec{S}_1 \| S_1 S_2 S_{12} S_3 S \rangle \right]$$

The reduced matrix element of the constituent spin operator

$$R_1 \equiv \langle S_1 S_2 S'_{12} S_3 S' \| \vec{S}_1 \| S_1 S_2 S_{12} S_3 S \rangle$$

has already been evaluated (Table 11.5) and it holds true that

$$R_{12} \equiv \langle S_1 S_2 S'_{12} S_3 S' \| \vec{S}_{12} \| S_1 S_2 S_{12} S_3 S \rangle \\ = \langle S_1 S_2 S'_{12} S_3 S' \| \vec{S}_1 \| S_1 S_2 S_{12} S_3 S \rangle \\ + \langle S_1 S_2 S'_{12} S_3 S' \| \vec{S}_2 \| S_1 S_2 S_{12} S_3 S \rangle = R_1 + R_2$$

Consequently

$$H_{IJ}^Z(c; d) = \mu_B [\hbar^{-1}] \sum_{q=-1}^{+1} (-1)^q (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} \\ \times [G''_{1,-q}(R_1 + R_2) + G'_{1,-q}R_1]$$

where the reduced matrix element R_3 does not occur, in accordance with its zero value for $S' \neq S$. The final matrix elements of the Zeeman operator are collected in Table 11.7.

We have seen that the construction of the Zeeman operator matrix for a general triad is a complex task: the Zeeman perturbation couples the states of the adjacent total spins and the states of the adjacent intermediate spins. Under certain assumptions, however, it can be considerably simplified.

Let us assume an equilateral triangle of the ABA type. Then the isotropic exchange matrix is diagonal with matrix elements, $\varepsilon_{S,S_{12}}^{(0)}$, given by Tables 11.3 and 11.4. The molecular-state g -tensors, $\bar{g}_{S,S_{12}}$, are easily constructed from the local g -tensors with the help of the combination coefficients collected in Tables 11.5 and 11.6. Since $S_1 = S_2 = S_A$ and $S_3 = S_B$, then

$$\bar{g}_{S,S_{12}} = \{\bar{g}_A[S(S+1) + S_{12}(S_{12}+1) - S_B(S_B+1)] \\ + \bar{g}_B[S(S+1) - S_{12}(S_{12}+1) + S_B(S_B+1)]\}/[2S(S+1)]$$

TABLE 11.7

Matrix elements of the Zeeman operator for a general triad^a

$$\begin{aligned}
H_{S_{12}, S, M'; S_{12}, S, M}^Z(a) &= \mu_B \sum_{q=-1}^{+1} (-1)^q G_{(a)1, -q} (-1)^{S-(M+q)} \begin{pmatrix} S & 1 & S \\ -(M+q) & q & M \end{pmatrix} [S(S+1)(2S+1)]^{1/2} \\
H_{S_{12}-1, S, M'; S_{12}, S, M}^Z(b) &= \mu_B \sum_{q=-1}^{+1} (-1)^q G_{(b)1, -q} (-1)^{S-(M+q)} \begin{pmatrix} S & 1 & S \\ -(M+q) & q & M \end{pmatrix} [S(S+1)(2S+1)]^{1/2} \\
H_{S_{12}, S-1, M'; S_{12}, S, M}^Z(c) &= \mu_B \sum_{q=-1}^{+1} (-1)^q (-1)^{(S-1)-(M+q)} \begin{pmatrix} S-1 & 1 & S \\ -(M+q) & q & M \end{pmatrix} \\
&\times \left[G'_{(c)1, -q} \frac{S_2(S_2+1) - S_1(S_1+1) - S_{12}(S_{12}+1)}{2S_{12}(S_{12}+1)} - G''_{(c)1, -q} \right] \frac{1}{2(S)^{1/2}} \\
&\times [(S+S_{12}-S_3)(S-S_{12}+S_3)(1-S+S_{12}+S_3)(1+S+S_{12}+S_3)]^{1/2} \\
H_{S_{12}-1, S-1, M'; S_{12}, S, M}^Z(d) &= \mu_B \sum_{q=-1}^{+1} (-1)^q (-1)^{(S-1)-(M+q)} \begin{pmatrix} S-1 & 1 & S \\ -(M+q) & q & M \end{pmatrix} G'_{(d)1, -q} \\
&\times \frac{-1}{4S_{12}[S(2S_{12}+1)(2S_{12}-1)]^{1/2}} \\
&\times [(S+S_{12}-S_3)(-1+S+S_{12}-S_3)(S+S_{12}+S_3)(1+S+S_{12}+S_3)]^{1/2} \\
&\times [(S_1+S_{12}-S_2)(1+S_1-S_{12}+S_2)(-S_1+S_{12}+S_2)(1+S_1+S_{12}+S_2)]^{1/2}
\end{aligned}$$

^aThe molecular g -tensors are: $\bar{g}_S = c_1 \bar{g}_1 + c_2 \bar{g}_2 + c_3 \bar{g}_3$; $\bar{g}' = \bar{g}_1 - \bar{g}_2$ and $\bar{g}'' = \bar{g}_2 - \bar{g}_3$. The magnetogyric vectors are: $\vec{G} = \vec{B} \cdot \bar{g}_S$; $\vec{G}' = \vec{B} \cdot \bar{g}'$; $\vec{G}'' = \vec{B} \cdot \bar{g}''$ with the spherical components $G_{1,0} = B_z g_{S,z}$, $G_{1,+1} = -(1/\sqrt{2})(B_x g_{S,x} + i B_y g_{S,y})$ and $G_{1,-1} = (1/\sqrt{2})(B_x g_{S,x} - i B_y g_{S,y})$; $\vec{G}_{(x)} = \vec{B} \cdot \bar{g}_{(S_{12}S'; S_{12}S)}$.

When the coupling of states of adjacent total spins and adjacent intermediate spins is neglected, the Zeeman matrix is diagonal

$$H_{S_{12}SM; S_{12}SM}^Z = \mu_B B g_{S, S_{12}} \left\langle \dots S_{12}SM \left| \hat{S}_z \right| \dots S_{12}SM \right\rangle$$

giving rise only to the first-order van Vleck coefficients

$$\varepsilon_S^{(1)} = \mu_B g_{S, S_{12}} M$$

Consequently the application of the van Vleck equation yields an analytic formula for the magnetic susceptibility in the form of

$$\bar{\chi}_{\text{mol}} = \frac{N_A \mu_0 \mu_B^2}{kT} \frac{\sum_{S_{12}=0}^{2S_A} \sum_{S=|S_{12}-S_B|}^{S_{12}+S_B} \frac{S(S+1)}{3} g_{S,S_{12}}^2 (2S+1) \exp(-\varepsilon_{S,S_{12}}/kT)}{\sum_{S_{12}=0}^{2S_A} \sum_{S=|S_{12}-S_B|}^{S_{12}+S_B} (2S+1) \exp(-\varepsilon_{S,S_{12}}/kT)}$$

Let us carry out a modelling for the linear cluster $\text{Mn}^{\text{II}}\text{--Cu}^{\text{II}}\text{--Mn}^{\text{II}}$: $S_{\text{Mn}} = 5/2$ and $S_{\text{Cu}} = 1/2$ with $J_{\text{Cu--Mn}} = J$ and $J_{\text{Mn--Mn}} = 0$. The zero-field energies and the molecular-state g -factors are collected in Table 11.8. The corresponding plot of the product function is shown in Fig. 11.3. For an antiferromag-

TABLE 11.8
Energy levels of a linear $\text{Mn}^{\text{II}}\text{--Cu}^{\text{II}}\text{--Mn}^{\text{II}}$ cluster

S	S_{12}	$\varepsilon_{S,S_{12}}$	$g_{S,S_{12}}$
9/2	5	0	$(12g_{\text{Mn}} - g_{\text{Cu}})/11$
11/2	5	$-(11/2)J$	$(10g_{\text{Mn}} + g_{\text{Cu}})/11$
7/2	4	$-(1/2)J$	$(10g_{\text{Mn}} - g_{\text{Cu}})/9$
9/2	4	$-5J$	$(8g_{\text{Mn}} + g_{\text{Cu}})/9$
5/2	3	$-J$	$(8g_{\text{Mn}} - g_{\text{Cu}})/7$
7/2	3	$-(9/2)J$	$(6g_{\text{Mn}} + g_{\text{Cu}})/7$
3/2	2	$-(3/2)J$	$(6g_{\text{Mn}} - g_{\text{Cu}})/5$
5/2	2	$-4J$	$(4g_{\text{Mn}} + g_{\text{Cu}})/5$
1/2	1	$-2J$	$(4g_{\text{Mn}} - g_{\text{Cu}})/3$
3/2	1	$-(7/2)J$	$(2g_{\text{Mn}} + g_{\text{Cu}})/3$
1/2	0	$-3J$	g_{Cu}

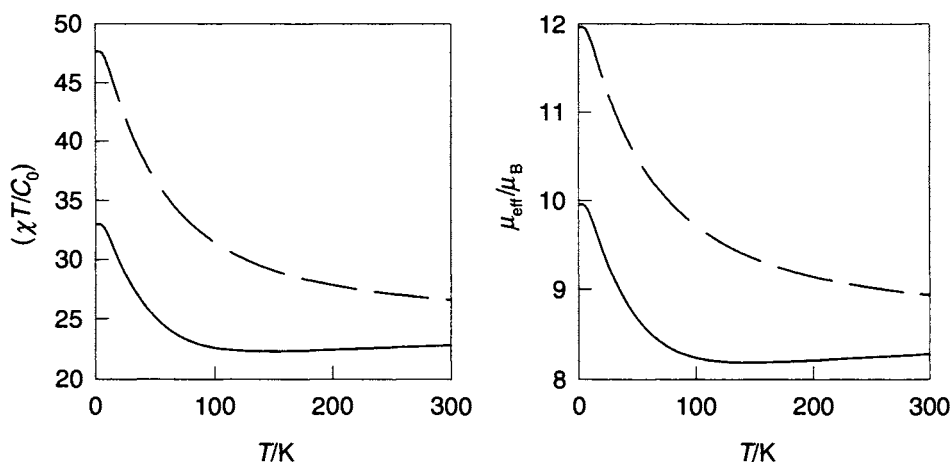


Fig. 11.3. Temperature variation of the product function and the effective magnetic moment for the linear $\text{Mn}^{\text{II}}\text{--Cu}^{\text{II}}\text{--Mn}^{\text{II}}$ cluster: $g_{\text{Mn}} = g_{\text{Cu}} = 2$, solid— $J/k = -50$ K, dashed— $J/k = +50$ K.

netic coupling the ground state is $S = 9/2$ and thus the (spin-only) effective magnetic moment

$$\mu_{\text{eff}}/\mu_B = 2\sqrt{S(S+1)}$$

reaches the value of $\mu_{\text{eff}}/\mu_B = 9.95$ near zero temperature when no other interactions assist. On temperature increase the magnetically less productive states are populated, as evidenced from Fig. 11.2 (for $J < 0$ the diagram is inverted). For $J/k = -50$ K the singlet state, which is magnetically unproductive, lies at the level $-3J = 150k$ K above the ground state and consequently the product function, χT , passes through a minimum. On further temperature increase again magnetically more productive states are populated and the product function increases up to a limiting (HT) value which is the sum of the contributions of the isolated centres

$$(\chi T/C_0)_{\text{HT}} = \sum_A \frac{S_A(S_A+1)}{3} g_A^2 = 2 \cdot \frac{1}{3} \cdot \frac{5}{2} \cdot \frac{7}{2} g_{\text{Mn}}^2 + \frac{1}{3} \cdot \frac{1}{2} \cdot \frac{3}{2} g_{\text{Cu}}^2 \approx 24.3$$

11.2.3 Asymmetric exchange

The Hamiltonian of the asymmetric exchange contains the local D -tensor terms as well as the pair-interaction D -tensors, hence

$$\begin{aligned} \hat{H}^{\text{asym}} = & [\vec{S}_1 \cdot \vec{\bar{D}}_1 \cdot \vec{S}_1 + \vec{S}_2 \cdot \vec{\bar{D}}_2 \cdot \vec{S}_2 + \vec{S}_3 \cdot \vec{\bar{D}}_3 \cdot \vec{S}_3 \\ & + \vec{S}_1 \cdot \vec{\bar{D}}_{12} \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{\bar{D}}_{13} \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{\bar{D}}_{23} \cdot \vec{S}_3] [\hbar^{-2}] \end{aligned}$$

Each D -tensor is symmetric and traceless, thus having five independent components. In fact, it represents an irreducible second-rank tensor since it holds true that

$$\begin{aligned} \vec{S}_i \cdot \vec{\bar{D}} \cdot \vec{S}_j &= \sqrt{5} [D_2 \cdot \hat{T}_2(\vec{S}_i \otimes \vec{S}_j)] \\ &= \sqrt{5} [\hat{T}_0(D_2 \otimes \hat{T}_2(\vec{S}_i \otimes \vec{S}_j))] = D_{2,+2} \hat{T}_{2,-2}(\vec{S}_i \otimes \vec{S}_j) \\ &\quad - D_{2,+1} \hat{T}_{2,-1}(\vec{S}_i \otimes \vec{S}_j) + D_{2,0} \hat{T}_{2,0}(\vec{S}_i \otimes \vec{S}_j) \\ &\quad - D_{2,-1} \hat{T}_{2,+1}(\vec{S}_i \otimes \vec{S}_j) + D_{2,-2} \hat{T}_{2,+2}(\vec{S}_i \otimes \vec{S}_j) \\ &= \sum_{q=-2}^{+2} (-1)^q D_{2,-q} \hat{T}_{2,q}(\vec{S}_i \otimes \vec{S}_j) \end{aligned}$$

and the scalar product runs over five spherical components. The Cartesian and spherical components of the D -tensor are related through the formulae (Table 1.13)

$$D_{2,2} = \frac{1}{2}[(D_{xx} - D_{yy}) + i(D_{xy} + D_{yx})] \rightarrow \frac{1}{2}(D_{xx} - D_{yy}) = E$$

$$D_{2,1} = -\frac{1}{2}[(D_{xz} + D_{zx}) + i(D_{yz} + D_{zy})] \rightarrow 0$$

$$\begin{aligned} D_{2,0} &= \frac{1}{\sqrt{6}}(2D_{zz} - D_{xx} - D_{yy}) \\ &= \frac{1}{\sqrt{6}}[3D_{zz} - (D_{xx} + D_{yy} + D_{zz})] \rightarrow \frac{3}{\sqrt{6}}D_{zz} = \frac{2}{\sqrt{6}}D \end{aligned}$$

$$D_{2,-1} = \frac{1}{2}[(D_{xz} + D_{zx}) - i(D_{yz} + D_{zy})] \rightarrow 0$$

$$D_{2,-2} = \frac{1}{2}[(D_{xx} - D_{yy}) - i(D_{xy} + D_{yx})] \rightarrow \frac{1}{2}(D_{xx} - D_{yy}) = E$$

where the simplifications (denoted as $\rightarrow$) are obtained for the traceless diagonal D -tensor so that only two parameters survive:

$$D = \frac{3}{2}D_{zz}$$

is the axial zero-field splitting parameter and

$$E = \frac{1}{2}(D_{xx} - D_{yy})$$

is the rhombic zero-field splitting parameter.

For a general evaluation of the matrix elements of the asymmetric exchange operator we need the reduced matrix elements

$$R_{ij(S'_1S'_2S'_3;S_1S_2)} \equiv \langle S_1S_2S'_1S'_2S'_3 | \hat{T}_2(\vec{S}_i \otimes \vec{S}_j) | S_1S_2S_1S_2S_3 \rangle$$

The tensor ranks for the decoupling formula are assigned as follows

	k_1	k_2	k_{12}	k_3	k
$\hat{T}_2(\vec{S}_1 \otimes \vec{S}_1)$	2	0	2	0	2
$\hat{T}_2(\vec{S}_2 \otimes \vec{S}_2)$	0	2	2	0	2
$\hat{T}_2(\vec{S}_3 \otimes \vec{S}_3)$	0	0	0	2	2
$\hat{T}_2(\vec{S}_1 \otimes \vec{S}_2)$	1	1	2	0	2
$\hat{T}_2(\vec{S}_1 \otimes \vec{S}_3)$	1	0	1	1	2
$\hat{T}_2(\vec{S}_2 \otimes \vec{S}_3)$	0	1	1	1	2

and then

$$\begin{aligned}
 R_{11} &= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 2 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 2 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 2 \end{Bmatrix} \\
 &\quad \times \langle S_1 \| \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 2 + 1)]^{1/2} \\
 &\quad \times \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S_3 & S_3 & 0 \\ S' & S & 2 \end{Bmatrix} \langle S_2 \| \hat{T}_0(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_0(\vec{S}_3) \| S_3 \rangle \\
 R_{22} &= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 2 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 2 \\ S'_{12} & S_{12} & 2 \end{Bmatrix} \\
 &\quad \times \langle S_1 \| \hat{T}_0(\vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 2 + 1)]^{1/2} \\
 &\quad \times \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S_3 & S_3 & 0 \\ S' & S & 2 \end{Bmatrix} \langle S_2 \| \hat{T}_2(\vec{S}_2 \otimes \vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_0(\vec{S}_3) \| S_3 \rangle \\
 R_{33} &= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 0 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 0 \end{Bmatrix} \\
 &\quad \times \langle S_1 \| \hat{T}_0(\vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 2 + 1)]^{1/2} \\
 &\quad \times \begin{Bmatrix} S'_{12} & S_{12} & 0 \\ S_3 & S_3 & 2 \\ S' & S & 2 \end{Bmatrix} \langle S_2 \| \hat{T}_0(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_2(\vec{S}_3 \otimes \vec{S}_3) \| S_3 \rangle
 \end{aligned}$$

$$R_{12} = [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 2 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 1 \\ S'_{12} & S_{12} & 2 \end{Bmatrix} \\ \times \langle S_1 \| \hat{T}_1(\vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 2 + 1)]^{1/2} \\ \times \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S_3 & S_3 & 0 \\ S' & S & 2 \end{Bmatrix} \langle S_2 \| \hat{T}_1(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_0(\vec{S}_3) \| S_3 \rangle$$

$$R_{13} = [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\ \times \langle S_1 \| \hat{T}_1(\vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 2 + 1)]^{1/2} \\ \times \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 1 \\ S' & S & 2 \end{Bmatrix} \langle S_2 \| \hat{T}_0(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_1(\vec{S}_3) \| S_3 \rangle$$

$$R_{23} = [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 1 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\ \times \langle S_1 \| \hat{T}_0(\vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 2 + 1)]^{1/2} \\ \times \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 1 \\ S' & S & 2 \end{Bmatrix} \langle S_2 \| \hat{T}_1(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_1(\vec{S}_3) \| S_3 \rangle$$

As the $9j$ -symbols containing one zero collapse in to $6j$ -symbols, the formulae are somewhat simplified, for example

$$R_{11} = (-1)^{2S_1+2S_2+S'_{12}+S_{12}+4} (-1)^{S'_{12}+S_{12}+S'+S+2S_3+4} \\ \times [(2S'_{12} + 1)(2S_{12} + 1)5]^{1/2} (-1)^{S_1+S'_{12}+2+S_2} \\ \times [(2 \cdot 2 + 1)(2S_2 + 1)]^{-1/2} \begin{Bmatrix} S_1 & S_1 & 2 \\ S_{12} & S'_{12} & S_2 \end{Bmatrix} \\ \times [(2S' + 1)(2S + 1)5]^{1/2} (-1)^{S_{12}+S'+2+S_3} \\ \times [(2 \cdot 2 + 1)(2S_3 + 1)]^{-1/2} \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S & S' & S_3 \end{Bmatrix} \\ \times [S_1(S_1 + 1)(2S_1 + 1)(2S_1 - 1)(2S_1 + 3)/6]^{1/2} \\ \times (2S_2 + 1)^{1/2} (2S_3 + 1)^{1/2} [\hbar^2]$$

The first two sign factors are associated with permutations of rows in the $9j$ -symbols. Analogous simplifications are possible for the other reduced matrix elements; the final formulae are collected in Table 11.9.

The formulae for the $6j$ -symbols can be found in Appendix 3. In dealing with the $9j$ -symbols we need to evaluate rather complex quantities which, however, can be expressed with the help of the $6j$ -symbols (Appendix 3)

$$\begin{aligned} \left\{ \begin{matrix} S'_{12} & S_{12} & 2 \\ S_2 & S_2 & 1 \\ S_1 & S_1 & 1 \end{matrix} \right\} &= \frac{1}{5 \left\{ \begin{matrix} S'_{12} & S_{12} & 2 \\ 1 & 1 & S_{12} \end{matrix} \right\}} \left[(-1)^{2S_{12}} \right. \\ &\quad \times \left\{ \begin{matrix} S_2 & S_2 & 1 \\ S_{12} & S_{12} & S_1 \end{matrix} \right\} \left\{ \begin{matrix} S_1 & S_1 & 1 \\ S_{12} & S'_{12} & S_2 \end{matrix} \right\} \\ &\quad + (-1)^{S_1+S_2+3S_{12}+1} \delta_{S'_{12}, S_{12}} \frac{1}{3(2S_{12}+1)} \\ &\quad \times \left\{ \begin{matrix} S_1 & S_1 & 1 \\ S_2 & S_2 & S_{12} \end{matrix} \right\} + (-1)^{3S_1+3S_2+S'_{12}+2S_{12}+1} \\ &\quad \times 3 \frac{[S'_{12}(S'_{12}+1) - S_{12}(S_{12}+1)]}{2[6S_2(S_2+1)(2S_2+1)]^{1/2}} \left\{ \begin{matrix} S'_{12} & S_{12} & 1 \\ 1 & 1 & S_{12} \end{matrix} \right\} \\ &\quad \left. \times \left\{ \begin{matrix} S_1 & S_1 & 1 \\ S'_{12} & S_{12} & S_2 \end{matrix} \right\} \right] \end{aligned}$$

and

$$\begin{aligned} \left\{ \begin{matrix} S' & S & 2 \\ S_3 & S_3 & 1 \\ S'_{12} & S_{12} & 1 \end{matrix} \right\} &= \frac{1}{5 \left\{ \begin{matrix} S' & S & 2 \\ 1 & 1 & S \end{matrix} \right\}} \left[(-1)^{2S} \left\{ \begin{matrix} S_3 & S_3 & 1 \\ S & S & S_{12} \end{matrix} \right\} \right. \\ &\quad \times \left\{ \begin{matrix} S'_{12} & S_{12} & 1 \\ S & S' & S_3 \end{matrix} \right\} + (-1)^{S'_{12}+S_3+3S+1} \delta_{S'_{12}, S_{12}} \\ &\quad \times \frac{1}{3(2S+1)} \left\{ \begin{matrix} S_{12} & S'_{12} & 1 \\ S_3 & S_3 & S \end{matrix} \right\} \\ &\quad + (-1)^{2S'_{12}+S_{12}+3S_3+S'+2S+1} \\ &\quad \times 3 \frac{S'(S'+1) - S(S+1) + S_{12}(S_{12}+1) - S'_{12}(S'_{12}+1)}{2[6S_3(S_3+1)(2S_3+1)]^{1/2}} \\ &\quad \left. \times \left\{ \begin{matrix} S' & S & 1 \\ 1 & 1 & S \end{matrix} \right\} \left\{ \begin{matrix} S_{12} & S'_{12} & 1 \\ S' & S & S_3 \end{matrix} \right\} \right] \end{aligned}$$

TABLE 11.9

Reduced matrix elements of the asymmetric exchange for a general triad

$R_{ij}(S'_{12}, S'; S_{12}, S)$	Restrictions
$R_{11} = (-1)^{3S_1+3S_2+3S_3+3S'_{12}+3S_{12}+2S'+S} \begin{Bmatrix} S_1 & S_1 & 2 \\ S_{12} & S'_{12} & S_2 \end{Bmatrix} \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S & S' & S_3 \end{Bmatrix}$ $\times [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'+1)(2S+1)]^{1/2}$ $\times [S_1(S_1+1)(2S_1+1)(2S_1-1)(2S_1+3)/6]^{1/2} [\hbar^2]$	$S'_{12} = S_{12}, S_{12} \pm 1,$ $S_{12} \pm 2$ $S' = S, S \pm 1, S \pm 2$
$R_{22} = (-1)^{S_1+S_2+3S_3+2S'_{12}+2S_{12}+2S'+S} \begin{Bmatrix} S_{12} & S'_{12} & 2 \\ S_2 & S_2 & S_1 \end{Bmatrix} \begin{Bmatrix} S & S' & 2 \\ S'_{12} & S_{12} & S_3 \end{Bmatrix}$ $\times [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'+1)(2S+1)]^{1/2}$ $\times [S_2(S_2+1)(2S_2+1)(2S_2-1)(2S_2+3)/6]^{1/2} [\hbar^2]$	$S'_{12} = S_{12}, S_{12} \pm 1,$ $S_{12} \pm 2$ $S' = S, S \pm 1, S \pm 2$
$R_{33} = \delta_{S'_{12}, S_{12}} (-1)^{S'+S_3+2+S_{12}} \begin{Bmatrix} S & S' & 2 \\ S_3 & S_3 & S_{12} \end{Bmatrix}$ $\times [(2S'+1)(2S+1)]^{1/2}$ $\times [S_3(S_3+1)(2S_3+1)(2S_3-1)(2S_3+3)/6]^{1/2} [\hbar^2]$	$S'_{12} = S_{12}$ $S' = S, S \pm 1, S \pm 2$
$R_{12} = (-1)^{2S_1+2S_2+3S_3+2S'_{12}+3S_{12}+2S'+S} \begin{Bmatrix} S & S' & 2 \\ S'_{12} & S_{12} & S_3 \end{Bmatrix} \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S_2 & S_2 & 1 \\ S_1 & S_1 & 1 \end{Bmatrix}$ $\times (5)^{1/2} [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'+1)(2S+1)]^{1/2}$ $\times [S_2(S_2+1)(2S_2+1)]^{1/2} [S_1(S_1+1)(2S_1+1)]^{1/2} [\hbar^2]$	$S'_{12} = S_{12}, S_{12} \pm 1,$ $S_{12} \pm 2$ $S' = S, S \pm 1, S \pm 2$
$R_{13} = (-1)^{1+3S_1+3S_2+2S_3+3S'_{12}+2S_{12}+S'+S} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_1 & S_1 & S_2 \end{Bmatrix} \begin{Bmatrix} S' & S & 2 \\ S_3 & S_3 & 1 \\ S'_{12} & S_{12} & 1 \end{Bmatrix}$ $\times (5)^{1/2} [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'+1)(2S+1)]^{1/2}$ $\times [S_3(S_3+1)(2S_3+1)]^{1/2} [S_1(S_1+1)(2S_1+1)]^{1/2} [\hbar^2]$	$S'_{12} = S_{12}, S_{12} \pm 1$ $S' = S, S \pm 1, S \pm 2$
$R_{23} = (-1)^{1+S_1+S_2+2S_3+2S'_{12}+S_{12}+S'+S} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} \begin{Bmatrix} S' & S & 2 \\ S_3 & S_3 & 1 \\ S'_{12} & S_{12} & 1 \end{Bmatrix}$ $\times (5)^{1/2} [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'+1)(2S+1)]^{1/2}$ $\times [S_2(S_2+1)(2S_2+1)]^{1/2} [S_3(S_3+1)(2S_3+1)]^{1/2} [\hbar^2]$	$S'_{12} = S_{12}, S_{12} \pm 1$ $S' = S, S \pm 1, S \pm 2$

The triangular conditions for non-zero $6j$ -symbols require $S'_{12} = S_{12} - 2$, $S'_{12} = S_{12} - 1$, $S'_{12} = S_{12}$, $S' = S - 2$, $S' = S - 1$ and $S' = S$. Thus the reduced matrix elements of the asymmetric exchange fill the places according to the recipe

Total spin	Intermediate spin	Reduced matrix elements		
$S' = S$	$S'_{12} = S_{12}$	a	b	c
	$S'_{12} = S_{12} - 1$	b	a	b
	$S'_{12} = S_{12} - 2$	c	b	a
$S' = S - 1$	$S'_{12} = S_{12}$	d	e	f
	$S'_{12} = S_{12} - 1$	e	d	e
	$S'_{12} = S_{12} - 2$	f	e	d
$S' = S - 2$	$S'_{12} = S_{12}$	g	h	i
	$S'_{12} = S_{12} - 1$	h	g	h
	$S'_{12} = S_{12} - 2$	i	h	g

From this scheme it is obvious that the evaluation of the matrix elements of the asymmetric exchange is a complex task. Much simplification is obtained when we restrict ourselves to the case of strong exchange coupling. In such a case only the blocks with $S' = S$ are considered. The asymmetric exchange Hamiltonian can be rewritten in the form

$$\hat{H}^{\text{asym}} = [\vec{S} \cdot \vec{\bar{D}}_S \cdot \vec{S}][\hbar^{-2}]$$

with the molecular-state D -tensor defined as

$$\vec{\bar{D}}_S = C_1 \vec{\bar{D}}_1 + C_2 \vec{\bar{D}}_2 + C_3 \vec{\bar{D}}_3 + C_{12} \vec{\bar{D}}_{12} + C_{13} \vec{\bar{D}}_{13} + C_{23} \vec{\bar{D}}_{23}$$

The combination coefficients depend upon the spin numbers (S_1, S_2, S_3, S_{12}, S). They can be evaluated with the help of the replacement theorem, hence

$$C_{ij} = \frac{\langle S_1 S_2 S'_{12} S_3 S' | \hat{T}_2(\vec{S}_i \otimes \vec{S}_j) | S_1 S_2 S_{12} S_3 S \rangle}{\langle S_1 S_2 S'_{12} S_3 S' | \hat{T}_2(\vec{S} \otimes \vec{S}) | S_1 S_2 S_{12} S_3 S \rangle} = \frac{R_{ij(S'_{12}, S; S_{12}, S)}}{R}$$

(with $C_i \equiv C_{ii}$). This formula is applicable only for $S' = S$ since the reduced matrix element of the total spin is diagonal

$$\begin{aligned} R &\equiv \langle \dots S' | \hat{T}_2(\vec{S} \otimes \vec{S}) | \dots S \rangle \\ &= \delta_{S', S} [S(S+1)(2S+1)(2S-1)(2S+3)/6]^{1/2} [\hbar^2] \end{aligned}$$

Owing to the addition of the spins

$$\begin{aligned}\hat{T}_2(\vec{S} \otimes \vec{S}) &= \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) + \hat{T}_2(\vec{S}_2 \otimes \vec{S}_2) + \hat{T}_2(\vec{S}_3 \otimes \vec{S}_3) \\ &\quad + 2\hat{T}_2(\vec{S}_1 \otimes \vec{S}_2) + 2\hat{T}_2(\vec{S}_1 \otimes \vec{S}_3) + 2\hat{T}_2(\vec{S}_2 \otimes \vec{S}_3)\end{aligned}$$

the combination coefficients fulfil the relationship

$$C_1 + C_2 + C_3 + 2C_{12} + 2C_{13} + 2C_{23} = 1$$

Some selected numerical data are presented in Table 11.6.

In the case of $S' = S$ and $S'_{12} = S_{12}$ the combination coefficients for the triple can be obtained through recurrence relationships. Two spins are added first

$$\overline{\overline{D}}_{AB} = C_1(S_1 S_2 S_{12})\overline{\overline{D}}_1 + C_2(S_1 S_2 S_{12})\overline{\overline{D}}_2 + C_{12}(S_1 S_2 S_{12})\overline{\overline{D}}_{12}$$

$$\overline{\overline{D}}_X = c_1(S_1 S_2 S_{12})\overline{\overline{D}}_{13} + c_2(S_1 S_2 S_{12})\overline{\overline{D}}_{23}$$

and then

$$\overline{\overline{D}}_S = C_1(S_{12} S_3 S)\overline{\overline{D}}_{AB} + C_2(S_{12} S_3 S)\overline{\overline{D}}_3 + C_{12}(S_{12} S_3 S)\overline{\overline{D}}_X$$

yielding

$$\begin{aligned}\overline{\overline{D}}_S &= C_1(S_{12} S_3 S) \cdot C_1(S_1 S_2 S_{12})\overline{\overline{D}}_1 + C_1(S_{12} S_3 S) \cdot C_2(S_1 S_2 S_{12})\overline{\overline{D}}_2 \\ &\quad + C_1(S_{12} S_3 S) \cdot C_{12}(S_1 S_2 S_{12})\overline{\overline{D}}_{12} + C_2(S_{12} S_3 S)\overline{\overline{D}}_3 \\ &\quad + C_{12}(S_{12} S_3 S) \cdot c_1(S_1 S_2 S_{12})\overline{\overline{D}}_{13} + C_{12}(S_{12} S_3 S) \cdot c_2(S_1 S_2 S_{12})\overline{\overline{D}}_{23}\end{aligned}$$

A comparison with

$$\begin{aligned}\overline{\overline{D}}_S &= C_1(S_1 S_2 S_{12} S_3 S)\overline{\overline{D}}_1 + C_2(S_1 S_2 S_{12} S_3 S)\overline{\overline{D}}_2 + C_3(S_1 S_2 S_{12} S_3 S)\overline{\overline{D}}_3 \\ &\quad + C_{12}(S_1 S_2 S_{12} S_3 S)\overline{\overline{D}}_{12} + C_{13}(S_1 S_2 S_{12} S_3 S)\overline{\overline{D}}_{13} \\ &\quad + C_{23}(S_1 S_2 S_{12} S_3 S)\overline{\overline{D}}_{23}\end{aligned}$$

implies that the triad-combination coefficients can be composed of the pair-combination coefficients of pairs, as shown in Table 11.10.

In the case of the strong exchange limit the spin Hamiltonian adopts the form of

$$\hat{H}\Big|_{S=S'} = \hat{H}^{\text{iso}} + \mu_B \vec{B} \cdot \vec{g}_S \cdot \vec{S}[\hbar^{-1}] + \vec{S} \cdot \overline{\overline{D}}_S \cdot \vec{S}[\hbar^{-2}]$$

TABLE 11.10

Recurrence formulae for evaluating the combination coefficients of g - and D -tensors for a trinuclear cluster^a

(a) Combination coefficients of the g -tensors

$$c_1(S_1 S_2 S_{12} S_3 S) = c_1(S_{12} S_3 S) \cdot c_1(S_1 S_2 S_{12})$$

$$c_2(S_1 S_2 S_{12} S_3 S) = c_1(S_{12} S_3 S) \cdot c_2(S_1 S_2 S_{12})$$

$$c_3(S_1 S_2 S_{12} S_3 S) = c_2(S_{12} S_3 S)$$

(b) Combination coefficients of the local D -tensors

$$C_1(S_1 S_2 S_{12} S_3 S) = C_1(S_{12} S_3 S) \cdot C_1(S_1 S_2 S_{12})$$

$$C_2(S_1 S_2 S_{12} S_3 S) = C_1(S_{12} S_3 S) \cdot C_2(S_1 S_2 S_{12})$$

$$C_3(S_1 S_2 S_{12} S_3 S) = C_2(S_{12} S_3 S)$$

(c) Combination coefficients of the pair-interaction D -tensors

$$C_{12}(S_1 S_2 S_{12} S_3 S) = C_1(S_{12} S_3 S) \cdot C_{12}(S_1 S_2 S_{12})$$

$$C_{13}(S_1 S_2 S_{12} S_3 S) = C_{12}(S_{12} S_3 S) \cdot c_1(S_1 S_2 S_{12})$$

$$C_{23}(S_1 S_2 S_{12} S_3 S) = C_{12}(S_{12} S_3 S) \cdot c_2(S_1 S_2 S_{12})$$

^aCombination coefficients for dinuclear systems are collected in Table 10.12.

and thus the Hamiltonian matrix takes a block-diagonal form. Its structure copies the following scheme where the individual types (a, b, c) of reduced matrix elements occur

Total spin	Intermediate spin	Matrix elements		
$S' = S$	$S'_{12} = S_{12}$	a(iso + Z + asym)	b(iso + Z + asym)	c(asym)
	$S'_{12} = S_{12} - 1$	b(iso + Z + asym)	a(iso + Z + asym)	b(iso + Z + asym)
	$S'_{12} = S_{12} - 2$	c(asym)	b(iso + Z + asym)	a(iso + Z + asym)

We assume that the D_S -tensors (more specifically $D_{S,S'_{12},S_{12}}$) are diagonal and traceless, hence

$$\begin{aligned} \vec{S} \cdot \vec{\bar{D}}_S \cdot \vec{S} &= D_{S,xx} \hat{S}_x^2 + D_{S,yy} \hat{S}_y^2 + D_{S,zz} \hat{S}_z^2 \\ &= \frac{D_S}{3} (3\hat{S}_z^2 - \hat{S}^2) + E_S (\hat{S}_x^2 - \hat{S}_y^2) \end{aligned}$$

where the axial zero-field splitting parameters are introduced through

$$D_S = \frac{3}{2} D_{S,zz}$$

and the rhombic zero-field splitting parameters are defined as

$$E_S = \frac{1}{2}(D_{S,xx} - D_{S,yy})$$

The matrix elements of the D_S -tensors are evaluated according to

$$\langle SM' | \vec{S} \cdot \bar{\bar{D}}_S \cdot \vec{S} | SM \rangle = \frac{D_S}{3} \langle SM' | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle + E_S \langle SM' | \hat{S}_x^2 - \hat{S}_y^2 | SM \rangle$$

The three situations are analysed in more detail.

1. The first integral is expressed via the Wigner–Eckart theorem as follows

$$\langle SM' | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle = \sqrt{6} \begin{pmatrix} S & 2 & S \\ -M' & 0 & M \end{pmatrix} (-1)^{S-M'} \langle S || \hat{T}_2(\vec{S} \otimes \vec{S}) || S \rangle$$

and the evaluation of the $3j$ -symbol and the reduced matrix element of the second-rank tensor operator yields

$$\langle SM' | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle = [3M^2 - S(S+1)][\hbar^2]\delta_{M',M}$$

Thus the diagonal of the interaction matrix is filled by the elements

$$H_{SM,SM}^{\text{asym}}(a_0) = \frac{D_S}{3} \langle SM | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle [\hbar^{-2}] = \frac{D_S}{3} [3M^2 - S(S+1)]$$

The second integral is reduced as follows

$$\begin{aligned} \langle SM' | \hat{S}_x^2 - \hat{S}_y^2 | SM \rangle &= \left[\begin{pmatrix} S & 2 & S \\ -M' & -2 & M \end{pmatrix} + \begin{pmatrix} S & 2 & S \\ -M' & +2 & M \end{pmatrix} \right] \\ &\times (-1)^{S-M'} \langle S || \hat{T}_2(\vec{S} \otimes \vec{S}) || S \rangle \end{aligned}$$

and the evaluation of the reduced matrix element and the $3j$ -symbols (restricted to either $M' = M - 2$ or $M' = M + 2$) finally yields

$$\begin{aligned} H_{S,M+2,S,M}^{\text{asym}}(a_2) &= E_S \langle SM' | \hat{S}_x^2 - \hat{S}_y^2 | SM \rangle [\hbar^{-2}] \\ &= \frac{E_S}{2} [(S-M-1)(S-M)(S+M+1)(S+M+2)]^{1/2} \end{aligned}$$

These matrix elements fill the places shifted by two positions out of the diagonal (the interaction matrix is symmetric).

2. The off-diagonal matrix elements

$$\begin{aligned}
 & \langle S'_{12} SM' | \vec{S} \cdot \vec{\bar{D}}_{S, S'_{12}, S_{12}} \cdot \vec{S} | S_{12} SM \rangle \\
 &= \frac{D_{S, S'_{12}, S_{12}}}{3} \langle S'_{12} SM' | 3\hat{S}_z^2 - \hat{S}^2 | S_{12} SM \rangle \\
 &+ E_{S, S'_{12}, S_{12}} \langle S'_{12} SM' | \hat{S}_x^2 - \hat{S}_y^2 | S_{12} SM \rangle
 \end{aligned}$$

for $S'_{12} = S_{12} - 1$ become

$$\begin{aligned}
 H_{S_{12}-1, S, M, S_{12}, S, M}^{\text{asym}}(b_0) &= \frac{D_{S, S_{12}-1, S_{12}}}{3} \langle SM | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle [\hbar^{-2}] \\
 &= \frac{D_{S, S_{12}-1, S_{12}}}{3} [3M^2 - S(S+1)]
 \end{aligned}$$

$$\begin{aligned}
 H_{S_{12}-1, S, M+2, S_{12}, S, M}^{\text{asym}}(b_2) &= E_{S, S_{12}-1, S_{12}} \langle SM' | \hat{S}_x^2 - \hat{S}_y^2 | SM \rangle [\hbar^{-2}] \\
 &= \frac{E_{S, S_{12}-1, S_{12}}}{2} [(S-M-1)(S-M) \\
 &\quad \times (S+M+1)(S+M+2)]^{1/2}
 \end{aligned}$$

3. For $S'_{12} = S_{12} - 2$ there is

$$\begin{aligned}
 H_{S_{12}-2, S, M, S_{12}, S, M}^{\text{asym}}(c_0) &= \frac{D_{S, S_{12}-2, S_{12}}}{3} \langle SM | 3\hat{S}_z^2 - \hat{S}^2 | SM \rangle [\hbar^{-2}] \\
 &= \frac{D_{S, S_{12}-2, S_{12}}}{3} [3M^2 - S(S+1)]
 \end{aligned}$$

$$\begin{aligned}
 H_{S_{12}-2, S, M+2, S_{12}, S, M}^{\text{asym}}(c_2) &= E_{S, S_{12}-2, S_{12}} \langle SM' | \hat{S}_x^2 - \hat{S}_y^2 | SM \rangle [\hbar^{-2}] \\
 &= \frac{E_{S, S_{12}-2, S_{12}}}{2} [(S-M-1)(S-M) \\
 &\quad \times (S+M+1)(S+M+2)]^{1/2}
 \end{aligned}$$

In the simplest case of the triple $S_1 = S_2 = S_3 = 1/2$, the structure of the exchange interaction matrix is

$$\mathbf{H}^{\text{asym}} = \left(\begin{array}{cccc|cccc} a_0 & 0 & a_2 & 0 & 0 & d_2 & 0 & e_2 \\ 0 & a_0 & 0 & a_2 & d_0 & 0 & e_0 & 0 \\ a_2 & 0 & a_0 & 0 & 0 & d_0 & 0 & e_0 \\ 0 & a_2 & 0 & a_0 & d_2 & 0 & e_2 & 0 \\ \hline 0 & d_0 & 0 & d_2 & a_0 & 0 & b_0 & 0 \\ d_2 & 0 & d_0 & 0 & 0 & a_0 & 0 & b_0 \\ \hline 0 & e_0 & 0 & e_2 & b_0 & 0 & a_0 & 0 \\ e_2 & 0 & e_0 & 0 & 0 & b_0 & 0 & a_0 \end{array} \right) \text{ for } \left[\begin{array}{l} S_{12} = 1 \quad S = 3/2 \quad M = -3/2 \\ \quad \quad \quad \quad \quad M = -1/2 \\ \quad \quad \quad \quad \quad M = +1/2 \\ \quad \quad \quad \quad \quad M = +3/2 \\ \hline S_{12} = 1 \quad S = 1/2 \quad M = -1/2 \\ \quad \quad \quad \quad \quad M = +1/2 \\ \hline S_{12} = 0 \quad S = 1/2 \quad M = -1/2 \\ \quad \quad \quad \quad \quad M = +1/2 \end{array} \right]$$

In the limit of the strong exchange coupling the matrix elements of d- and e-type are neglected. The molecular-state D -tensors are composed with the help of Table 11.6, as follows:

(a) for the highest multiplicity state

$$\overline{\overline{D}}_{S=3/2} = \frac{1}{6}\overline{\overline{D}}_{12} + \frac{1}{6}\overline{\overline{D}}_{13} + \frac{1}{6}\overline{\overline{D}}_{23} = \frac{1}{2}\overline{\overline{D}}_{AB}$$

(b) for the diagonal blocks (a-type)

$$\overline{\overline{D}}_{S=1/2, S'_{12}=0, S_{12}=0} = 0$$

$$\overline{\overline{D}}_{S=1/2, S'_{12}=1, S_{12}=1} = 0$$

(c) for the off-diagonal blocks (b-type)

$$\overline{\overline{D}}_{S=1/2, S'_{12}=0, S_{12}=1} = 0$$

Since the local D -tensors for $S_i = 1/2$ all vanish, the only contribution arises from the pair-interaction D -tensors with

$$D_{3/2} = \frac{3}{2}D_{3/2,zz} = \frac{3}{2} \cdot \frac{1}{2}D_{AB,zz}$$

$$E_{3/2} = \frac{1}{2}(D_{3/2,xx} - D_{3/2,yy}) = \frac{1}{2} \cdot \frac{1}{2}(D_{AB,xx} - D_{AB,yy})$$

After the evaluation of the matrix elements one gets the contribution of the asymmetric exchange in the form

$$\mathbf{H}^{\text{asym}} = \left(\begin{array}{cccc|cccc} +D_{3/2} & 0 & \sqrt{3}E_{3/2} & 0 & & & & \\ 0 & -D_{3/2} & 0 & \sqrt{3}E_{3/2} & & & & \\ \sqrt{3}E_{3/2} & 0 & -D_{3/2} & 0 & & & & \\ 0 & \sqrt{3}E_{3/2} & 0 & +D_{3/2} & & & & \\ \hline & & & & 0 & 0 & 0 & 0 \\ & & & & 0 & 0 & 0 & 0 \\ \hline & & & & 0 & 0 & 0 & 0 \\ & & & & 0 & 0 & 0 & 0 \end{array} \right)$$

This term should be added to the isotropic exchange term which, for a general triad, becomes

$$\mathbf{H}^{\text{iso}} = \left(\begin{array}{cccc|cccc} A_{3/2} & 0 & 0 & 0 & & & & \\ 0 & A_{3/2} & 0 & 0 & & & & \\ 0 & 0 & A_{3/2} & 0 & & & & \\ 0 & 0 & 0 & A_{3/2} & & & & \\ \hline & & & & A_{1/2} & 0 & B_{1/2} & 0 \\ & & & & 0 & A_{1/2} & 0 & B_{1/2} \\ \hline & & & & B_{1/2} & 0 & A'_{1/2} & 0 \\ & & & & 0 & B_{1/2} & 0 & A'_{1/2} \end{array} \right)$$

with the matrix elements as determined by Table 11.3, i.e.

$$A_{3/2} = -(1/4)J_{12} - (1/4)(J_{13} + J_{23})$$

$$A_{1/2} = -(1/4)J_{12} + (1/2)(J_{13} + J_{23})$$

$$A'_{1/2} = +(3/4)J_{12}$$

$$B_{1/2} = -(\sqrt{3}/4)(J_{23} - J_{13})$$

The Zeeman matrix requires the evaluation of the molecular-state g -tensors which, with the help of Tables 11.5 and 11.6, are

$$\bar{g}(a_{3/2}) \equiv \bar{g}_{S=3/2} = \frac{1}{3}\bar{g}_1 + \frac{1}{3}\bar{g}_2 + \frac{1}{3}\bar{g}_3 \rightarrow \bar{g}_A$$

$$\bar{g}(a_{1/2}) \equiv \bar{g}_{S=1/2, S'_{12}=S_{12}=1} = \frac{2}{3}\bar{g}_1 + \frac{2}{3}\bar{g}_2 - \frac{1}{3}\bar{g}_3 \rightarrow \bar{g}_A$$

$$\bar{g}(a'_{1/2}) \equiv \bar{g}_{S=1/2, S'_{12}=S_{12}=0} = 0 \cdot \bar{g}_1 + 0 \cdot \bar{g}_2 + 1 \cdot \bar{g}_3 \rightarrow \bar{g}_A$$

$$\bar{g}(b_{1/2}) \equiv \bar{g}_{S=1/2, S'_{12}=0, S_{12}=1} = -\frac{\sqrt{3}}{3} \cdot \bar{g}_1 + \frac{\sqrt{3}}{3} \cdot \bar{g}_2 + 0 \cdot \bar{g}_3 \rightarrow 0$$

where we have assumed identical local g -tensors $\bar{g}_A$ (which is not necessarily fulfilled). The remaining g -tensors vanish as well in this particular case since they are introduced through the differences of the local ones

$$\bar{g}'(c; d) = \bar{g}_1 - \bar{g}_2 \rightarrow 0$$

$$\bar{g}''(c) = \bar{g}_2 - \bar{g}_3 \rightarrow 0$$

The spherical transforms are introduced as follows

$$G_{1,+1} = -\frac{1}{\sqrt{2}}(B_x g_{A,x} + iB_y g_{A,y})$$

$$G_{1,-1} = \frac{1}{\sqrt{2}}(B_x g_{A,x} - iB_y g_{A,y})$$

$$G_{1,0} = B_z g_{A,z}$$

(all of them are identical when identical $\bar{g}_A$ occur). According to Table 11.7

$$\begin{aligned} H_{S_{12}, S, M'; S_{12}, S, M}^Z(a) &= \mu_B \sum_{q=-1}^{+1} (-1)^q G_{(a)1, -q} (-1)^{S-(M+q)} \\ &\quad \times \begin{pmatrix} S & 1 & S \\ -(M+q) & q & M \end{pmatrix} [S(S+1)(2S+1)]^{1/2} \end{aligned}$$

and then only the term $q = 0$ contributes to $M' = M$

$$\begin{aligned} H_{S_{12}, S, M; S_{12}, S, M}^Z(a) &= \mu_B (-1)^0 G_{(a)1, 0} (-1)^{S-M} \begin{pmatrix} S & 1 & S \\ -M & 0 & M \end{pmatrix} \\ &\quad \times [S(S+1)(2S+1)]^{1/2} \\ &= \mu_B (-1)^0 G_{(a)1, 0} (-1)^{S-M} (-1)^{M-S} \\ &\quad \times \frac{M}{[S(S+1)(2S+1)]^{1/2}} [S(S+1)(2S+1)]^{1/2} \\ &= \mu_B G_{(a)1, 0} M = \mu_B g_{S,z} M \end{aligned}$$

Analogously, only the term $q = 1$ contributes to $M' = M + 1$

$$\begin{aligned}
 H_{S_{12}, S, M+1; S_{12}, S, M}^Z(\mathbf{a}) &= \mu_B (-1)^1 G_{(a)1, -1} (-1)^{S-(M+1)} \\
 &\quad \times \begin{pmatrix} S & 1 & S \\ -(M+1) & 1 & M \end{pmatrix} [S(S+1)(2S+1)]^{1/2} \\
 &= \mu_B (-1)^1 G_{(a)1, 0} (-1)^{S-(M+1)} (-1)^{M-S} \\
 &\quad \times \left[\frac{(S-M)(S+M+1)}{2S(S+1)(2S+1)} \right]^{1/2} [S(S+1)(2S+1)]^{1/2} \\
 &= \mu_B G_{(a)1, -1} \left[\frac{(S-M)(S+M+1)}{2} \right]^{1/2} \\
 &= \mu_B [(S-M)(S+M+1)]^{1/2} \frac{1}{2} (B_x g_{A,x} - i B_y g_{A,y})
 \end{aligned}$$

Then the Zeeman matrix takes the form

$$\mathbf{H}^Z = \mu_B \begin{pmatrix} (3/2)G_{1,0} & (\sqrt{3/2})G_{1,-1}^* & 0 & 0 \\ (\sqrt{3/2})G_{1,-1} & (1/2)G_{1,0} & (\sqrt{2})G_{1,-1}^* & 0 \\ 0 & (\sqrt{2})G_{1,-1} & -(1/2)G_{1,0} & (\sqrt{3/2})G_{1,-1}^* \\ 0 & 0 & (\sqrt{3/2})G_{1,-1} & -(3/2)G_{1,0} \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \hline (1/2)G_{1,0} & -(1/\sqrt{2})G_{1,-1}^* & 0 & 0 \\ (1/\sqrt{2})G_{1,-1} & -(1/2)G_{1,0} & 0 & 0 \\ \hline 0 & 0 & (1/2)G_{1,0} & -(1/\sqrt{2})G_{1,-1}^* \\ 0 & 0 & (1/\sqrt{2})G_{1,-1} & -(1/2)G_{1,0} \end{pmatrix}$$

Now, in the z -direction (the spherical component $q = 0$) we get the total interaction matrix, involving the isotropic exchange, asymmetric exchange and the Zeeman interaction, in the form

and finally, in the y -direction the interaction matrix is complex Hermitian

$$H_y = \begin{pmatrix} A_{3/2} + D_{3/2} & +i(\sqrt{3}/2)\mu_B B_y g_{A,y} & \sqrt{3}E_{3/2} & 0 \\ -i(\sqrt{3}/2)\mu_B B_y g_{A,y} & A_{3/2} - D_{3/2} & +i\mu_B B_y g_{A,y} & \sqrt{3}E_{3/2} \\ \sqrt{3}E_{3/2} & -i\mu_B B_y g_{A,y} & A_{3/2} - D_{3/2} & +i(\sqrt{3}/2)\mu_B B_y g_{A,y} \\ 0 & \sqrt{3}E_{3/2} & -i(\sqrt{3}/2)\mu_B B_y g_{A,y} & A_{3/2} + D_{3/2} \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \hline A_{1/2} & +i(1/2)\mu_B B_y g_{A,y} & B_{1/2} & 0 \\ -i(1/2)\mu_B B_y g_{A,y} & A_{1/2} & 0 & B_{1/2} \\ \hline B_{1/2} & 0 & A'_{1/2} & +i(1/2)\mu_B B_y g_{A,y} \\ 0 & B_{1/2} & -i(1/2)\mu_B B_y g_{A,y} & A'_{1/2} \end{pmatrix}$$

The eigenvalues can be easily obtained by assuming no rhombic anisotropy (i.e., $E_{3/2} = 0$) and no general triangle (i.e., $B_{1/2} = 0$, which is equivalent to $J_{13} = J_{23}$):

1. In the z -direction

- the block for $S = 3/2$ is already diagonal and yields eigenvalues evidencing a zero-field splitting similar to the case of mononuclear complexes;
- the two sub-blocks for $S = 1/2$ are diagonal as well; they become degenerate for $A_{1/2} = A'_{1/2}$ (an isosceles triangle).

2. In the x -direction

- the sub-block for $S = 3/2$ reduces to the standard treatment for zero-field splitting. There are two degenerate levels ($H_{ii}^{(0)} = A_{3/2} - D_{3/2}$) coupled by an off-diagonal element ($H_{ij} = \mu_B B g_{A,x}$) so that first-order perturbation theory is applied first and, after solving the corresponding secular determinant, the first-order energies are obtained: $\varepsilon_i^{(1)} = \pm \mu_B B g_{A,x}$. Then second-order perturbation theory is used, $\varepsilon_i^{(2)} = \sum_{j \neq i} H_{ij}^2 / (H_{ii}^{(0)} - H_{jj}^{(0)})$, for all four energy levels.

- the two sub-blocks for $S = 1/2$ are solved separately, yielding only the first-order van Vleck coefficients (Table 11.11).

TABLE 11.11

Van Vleck coefficients for the equilateral triangle ($J_{12} = J$ and $J_{13} = J_{23} = J'$) with $S_1 = S_2 = S_3 = 1/2$

	$\varepsilon_z^{(0)}$	$\varepsilon_z^{(1)}/\mu_B$	$\varepsilon_z^{(2)}/\mu_B^2$	$\varepsilon_x^{(0)}$	$\varepsilon_x^{(1)}/\mu_B$	$\varepsilon_x^{(2)}/\mu_B^2$
1	$A_{3/2} + D_{3/2}$	$+(3/2)g_{A,z}$	—	$A_{3/2} + D_{3/2}$	—	$+\frac{3}{8}\frac{(g_{A,x})^2}{D_{3/2}}$
2	$A_{3/2} - D_{3/2}$	$+(1/2)g_{A,z}$	—	$A_{3/2} - D_{3/2}$	$+g_{A,x}$	$-\frac{3}{8}\frac{(g_{A,x})^2}{D_{3/2}}$
3	$A_{3/2} - D_{3/2}$	$-(1/2)g_{A,z}$	—	$A_{3/2} - D_{3/2}$	$-g_{A,x}$	$-\frac{3}{8}\frac{(g_{A,x})^2}{D_{3/2}}$
4	$A_{3/2} + D_{3/2}$	$-(3/2)g_{A,z}$	—	$A_{3/2} + D_{3/2}$	—	$+\frac{3}{8}\frac{(g_{A,x})^2}{D_{3/2}}$
5	$A_{1/2}$	$+(1/2)g_{A,z}$	—	$A_{1/2}$	$+(1/2)g_{A,x}$	—
6	$A'_{1/2}$	$+(1/2)g_{A,z}$	—	$A'_{1/2}$	$+(1/2)g_{A,x}$	—
7	$A_{1/2}$	$-(1/2)g_{A,z}$	—	$A_{1/2}$	$-(1/2)g_{A,x}$	—
8	$A'_{1/2}$	$-(1/2)g_{A,z}$	—	$A'_{1/2}$	$-(1/2)g_{A,x}$	—

With the van Vleck coefficients determined, one can apply the van Vleck formula to the parallel and perpendicular components of the magnetic susceptibility, hence

$$\chi_z = \frac{N_A \mu_0 \mu_B^2}{k} \frac{g_{A,z}^2}{T} \frac{2}{Z_0} \frac{1}{4} \{ 9 \exp[(-A_{3/2} - D_{3/2})/kT] \\ + \exp[(-A_{3/2} + D_{3/2})/kT] \\ + \exp[-A_{1/2}/kT] + \exp[-A'_{1/2}/kT] \}$$

$$\chi_x = \frac{N_A \mu_0 \mu_B^2}{k} \frac{g_{A,x}^2}{T} \frac{2}{Z_0} \frac{1}{4} \{ -(3/x) \exp[(-A_{3/2} - D_{3/2})/kT] \\ + [4 + (3/x)] \exp[(-A_{3/2} + D_{3/2})/kT] + \exp[-A_{1/2}/kT] \\ + \exp[-A'_{1/2}/kT] \}$$

with

$$x = D_{3/2}/kT$$

and

$$Z_0 = 2 \{ \exp[(-A_{3/2} - D_{3/2})/kT] + \exp[(-A_{3/2} + D_{3/2})/kT] \\ + \exp[-A_{1/2}/kT] + \exp[-A'_{1/2}/kT] \}$$

For completeness, we repeat the expressions for the equilateral triangle

$$A_{3/2} = -(1/4)J_{12} - (1/4)(J_{13} + J_{23}) = -(1/4)J - (1/2)J'$$

$$A_{1/2} = -(1/4)J_{12} + (1/2)(J_{13} + J_{23}) = -(1/4)J + J'$$

$$A'_{1/2} = +(3/4)J_{12} = (3/4)J$$

The corresponding plots are shown in Figs. 11.4 and 11.5.

The net effect of the axial asymmetry parameter is seen in Fig. 11.6 where, for comparison, the case of pure ferromagnetic isotropic exchange is included. The upturn of the product function and/or effective magnetic moment on temperature lowering is due to the depopulation of the magnetically productive $|3/2, \pm 3/2\rangle$ state.

The effect of the axial asymmetry is less pronounced in the case of anti-ferromagnetic exchange coupling, as seen from Fig. 11.7. The ferro- and antiferromagnetic coupling are compared in Fig. 11.8.

11.2.4 Antisymmetric exchange

The generalisation of the antisymmetric exchange operator, as introduced for dinuclear systems, leads to the operator

$$\hat{H}^{\text{anti}} = \sum_i \sum_{j < i} \vec{d}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) [\hbar^{-2}] = \sum_i \sum_{j < i} \vec{d}_{ij} \cdot \vec{A}_{ij}$$

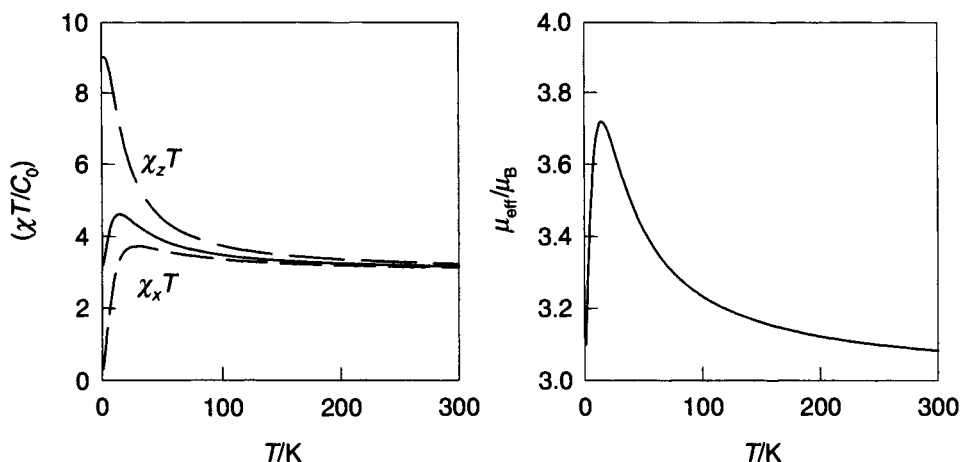


Fig. 11.4. Temperature variation of the product functions for an equilateral triangle with $S_1 = S_2 = S_3 = 1/2$, including asymmetric exchange: $g_A = 2.0$, $J/k = 50$ K, $J'/k = 25$ K, $D_{3/2}/k = -10$ K; solid— $\chi_{\text{av}} T$.

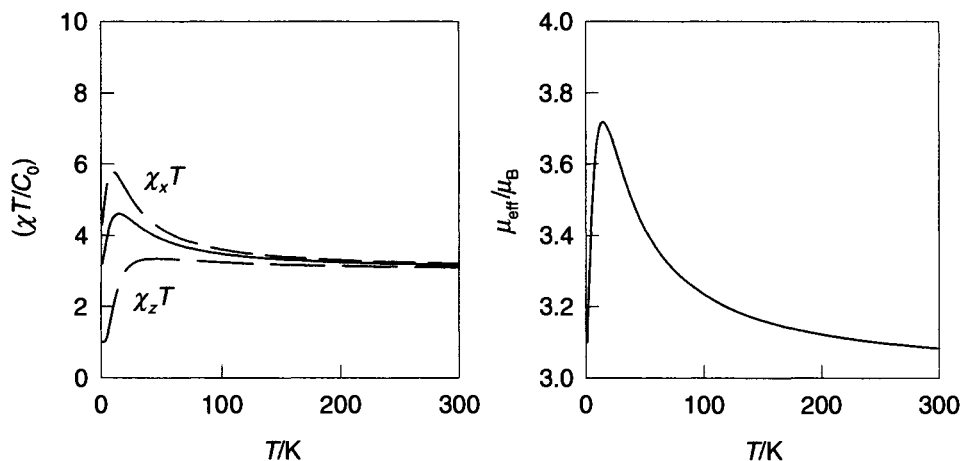


Fig. 11.5. Temperature variation of the product functions for an equilateral triangle with $S_1 = S_2 = S_3 = 1/2$, including asymmetric exchange: $g_A = 2.0$, $J/k = 50$ K, $J'/k = 25$ K, $D_{3/2}/k = +10$ K; solid— $\chi_{\text{av}} T$.

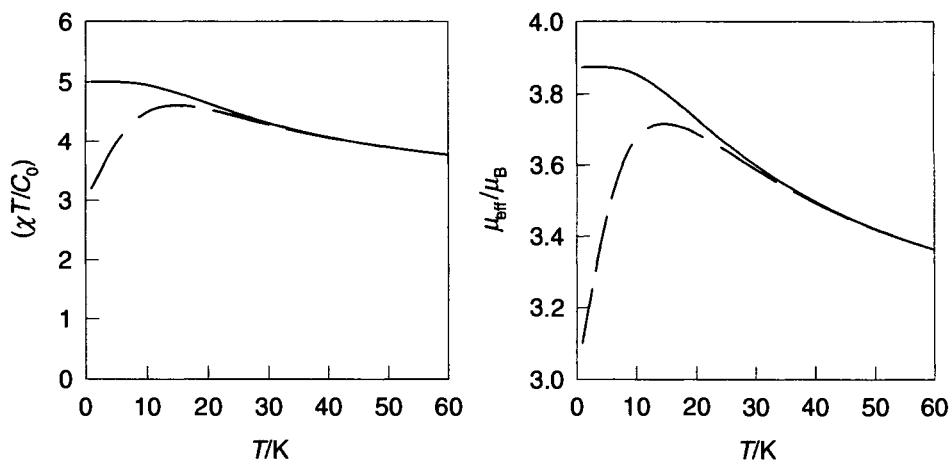


Fig. 11.6. Temperature variation of the product functions for an equilateral triangle with $S_1 = S_2 = S_3 = 1/2$, including isotropic exchange: solid— $g_A = 2.0$, $J/k = 50$ K, $J'/k = 25$ K; dashed—effect of $D_{3/2}/k = \pm 10$ K.

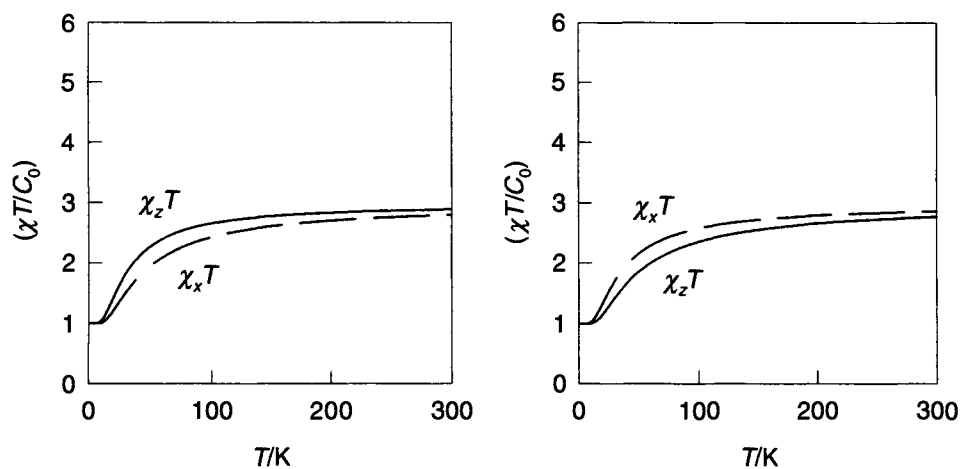


Fig. 11.7. Temperature variation of the product functions for an equilateral triangle with $S_1 = S_2 = S_3 = 1/2$, including asymmetric exchange: $g_A = 2.0$, $J/k = -50$ K, $J'/k = -25$ K; left— $D_{3/2}/k = -10$ K; right— $D_{3/2}/k = +10$ K.

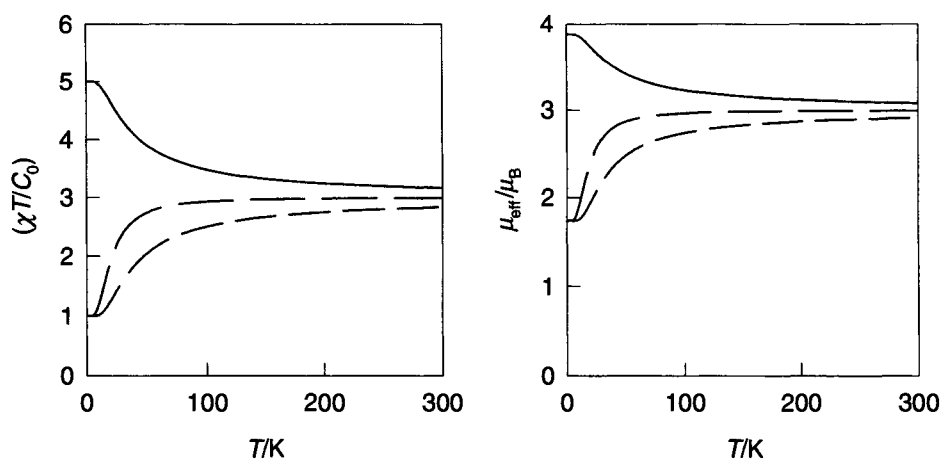


Fig. 11.8. Temperature variation of the product functions for an equilateral triangle with $S_1 = S_2 = S_3 = 1/2$, including isotropic exchange: $g_A = 2.0$; solid— $J/k = +50$ K, $J'/k = +25$ K; long dashed $J/k = +50$ K, $J'/k = -25$ K; short dashed— $J/k = -50$ K, $J'/k = -25$ K.

where $\vec{d}_{ij}(d_{ij,x}, d_{ij,y}, d_{ij,z})$ are parameters related to the antisymmetric part of the exchange coupling tensors. The scalar product of two vectors can be written in terms of the spherical components as follows

$$\vec{d} \cdot \vec{A} = -d_{1,+1}\hat{A}_{1,-1} + d_{1,0}\hat{A}_{1,0} - d_{1,-1}\hat{A}_{1,+1} = \sum_{q=-1}^{+1} (-1)^q d_{1,-q} \hat{A}_{1,q}$$

with spherical transform of the antisymmetric exchange parameters

$$d_{1,+1} = -\frac{1}{\sqrt{2}}(d_x + id_y)$$

$$d_{1,-1} = \frac{1}{\sqrt{2}}(d_x - id_y)$$

$$d_{1,0} = d_z$$

Each cross-product can be expressed through the first-order tensor product as follows

$$\hat{A}_{ij,1,q} = (\vec{S}_i \times \vec{S}_j)_{1,q} [\hbar^{-2}] = -i\sqrt{2} \left\{ \hat{T}_{1,q}(\vec{S}_i \otimes \vec{S}_j) \right\} [\hbar^{-2}]$$

and the application of the Wigner-Eckart theorem for the spherical ($q = 0, \pm 1$) components yields

$$A_{S'M'SM,ij,1,q} = (-i\sqrt{2})(-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} \langle \dots S' \| \hat{T}_1(\vec{S}_i \otimes \vec{S}_j) \| \dots S \rangle [\hbar^{-2}]$$

The reduced matrix elements are evaluated according to the general decoupling formula (Section 1.5.4) where the tensor ranks are assigned as follows

Tensor operator	k_1	k_2	k_{12}	k_3	k
$\hat{T}_1(\vec{S}_1 \otimes \vec{S}_2)$	1	1	1	0	1
$\hat{T}_1(\vec{S}_1 \otimes \vec{S}_3)$	1	0	1	1	1
$\hat{T}_1(\vec{S}_2 \otimes \vec{S}_3)$	0	1	1	1	1

The reduced matrix elements of the constituent spins

$$R_{ij} \equiv \langle S_1 S_2 S'_1 S_3 S' \| \hat{T}_1(\vec{S}_i \otimes \vec{S}_j) \| S_1 S_2 S_1 S_3 S \rangle$$

are expressed as

$$R_{12} = [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 1 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\ \times \langle S_1 \| \hat{T}_1(\vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 1 + 1)]^{1/2} \\ \times \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 0 \\ S' & S & 1 \end{Bmatrix} \langle S_2 \| \hat{T}_1(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_0(\vec{S}_3) \| S_3 \rangle$$

$$R_{13} = [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\ \times \langle S_1 \| \hat{T}_1(\vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 1 + 1)]^{1/2} \\ \times \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 1 \\ S' & S & 1 \end{Bmatrix} \langle S_2 \| \hat{T}_0(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_1(\vec{S}_3) \| S_3 \rangle$$

$$R_{23} = [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 1 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\ \times \langle S_1 \| \hat{T}_0(\vec{S}_1) \| S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 1 + 1)]^{1/2} \\ \times \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 1 \\ S' & S & 1 \end{Bmatrix} \langle S_2 \| \hat{T}_1(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_1(\vec{S}_3) \| S_3 \rangle$$

A simplification is obtained when the $9j$ -symbols are further manipulated by utilising special formulae (Appendix 3) resulting only in $6j$ -symbols, i.e.

$$\begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 1 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} = \frac{S_{12}(S_{12} + 1) - S'_{12}(S'_{12} + 1)}{2[1 \cdot 2 \cdot 3 \cdot S_1(S_1 + 1)(2S_1 + 1)]^{1/2}} (-1)^{S'_{12} + S_2 + 1 + S_1} \\ \times \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix}$$

and

$$\begin{aligned}
 \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & 1 \\ S' & S & 1 \end{Bmatrix} &= (-1)^{S'_{12}+S_{12}+2S_3+S'+S+3} \begin{Bmatrix} S_3 & S_3 & 1 \\ S'_{12} & S_{12} & 1 \\ S' & S & 1 \end{Bmatrix} \\
 &= (-1)^{S'_{12}+S_{12}+2S_3+S'+S+3} \\
 &\quad \times \frac{S(S+1) - S'(S'+1) + S'_{12}(S'_{12}+1) - S_{12}(S_{12}+1)}{2[1 \cdot 2 \cdot 3 \cdot S_3(S_3+1)(2S_3+1)]^{1/2}} \\
 &\quad \times (-1)^{S'+S_{12}+1+S_3} \begin{Bmatrix} S & S' & 1 \\ S'_{12} & S_{12} & S_3 \end{Bmatrix}
 \end{aligned}$$

The reduced matrix elements containing only the $6j$ -symbols are

$$\begin{aligned}
 R_{12} &= (-1)^{2S_3+S'_{12}+S_{12}+S'+S+2} \frac{S_{12}(S_{12}+1) - S'_{12}(S'_{12}+1)}{2[2]^{1/2}} \\
 &\quad \times [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'+1)(2S+1)]^{1/2} [S_2(S_2+1)(2S_2+1)]^{1/2} \\
 &\quad \times (-1)^{S'_{12}+S_2+1+S_1} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} (-1)^{S'+S_{12}+1+S_3} \begin{Bmatrix} S & S' & 1 \\ S'_{12} & S_{12} & S_3 \end{Bmatrix} [\hbar^2] \\
 R_{13} &= (-1)^{2S_1+2S_2+S'_{12}+S_{12}+2} \\
 &\quad \times \frac{S(S+1) - S'(S'+1) + S'_{12}(S'_{12}+1) - S_{12}(S_{12}+1)}{2[2]^{1/2}} \\
 &\quad \times [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'+1)(2S+1)]^{1/2} [S_1(S_1+1)(2S_1+1)]^{1/2} \\
 &\quad \times (-1)^{S'_{12}+S_{12}+2S_3+S'+S+3} (-1)^{S'_{12}+S_1+1+S_2} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_1 & S_1 & S_2 \end{Bmatrix} \\
 &\quad \times (-1)^{S'+S_{12}+1+S_3} \begin{Bmatrix} S & S' & 1 \\ S'_{12} & S_{12} & S_3 \end{Bmatrix} [\hbar^2]
 \end{aligned}$$

$$\begin{aligned}
R_{23} = & \frac{S(S+1) - S'(S'+1) + S'_{12}(S'_{12}+1) - S_{12}(S_{12}+1)}{2[2]^{1/2}} \\
& \times [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'+1)(2S+1)]^{1/2} [S_2(S_2+1)(2S_2+1)]^{1/2} \\
& \times (-1)^{S'_{12}+S_{12}+2S_3+S'+S+3} (-1)^{S'_{12}+S_2+1+S_1} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} \\
& \times (-1)^{S'+S_{12}+1+S_3} \begin{Bmatrix} S & S' & 1 \\ S'_{12} & S_{12} & S_3 \end{Bmatrix} [\hbar^2]
\end{aligned}$$

The triangular restriction for the $6j$ -symbol implies that $S' = S, S \pm 1$ and $S'_{12} = S_{12}, S_{12} \pm 1$ should be fulfilled. A further restriction follows from the expansion of the $9j$ -symbols containing three 1s. Consequently the reduced matrix elements can fill only the places according to the recipe

Total spin	Intermediate spin	Reduced matrix elements	
$S' = S$	$S'_{12} = S_{12}$	0	b
	$S'_{12} = S_{12} - 1$	b	0
$S' = S - 1$	$S'_{12} = S_{12}$	c	d
	$S'_{12} = S_{12} - 1$	d	c

The $6j$ -symbols become expressed through special formulae (Appendix 3, [4, 5]), yielding finally the simple formulae listed in Table 11.12.

Since the operator of the antisymmetric exchange is

$$\hat{H}^{\text{anti}} = \sum_i \sum_{j < i} \sum_{q=-1}^{+1} (-1)^q d_{ij,1,-q} \hat{A}_{ij,1,q}$$

its matrix elements become

$$H_{S'_{12}S'M', S_{12}SM}^{\text{anti}} = \sum_i \sum_{j < i} \sum_{q=-1}^{+1} (-1)^q d_{ij,1,-q} A_{S'_{12}S'M', S_{12}SM, ij, 1, q}$$

with the contributions of integrals

$$A_{S'_{12}S'M', S_{12}SM, ij, 1, q} = (-i\sqrt{2})(-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} R_{ij(S'_{12}, S'; S_{12}, S)} [\hbar^{-2}]$$

Then, after substitution, one gets

$$\begin{aligned}
 H_{S'_{12}S'M', S_{12}SM}^{\text{anti}} &= \sum_i \sum_{j < i} \sum_{q=-1}^{+1} (-1)^q d_{ij,1,-q} (-i\sqrt{2}) (-1)^{S'-M'} \\
 &\quad \times \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} R_{ij(S'_{12}, S'; S_{12}, S)}[\hbar^{-2}] \\
 &= \sum_i \sum_{j < i} \left\{ (-1) \left[-\frac{1}{\sqrt{2}} (d_x + id_y) \right] (-i\sqrt{2}) (-1)^{S'-M'} \right. \\
 &\quad \times \begin{pmatrix} S' & 1 & S \\ -M' & -1 & M \end{pmatrix} \\
 &\quad + d_z (-i\sqrt{2}) (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & 0 & M \end{pmatrix} \\
 &\quad + (-1) \left[\frac{1}{\sqrt{2}} (d_x - id_y) \right] (-i\sqrt{2}) (-1)^{S'-M'} \\
 &\quad \left. \times \begin{pmatrix} S' & 1 & S \\ -M' & +1 & M \end{pmatrix} \right\} R_{ij(S'_{12}, S'; S_{12}, S)}[\hbar^{-2}]
 \end{aligned}$$

Owing to the restriction for the non-zero $3j$ -symbols, namely $M' = M + q$, only one of the three terms can contribute, i.e.

$$\begin{aligned}
 H_{S'_{12}S', M-1, S_{12}SM}^{\text{anti}}(x_-) &= (-i\sqrt{2}) (-1)^{S'-(M-1)} \begin{pmatrix} S' & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} \\
 &\quad \times \sum_i \sum_{j < i} (-1) \left[-\frac{1}{\sqrt{2}} (d_{ij,x} + id_{ij,y}) \right] \\
 &\quad \times R_{ij(S'_{12}, S'; S_{12}, S)}[\hbar^{-2}]
 \end{aligned}$$

$$\begin{aligned}
 H_{S'_{12}S'M, S_{12}SM}^{\text{anti}}(x_0) &= (-i\sqrt{2}) (-1)^{S'-M} \begin{pmatrix} S' & 1 & S \\ -M & 0 & M \end{pmatrix} \\
 &\quad \times \sum_i \sum_{j < i} d_{ij,z} R_{ij(S'_{12}, S'; S_{12}, S)}[\hbar^{-2}]
 \end{aligned}$$

$$\begin{aligned}
 H_{S'_{12}S', M+1, S_{12}SM}^{\text{anti}}(x_+) &= (-i\sqrt{2}) (-1)^{S'-(M+1)} \begin{pmatrix} S' & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} \\
 &\quad \times \sum_i \sum_{j < i} (-1) \left[\frac{1}{\sqrt{2}} (d_{ij,x} - id_{ij,y}) \right] \\
 &\quad \times R_{ij(S'_{12}, S'; S_{12}, S)}[\hbar^{-2}]
 \end{aligned}$$

TABLE 11.12

Reduced matrix elements of the antisymmetric exchange for a general triad^a

$R_{ij}(S'_{12}, S'; S_{12}, S)$	Restrictions
$R_{12}(b) = B$	$S' = S$ $S'_{12} = S_{12} - 1$
$R_{13}(b) = -(-1)^{2S_1+2S_2+2S_{12}} B$ $R_{23}(b) = B$	
$B = (-1)^{2S_3+2S_{12}+2S} \frac{(2S+1)^{1/2}}{4[2S(S+1)(2S_{12}-1)(2S_{12}+1)]^{1/2}}$ $\times [(1+S_1+S_2-S_{12})(S_1-S_2+S_{12})(-S_1+S_2+S_{12})(1+S_1+S_2+S_{12})]^{1/2}$ $\times [(1+S_3+S-S_{12})(S_3-S+S_{12})(-S_3+S+S_{12})(1+S_3+S+S_{12})]^{1/2} [\hbar^2]$	
$R_{12}(c) = 0$	$S' = S - 1$ $S'_{12} = S_{12}$
$R_{13}(c) = (-1)^{2S_1+2S_2+2S_{12}} C[S_1(S_1+1) - S_2(S_2+1) + S_{12}(S_{12}+1)]$ $R_{23}(c) = C[-S_1(S_1+1) + S_2(S_2+1) + S_{12}(S_{12}+1)]$	
$C = (-1)^{2S_3+2S_{12}+2S} \frac{(S)^{1/2}}{4S_{12}(S_{12}+1)(2)^{1/2}}$ $\times [(1+S_3-S+S_{12})(S_3+S-S_{12})(-S_3+S+S_{12})(1+S_3+S+S_{12})]^{1/2} [\hbar^2]$	
$R_{12}(d) = D$	$S' = S - 1$ $S'_{12} = S_{12} - 1$
$R_{13}(d) = (-1)^{2S_1+2S_2+2S_{12}} \frac{S - S_{12}}{S_{12}} D$	
$R_{23}(d) = (-1) \frac{S - S_{12}}{S_{12}} D$	
$D = (-1)^{2S_3+2S_{12}+2S} \frac{1}{4[2S(2S_{12}-1)(2S_{12}+1)]^{1/2}}$ $\times [(1+S_1+S_2-S_{12})(S_1-S_2+S_{12})(-S_1+S_2+S_{12})(1+S_1+S_2+S_{12})]^{1/2}$ $\times [(-1-S_3+S_{12}+S)(-S_3+S_{12}+S)(S_3+S_{12}+S)(1+S_3+S_{12}+S)]^{1/2} [\hbar^2]$	

^aFor zero numerator the reduced matrix element is equal to zero. For zero denominator it equals 1.

TABLE 11.13

Matrix elements of the antisymmetric exchange for a general triad^a

$$H_{S_{12}-1, S, M-1, S_{12}SM}^{\text{anti}}(\mathbf{b}_-) = -i \left[\frac{(S-M+1)(S+M)}{2S(S+1)(2S+1)} \right]^{1/2} \sum_i \sum_{j<i} (d_{ij,x} + id_{ij,y}) R_{ij(S_{12}-1, S; S_{12}, S)} [\hbar^{-2}]$$

$$H_{S_{12}-1, SM, S_{12}SM}^{\text{anti}}(\mathbf{b}_0) = -i\sqrt{2} \frac{M}{[S(S+1)(2S+1)]^{1/2}} \sum_i \sum_{j<i} d_{ij,z} R_{ij(S_{12}-1, S; S_{12}, S)} [\hbar^{-2}]$$

$$H_{S_{12}-1, S, M+1, S_{12}SM}^{\text{anti}}(\mathbf{b}_+) = -i \left[\frac{(S-M)(S+M+1)}{2S(S+1)(2S+1)} \right]^{1/2} \sum_i \sum_{j<i} (d_{ij,x} - id_{ij,y}) R_{ij(S_{12}-1, S; S_{12}, S)} [\hbar^{-2}]$$

$$H_{S_{12}, S-1, M-1, S_{12}SM}^{\text{anti}}(\mathbf{c}_-) = -i(-1)^{2S-2M} \left[\frac{(S+M-1)(S+M)}{2S(2S-1)(2S+1)} \right]^{1/2} \\ \times \sum_i \sum_{j<i} (d_{ij,x} + id_{ij,y}) R_{ij(S_{12}, S-1; S_{12}, S)} [\hbar^{-2}]$$

$$H_{S_{12}, S-1, M, S_{12}SM}^{\text{anti}}(\mathbf{c}_0) = i\sqrt{2}(-1)^{2S-2M} \left[\frac{(S-M)(S+M)}{S(2S-1)(2S+1)} \right]^{1/2} \\ \times \sum_i \sum_{j<i} d_{ij,z} R_{ij(S_{12}, S-1; S_{12}, S)} [\hbar^{-2}]$$

$$H_{S_{12}, S-1, M+1, S_{12}SM}^{\text{anti}}(\mathbf{c}_+) = i(-1)^{2S-2M} \left[\frac{(S-M-1)(S-M)}{2S(2S-1)(2S+1)} \right]^{1/2} \\ \times \sum_i \sum_{j<i} (d_{ij,x} - id_{ij,y}) R_{ij(S_{12}, S-1; S_{12}, S)} [\hbar^{-2}]$$

$$H_{S_{12}-1, S-1, M-1, S_{12}SM}^{\text{anti}}(\mathbf{d}_-) = -i(-1)^{2S-2M} \left[\frac{(S+M-1)(S+M)}{2S(2S-1)(2S+1)} \right]^{1/2} \\ \times \sum_i \sum_{j<i} (d_{ij,x} + id_{ij,y}) R_{ij(S_{12}-1, S-1; S_{12}, S)} [\hbar^{-2}]$$

$$H_{S_{12}-1, S-1, M, S_{12}SM}^{\text{anti}}(\mathbf{d}_0) = i\sqrt{2}(-1)^{2S-2M} \left[\frac{(S-M)(S+M)}{S(2S-1)(2S+1)} \right]^{1/2} \sum_i \sum_{j<i} d_{ij,z} R_{ij(S_{12}-1, S-1; S_{12}, S)} [\hbar^{-2}]$$

$$H_{S_{12}-1, S-1, M+1, S_{12}SM}^{\text{anti}}(\mathbf{d}_+) = i(-1)^{2S-2M} \left[\frac{(S-M-1)(S-M)}{2S(2S-1)(2S+1)} \right]^{1/2} \\ \times \sum_i \sum_{j<i} (d_{ij,x} - id_{ij,y}) R_{ij(S_{12}-1, S-1; S_{12}, S)} [\hbar^{-2}]$$

^aThe reduced matrix elements $R_{ij(S_{12}, S; S_{12}, S)}$ are collected in Table 11.12. The spherical transforms are $d_{1,+1} = -(d_x + id_y)/\sqrt{2}$, $d_{1,-1} = (d_x - id_y)/\sqrt{2}$ and $d_{1,0} = d_z$.

The expressions for the corresponding $3j$ -symbols can be found in Appendix 3. Using them, the final formulae are obtained (Table 11.13).

As an example, for the $S_1 = S_2 = S_3 = 1/2$ cluster the structure of the antisymmetric exchange matrix is

$$\mathbf{H}^{\text{anti}} = \left(\begin{array}{cccc|cccc} 0 & 0 & 0 & 0 & c_+^* & 0 & d_+^* & 0 \\ 0 & 0 & 0 & 0 & c_0^* & c_+^* & d_0^* & d_+^* \\ 0 & 0 & 0 & 0 & c_-^* & c_0^* & d_-^* & d_0^* \\ 0 & 0 & 0 & 0 & 0 & c_-^* & 0 & d_-^* \\ \hline c_+ & c_0 & c_- & 0 & 0 & 0 & b_0^* & b_+^* \\ 0 & c_+ & c_0 & c_- & 0 & 0 & b_-^* & b_0^* \\ \hline d_+ & d_0 & d_- & 0 & b_0 & b_- & 0 & 0 \\ 0 & d_+ & d_0 & d_- & b_+ & b_0 & 0 & 0 \end{array} \right)$$

for

$$\left[\begin{array}{lll} S_{12} = 1 & S = 3/2 & M = -3/2 \\ & & M = -1/2 \\ & & M = +1/2 \\ & & M = +3/2 \\ \hline S_{12} = 1 & S = 1/2 & M = -1/2 \\ & & M = +1/2 \\ \hline S_{12} = 0 & S = 1/2 & M = -1/2 \\ & & M = +1/2 \end{array} \right]$$

The letters indicate the type of reduced matrix element (common within a block); the lower indices ($q = 0, \pm 1$) indicate different angular parts (different $3j$ -symbols) owing to the application of the Wigner-Eckart theorem.

Evaluation of the reduced matrix elements according to Table 11.12 yields the result: $R_{12}(b) = +1/2$, $R_{13}(b) = -1/2$, $R_{23}(b) = +1/2$, $R_{12}(c) = 0$, $R_{13}(c) = +\sqrt{3/8}$, $R_{23}(c) = +\sqrt{3/8}$, $R_{12}(d) = +1/\sqrt{2}$, $R_{13}(d) = +1/\sqrt{8}$ and $R_{23}(d) = -1/\sqrt{8}$ (all in units of $[\hbar^2]$). A matrix element of the antisymmetric exchange, for example, is

$$d_+(M = -3/2) = i \frac{-1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}} d_{12,-1} + \frac{1}{\sqrt{8}} d_{13,-1} - \frac{1}{\sqrt{8}} d_{23,-1} \right)$$

In the general case these matrix elements contain nine (spherical or Cartesian) parameters $d_{ij,q}$. For an isosceles triangle they simplify to only

three components, d_q , and the interaction matrix becomes

$$\mathbf{H}^{\text{anti}} = i \left(\begin{array}{cccc|cc|cc} 0 & 0 & 0 & 0 & * & 0 & * & 0 \\ 0 & 0 & 0 & 0 & * & * & * & * \\ 0 & 0 & 0 & 0 & * & * & * & * \\ 0 & 0 & 0 & 0 & 0 & * & 0 & * \\ \hline \frac{-\sqrt{3}}{2}d_{-1} & \frac{+1}{\sqrt{2}}d_0 & \frac{-1}{2}d_{+1} & 0 & 0 & 0 & * & * \\ 0 & \frac{-1}{2}d_{-1} & \frac{+1}{\sqrt{2}}d_0 & \frac{-\sqrt{3}}{2}d_{+1} & 0 & 0 & * & * \\ \hline \frac{-1}{2}d_{-1} & \frac{+1}{\sqrt{6}}d_0 & \frac{-1}{\sqrt{12}}d_{+1} & 0 & \frac{+1}{2\sqrt{3}}d_0 & \frac{-1}{\sqrt{6}}d_{+1} & 0 & 0 \\ 0 & \frac{-1}{\sqrt{12}}d_{-1} & \frac{+1}{\sqrt{6}}d_0 & \frac{-1}{2}d_{+1} & \frac{+1}{\sqrt{6}}d_{-1} & \frac{-1}{2\sqrt{3}}d_0 & 0 & 0 \end{array} \right)$$

where the asterisk indicates a filled space determined by the hermitian property of the matrix.

The effect of the antisymmetric exchange lies in a second-order splitting of degenerate energy levels. Thus the antisymmetric exchange leads to zero-field splitting. In the above case of the $S_1 = S_2 = S_3 = 1/2$ cluster the zero-field energy levels $\varepsilon(S_{12}, S)$ are accidentally degenerate for an isosceles triangle:

$$\varepsilon(1, 1/2) = \varepsilon(0, 1/2) = A_{1/2} = (3/4)J$$

Asymmetric exchange is incapable of removing this kind of degeneracy since there are no interaction elements between $|1, 1/2\rangle$ and $|0, 1/2\rangle$ kets. Only antisymmetric exchange couples the above states, which lead to the removal of the accidental degeneracy of the two Kramers doublets, yielding

$$\varepsilon_{\pm} = (3/4)J \pm d_z/(2\sqrt{3})$$

Some consequences of antisymmetric exchange for trinuclear systems are discussed elsewhere [6].

11.2.5 Biquadratic exchange

The operator of biquadratic exchange involves not only the pair-interaction terms but also the triad-interaction ones

$$\begin{aligned} \hat{H}^{\text{bi}} = & -J[(\hat{S}_1 \cdot \hat{S}_2)^2 + (\hat{S}_1 \cdot \hat{S}_3)^2 + (\hat{S}_2 \cdot \hat{S}_3)^2][\hbar^{-4}] \\ & -J'[(\hat{S}_1 \cdot \hat{S}_2)(\hat{S}_1 \cdot \hat{S}_3) + (\hat{S}_1 \cdot \hat{S}_2)(\hat{S}_2 \cdot \hat{S}_3) + (\hat{S}_1 \cdot \hat{S}_3)(\hat{S}_2 \cdot \hat{S}_3)][\hbar^{-4}] \end{aligned}$$

Nevertheless, biquadratic exchange spans the class of isotropic exchange. The individual terms are of the general type

$$\hat{T} = (\hat{S}_A \cdot \hat{S}_B)(\hat{S}_C \cdot \hat{S}_D)$$

and can be expressed via a scalar product of two second-rank tensors

$$\begin{aligned} & \sqrt{5} \left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_A \otimes \vec{S}_C) \} \otimes \{ T_2(\vec{S}_B \otimes \vec{S}_D) \} \right\} \\ &= \sum_{q=-2}^{+2} (-1)^q \hat{T}_{2,-q}(\vec{S}_A \otimes \vec{S}_C) \hat{T}_{2,q}(\vec{S}_B \otimes \vec{S}_D) \\ &= \frac{1}{2} [(\vec{S}_A \cdot \vec{S}_B)(\vec{S}_C \cdot \vec{S}_D) + (\vec{S}_A \cdot \vec{S}_D)(\vec{S}_B \cdot \vec{S}_C)] - \frac{1}{3} (\vec{S}_A \cdot \vec{S}_C)(\vec{S}_B \cdot \vec{S}_D) \end{aligned}$$

Those second-rank tensors on the left side are constructed from first-rank tensors (spherical vectors) as follows (Table 1.14)

$$\begin{aligned} \hat{T}_{2,+2}(\vec{S}_A \otimes \vec{S}_C) &= \hat{T}_{1,+1}(\vec{S}_A) \hat{T}_{1,+1}(\vec{S}_C) \\ \hat{T}_{2,+1}(\vec{S}_A \otimes \vec{S}_C) &= \frac{1}{\sqrt{2}} [\hat{T}_{1,+1}(\vec{S}_A) \hat{T}_{1,0}(\vec{S}_C) + \hat{T}_{1,0}(\vec{S}_A) \hat{T}_{1,+1}(\vec{S}_C)] \\ \hat{T}_{2,0}(\vec{S}_A \otimes \vec{S}_C) &= \frac{2}{\sqrt{6}} \hat{T}_{1,0}(\vec{S}_A) \hat{T}_{1,0}(\vec{S}_C) \\ &\quad + \frac{1}{\sqrt{6}} [\hat{T}_{1,+1}(\vec{S}_A) \hat{T}_{1,-1}(\vec{S}_C) + \hat{T}_{1,-1}(\vec{S}_A) \hat{T}_{1,+1}(\vec{S}_C)] \\ \hat{T}_{2,-1}(\vec{S}_A \otimes \vec{S}_C) &= \frac{1}{\sqrt{2}} [\hat{T}_{1,-1}(\vec{S}_A) \hat{T}_{1,0}(\vec{S}_C) + \hat{T}_{1,0}(\vec{S}_A) \hat{T}_{1,-1}(\vec{S}_C)] \\ \hat{T}_{2,-2}(\vec{S}_A \otimes \vec{S}_C) &= \hat{T}_{1,-1}(\vec{S}_A) \hat{T}_{1,-1}(\vec{S}_C) \end{aligned}$$

and analogously for $\hat{T}_{2,q}(\vec{S}_B \otimes \vec{S}_D)$. The scalar products on the right side are evaluated as

$$\begin{aligned} (\vec{S}_A \cdot \vec{S}_C) &= -\sqrt{3} \left\{ \hat{T}_0(\vec{S}_A \otimes \vec{S}_C) \right\} = \sum_{q=-1}^{+1} (-1)^q \hat{T}_{1,-q}(\vec{S}_A) \hat{T}_{1,q}(\vec{S}_C) \\ &= -\hat{T}_{1,+1}(\vec{S}_A) \hat{T}_{1,-1}(\vec{S}_C) + \hat{T}_{1,0}(\vec{S}_A) \hat{T}_{1,0}(\vec{S}_C) - \hat{T}_{1,-1}(\vec{S}_A) \hat{T}_{1,+1}(\vec{S}_C) \end{aligned}$$

and analogously for the other combinations. After substitution into the right and left sides the above expression is easily proven.

There are two relevant cases:

1. For $A = C = 1$ and $B = D = 2$ we get the result already obtained in the case of dinuclear systems

$$\begin{aligned} & \sqrt{5} \left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \} \otimes \{ T_2(\vec{S}_2 \otimes \vec{S}_2) \} \right\} \\ &= (\vec{S}_1 \cdot \vec{S}_2)(\vec{S}_1 \cdot \vec{S}_2) - \frac{1}{3}(\vec{S}_1 \cdot \vec{S}_1)(\vec{S}_2 \cdot \vec{S}_2) \end{aligned}$$

2. For $A = C = 1$, $B = 2$ and $D = 3$ we get an expression of the type

$$\begin{aligned} & \sqrt{5} \left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \} \otimes \{ T_2(\vec{S}_2 \otimes \vec{S}_3) \} \right\} \\ &= \frac{1}{2} [(\vec{S}_1 \cdot \vec{S}_2)(\vec{S}_1 \cdot \vec{S}_3) + (\vec{S}_1 \cdot \vec{S}_3)(\vec{S}_2 \cdot \vec{S}_1)] - \frac{1}{3}(\vec{S}_1 \cdot \vec{S}_1)(\vec{S}_2 \cdot \vec{S}_3) \end{aligned}$$

The matrix elements of the tensor product are evaluated by applying the Wigner-Eckart theorem

$$\begin{aligned} & \left\langle S' M' \left| \left\{ \hat{T}_{0,0} \{ \hat{T}_2(\vec{S}_A \otimes \vec{S}_C) \} \otimes \{ T_2(\vec{S}_B \otimes \vec{S}_D) \} \right\} \right| S M \right\rangle \\ &= (-1)^{S'-M'} \begin{pmatrix} S' & 0 & S \\ -M' & 0 & M \end{pmatrix} \\ & \quad \times \left\langle S' \left\| \left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_A \otimes \vec{S}_C) \} \otimes \{ T_2(\vec{S}_B \otimes \vec{S}_D) \} \right\} \right\| S \right\rangle \end{aligned}$$

with the special $3j$ -symbol

$$\begin{pmatrix} S' & 0 & S \\ -M' & 0 & M \end{pmatrix} = (-1)^{S-M} (2S+1)^{-1/2} \delta_{S,S'} \delta_{M,M'}$$

The tensor ranks for the decoupling formula are assigned as follows

Tensor operator	k_1	k_2	k_{ij}	k_3	k
$\left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \} \otimes \{ T_2(\vec{S}_2 \otimes \vec{S}_2) \} \right\}$	2	2	$k_{12} = 0$	0	0
$\left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \} \otimes \{ T_2(\vec{S}_3 \otimes \vec{S}_3) \} \right\}$	2	0	$k_{12} = 2$	2	0
$\left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_2 \otimes \vec{S}_2) \} \otimes \{ T_2(\vec{S}_3 \otimes \vec{S}_3) \} \right\}$	0	2	$k_{12} = 2$	2	0
$\left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \} \otimes \{ T_2(\vec{S}_2 \otimes \vec{S}_3) \} \right\}$	2	1	$k_{23} = 2$	1	0
$\left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_2 \otimes \vec{S}_2) \} \otimes \{ T_2(\vec{S}_1 \otimes \vec{S}_3) \} \right\}$	1	2	$k_{13} = 2$	1	0
$\left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_3 \otimes \vec{S}_3) \} \otimes \{ T_2(\vec{S}_1 \otimes \vec{S}_2) \} \right\}$	1	1	$k_{12} = 2$	2	0

The decoupling formula for the reduced matrix element yields

(a) the first type (pair-interaction) reduced matrix elements, which are straightforward

$$R_{1122} \equiv \langle S_1 S_2 S'_{12} S_3 S' | \{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \} \otimes \{ T_2(\vec{S}_2 \otimes \vec{S}_2) \} \} | S_1 S_2 S_{12} S_3 S \rangle$$

$$= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 0 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 2 \\ S_2 & S_2 & 2 \\ S'_{12} & S_{12} & 0 \end{Bmatrix}$$

$$\times \langle S_1 | \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) | S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 0 + 1)]^{1/2}$$

$$\times \begin{Bmatrix} S'_{12} & S_{12} & 0 \\ S_3 & S_3 & 0 \\ S' & S & 0 \end{Bmatrix} \langle S_2 | \hat{T}_2(\vec{S}_2 \otimes \vec{S}_2) | S_2 \rangle \langle S_3 | \hat{T}_0(\vec{S}_3) | S_3 \rangle$$

$$R_{1133} \equiv \langle S_1 S_2 S'_{12} S_3 S' | \{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \} \otimes \{ T_2(\vec{S}_3 \otimes \vec{S}_3) \} \} | S_1 S_2 S_{12} S_3 S \rangle$$

$$= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 2 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 2 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 2 \end{Bmatrix}$$

$$\times \langle S_1 | \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) | S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 0 + 1)]^{1/2}$$

$$\times \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S_3 & S_3 & 2 \\ S' & S & 0 \end{Bmatrix} \langle S_2 | \hat{T}_0(\vec{S}_2) | S_2 \rangle \langle S_3 | \hat{T}_2(\vec{S}_3 \otimes \vec{S}_3) | S_3 \rangle$$

$$R_{2233} \equiv \langle S_1 S_2 S'_{12} S_3 S' | \{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_2 \otimes \vec{S}_2) \} \otimes \{ T_2(\vec{S}_3 \otimes \vec{S}_3) \} \} | S_1 S_2 S_{12} S_3 S \rangle$$

$$= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 2 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 2 \\ S'_{12} & S_{12} & 2 \end{Bmatrix}$$

$$\times \langle S_1 | \hat{T}_0(\vec{S}_1) | S_1 \rangle [(2S' + 1)(2S + 1)(2 \cdot 0 + 1)]^{1/2}$$

$$\times \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S_3 & S_3 & 2 \\ S' & S & 0 \end{Bmatrix} \langle S_2 | \hat{T}_2(\vec{S}_2 \otimes \vec{S}_2) | S_2 \rangle \langle S_3 | \hat{T}_2(\vec{S}_3 \otimes \vec{S}_3) | S_3 \rangle$$

(b) the second type (triad-interaction) reduced matrix elements, such as

$$\begin{aligned}
 R_{1123} &\equiv \langle S_1 S_2 S_3 S'_{23} S' \| \{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \} \otimes \{ T_2(\vec{S}_2 \otimes \vec{S}_3) \} \} \| S_1 S_2 S_3 S_{23} S \rangle \\
 &= [(2S' + 1)(2S + 1)(2 \cdot 0 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 2 \\ S'_{23} & S_{23} & 2 \\ S' & S & 0 \end{Bmatrix} \\
 &\quad \times \langle S_1 \| \hat{T}_2(\vec{S}_1 \otimes \vec{S}_1) \| S_1 \rangle [(2S'_{23} + 1)(2S_{23} + 1)(2 \cdot 2 + 1)]^{1/2} \\
 &\quad \times \begin{Bmatrix} S_2 & S_2 & 1 \\ S_3 & S_3 & 1 \\ S'_{23} & S_{23} & 2 \end{Bmatrix} \langle S_2 \| \hat{T}_1(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_1(\vec{S}_3) \| S_3 \rangle
 \end{aligned}$$

which needs recoupling to the common coupling order with the help of the $6j$ -symbols (Section 1.4.8)

$$\begin{aligned}
 |S_1 S_2 S_{12} S_3 S\rangle &= \sum_{S_{23}} |S_1 S_2 S_3 S_{23} S\rangle \cdot \langle S_1 S_2 S_{12} S_3 S | S_1 S_2 S_3 S_{23} S \rangle \\
 &= \sum_{S_{23}=|S_2-S_3|}^{S_2+S_3} |S_1 S_2 S_3 S_{23} S\rangle [(2S_{12} + 1)(2S_{23} + 1)]^{1/2} \\
 &\quad \times (-1)^{-(S_1+S_2+S_3+S)} \begin{Bmatrix} S_1 & S_2 & S_{12} \\ S_3 & S & S_{23} \end{Bmatrix}
 \end{aligned}$$

The triad-interaction matrix elements will not be considered in more detail.

The $9j$ -symbols containing one zero collapse into $6j$ -symbols and since

$$\begin{aligned}
 \langle S_A \| \hat{T}_0(\vec{S}_A) \| S_A \rangle &= (2S_A + 1)^{1/2} \\
 \langle S_A \| \hat{T}_2(\vec{S}_A \otimes \vec{S}_A) \| S_A \rangle \\
 &= [S_A(S_A + 1)(2S_A + 1)(2S_A + 3)(2S_A - 1)/6]^{1/2} [\hbar^2]
 \end{aligned}$$

some simplifications are obtained for the pair-interaction reduced matrix elements (Table 11.14). The triangular restrictions for the $6j$ -symbols imply $S'_{12} = S_{12}$, $S'_{12} \pm 1$, $S'_{12} \pm 2$, and the formulae for the $6j$ -symbols are collected in Appendix 3.

TABLE 11.14

Pair-interaction reduced matrix elements of the biquadratic exchange for a general triad^a

$R_{AABB}(S'_{12}, S, S_{12}, S)$	Restrictions
$R_{1122} = \delta_{S_{12}, S'_{12}} \delta_{S', S} \frac{(2S+1)^{1/2}}{(5)^{1/2}} (-1)^{S_1+S_2+S_{12}} \begin{Bmatrix} S_1 & S_1 & 2 \\ S_2 & S_2 & S_{12} \end{Bmatrix}$ $\times [S_1(S_1+1)(2S_1+1)(2S_1+3)(2S_1-1)/6]^{1/2}$ $\times [S_2(S_2+1)(2S_2+1)(2S_2+3)(2S_2-1)/6]^{1/2} [\hbar^4]$	$S'_{12} = S_{12}$
$R_{1133} = \delta_{S, S'} (-1)^{2S_1+2S_2+S'_{12}+S_{12}} \frac{[(2S+1)(2S'_{12}+1)(2S_{12}+1)]^{1/2}}{(5)^{1/2}}$ $\times (-1)^{S_{12}+S_3+S} \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S_3 & S_3 & S \end{Bmatrix} (-1)^{S'_{12}+S_1+S_2} \begin{Bmatrix} S_{12} & S'_{12} & 2 \\ S_1 & S_1 & S_2 \end{Bmatrix}$ $\times [S_1(S_1+1)(2S_1+1)(2S_1+3)(2S_1-1)/6]^{1/2}$ $\times [S_3(S_3+1)(2S_3+1)(2S_3+3)(2S_3-1)/6]^{1/2} [\hbar^4]$	$S'_{12} = S_{12}, S_{12} \pm 1, S_{12} \pm 2$
$R_{2233} = \delta_{S, S'} \frac{[(2S+1)(2S'_{12}+1)(2S_{12}+1)]^{1/2}}{(5)^{1/2}}$ $\times (-1)^{S'_{12}+S_2+S_1} \begin{Bmatrix} S_{12} & S'_{12} & 2 \\ S_2 & S_2 & S_1 \end{Bmatrix} (-1)^{S_{12}+S_3+S} \begin{Bmatrix} S'_{12} & S_{12} & 2 \\ S_3 & S_3 & S \end{Bmatrix}$ $\times [S_2(S_2+1)(2S_2+1)(2S_2+3)(2S_2-1)/6]^{1/2}$ $\times [S_3(S_3+1)(2S_3+1)(2S_3+3)(2S_3-1)/6]^{1/2} [\hbar^4]$	$S'_{12} = S_{12}, S_{12} \pm 1, S_{12} \pm 2$

^aFor zero numerator the reduced matrix element is equal to zero. For zero denominator it equals 1.

The structure of the interaction matrix is

Total spin	Intermediate spin	Reduced matrix elements		
$S' = S$	$S'_{12} = S_{12}$	a	b	c
	$S'_{12} = S_{12} - 1$	b	a	b
	$S'_{12} = S_{12} - 2$	c	b	a

Application of the Wigner–Eckart theorem yields

$$\begin{aligned}
 & \langle S'_{12} S' M' | \{ \hat{T}_{0,0} \{ \hat{T}_2(\vec{S}_A \otimes \vec{S}_C) \} \otimes \{ T_2(\vec{S}_B \otimes \vec{S}_D) \} \} | S_{12} S M \rangle \\
 &= (2S+1)^{-1/2} \delta_{S, S'} \delta_{M, M'} \\
 & \quad \times \langle S'_{12} S | \{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_A \otimes \vec{S}_C) \} \otimes \{ T_2(\vec{S}_B \otimes \vec{S}_D) \} \} | S_{12} S \rangle
 \end{aligned}$$

and then the pair-interaction terms have the following matrix elements irrespective of the magnetic quantum number M

$$\begin{aligned} \langle S'_{12} SM | (\vec{S}_A \cdot \vec{S}_B)^2 | S_{12} SM \rangle &= \sqrt{\frac{5}{2S+1}} R_{AABB}(S'_{12}, S, S_{12}, S) \\ &\quad + \delta_{S'_{12}, S_{12}} \frac{1}{3} S_A(S_A+1) S_B(S_B+1) [\hbar^4] \end{aligned}$$

Biquadratic exchange applies side by side with bilinear exchange, hence

$$\begin{aligned} \langle S'_{12} SM | \hat{H} | S_{12} SM \rangle &= \sum_A \sum_{B>A} \left\{ -J_{AB} \langle S'_{12} SM | (\vec{S}_A \cdot \vec{S}_B) | S_{12} SM \rangle [\hbar^{-2}] \right. \\ &\quad \left. - j_{AB} \langle S'_{12} SM | (\vec{S}_A \cdot \vec{S}_B)^2 | S_{12} SM \rangle [\hbar^{-4}] \right\} \end{aligned}$$

More details about biquadratic exchange can be found elsewhere [6–8]. Since biquadratic exchange can couple kets $|S_{12}, S\rangle$ of different intermediate spins, it can result in a splitting of degenerate energy levels. For example, in the system $S_1 = S_2 = S_3 = 1$ an accidental degeneracy of energy levels occurs for an equilateral triangle: $\varepsilon(S_{12}, S) = \varepsilon(0, 1) = \varepsilon(1, 1) = \varepsilon(2, 1) = 2J$; the degeneracy is partially removed by the biquadratic exchange (Table 11.15). This may have a consequence in the alteration of the ground state, as evidenced from Fig. 11.9.

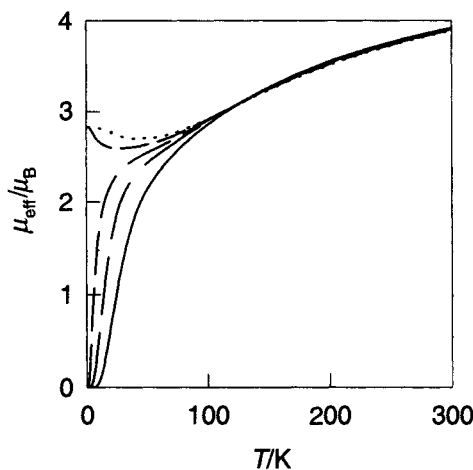


Fig. 11.9. Effect of biquadratic exchange on the temperature dependence of the effective magnetic moment for the $S_1 = S_2 = S_3 = 1$ system: $J/k = -100$ K, individual curves (from bottom to top) correspond to $j/k = 0, 10, 15, 20$ and 25 K.

TABLE 11.15

Matrix elements of the biquadratic exchange for the $S_1 = S_2 = S_3 = 1$ system (an isosceles triangle)

S'_{12}	S_{12}	S	Matrix element	Eigenvalues
1	1	0	$3J - (3/2)j$	$3J - (3/2)j$
0	0	1	$2J - (17/3)j$	$2J - 7j$
1	1	1	$2J - 4j$	$2J - 4j$
0	1	1	0	
2	2	1	$2J - (16/3)j$	$2J - 4j$
1	2	1	0	
0	2	1	$-(2\sqrt{5}/3)j$	
2	2	2	$-3j$	$-3j$
1	2	2	0	
1	1	2	$-3j$	$-3j$
2	2	3	$-3J - (9/2)j$	$-3J - (9/2)j$

11.2.6 Double exchange

Mixed-valence trinuclear systems involve two groups:

- (1) $d^n-d^n-d^{n+1}$ systems with an extra electron (electron delocalisation);
- (2) $d^n-d^n-d^{n-1}$ systems with an extra hole (hole delocalisation).

The localisation of the extra electron (hole) on a definite centre is denoted by $\bullet$, i.e. $|A\bullet BC\rangle$, $|AB\bullet C\rangle$ and $|ABC\bullet\rangle$. Each ket is constructed by means a coupling scheme, for example

$$|A\bullet BC\rangle: S_A + s = S_{As}, S_B + S_C = S_{BC}, S_{As} + S_{BC} = S$$

$$|AB\bullet C\rangle: S_A + S_C = S_{AC}, S_B + s = S_{Bs}, S_{AC} + S_{Bs} = S$$

$$|ABC\bullet\rangle: S_A + S_B = S_{AB}, S_C + s = S_{Cs}, S_{AB} + S_{Cs} = S$$

where $s = 1/2$ is the spin number of the extra electron. Any pair of kets is related through a recoupling formula which, for the four spins involved, contains 9j-symbols (Section 1.4.9), say

$$\begin{aligned}
 |A\bullet BC\rangle &= [(2S_{AB} + 1)(2S_{BC} + 1)(2S_A + 2s + 1)(2S_C + 2s + 1)]^{1/2} \\
 &\times \left\{ \begin{array}{ccc} S_A & S_B & S_{AB} \\ s & S_C & (S_C + s) \\ (S_A + s) & S_{BC} & S \end{array} \right\} |ABC\bullet\rangle \\
 &= R(S_A, S_B, S_C, S_{AB}, S_{BC}, S) |ABC\bullet\rangle
 \end{aligned}$$

In accordance with the addition of angular momenta the intermediate spin numbers are

$$S_{AB} = |S_A - S_B|, \dots, (S_A + S_B)$$

$$S_{BC} = |S_B - S_C|, \dots, (S_B + S_C)$$

Since only one possibility exists for the intermediate states $S_{As} = S_A + s$ and $S_{Cs} = S_C + s$, a single term arises in the recoupling formula. For electron delocalisation $s = +1/2$ whereas for the case of hole delocalisation $s = -1/2$ can be applied.

For a homonuclear system, $S_A = S_B = S_C \equiv S_i$ (which is the most frequent case of mixed-valence systems), the $9j$ -symbol can be expressed through $6j$ -symbols and the recoupling coefficients become [9]

$$\begin{aligned} R_+(S_0, S_{ij}, S_{jk}, S) &= (2S_0 + 2)[(2S_{ij} + 1)(2S_{jk} + 1)]^{1/2} \\ &\times \left\{ \begin{array}{ccc} S_0 & S_0 & S_{ij} \\ 1/2 & S_0 & (S_0 + 1/2) \\ (S_0 + 1/2) & S_{jk} & S \end{array} \right\} = (-1)^{S+3S_0+1/2} \frac{(2S_{ij} + 1)^{1/2}}{(2S_0 + 1)(2S_{jk} + 1)^{1/2}} \\ &\times \left(\left\{ \begin{array}{ccc} S_{ij} & S & (S_0 + 1/2) \\ (S_{jk} + 1/2) & S_0 & S_0 \end{array} \right\} \right. \\ &\times [(S_{jk} - S_0 + S + 1/2)(S - S_{jk} + S_0 + 1/2)(2S_0 + S_{jk} + 2)(S_{jk} + 1)]^{1/2} \\ &- \left. \left\{ \begin{array}{ccc} S_{ij} & S & (S_0 + 1/2) \\ (S_{jk} - 1/2) & S_0 & S_0 \end{array} \right\} \right. \\ &\times \left. [(S_{jk} + S_0 + S + 3/2)(-S + S_{jk} + S_0 + 1/2)(2S_0 - S_{jk} + 1)S_{jk}]^{1/2} \right) \end{aligned}$$

and

$$\begin{aligned} R_-(S_0, S_{ij}, S_{jk}, S) &= (2S_0 + 1)[(2S_{ij} + 1)(2S_{jk} + 1)]^{1/2} \\ &\times \left\{ \begin{array}{ccc} S_0 & S_0 & S_{ij} \\ 1/2 & S_0 & (S_0 - 1/2) \\ (S_0 - 1/2) & S_{jk} & S \end{array} \right\} = (-1)^{S+3S_0-1/2} \frac{(2S_{ij} + 1)^{1/2}}{2S_0(2S_{jk} + 1)^{1/2}} \\ &\times \left(\left\{ \begin{array}{ccc} S_{ij} & S & (S_0 - 1/2) \\ (S_{jk} + 1/2) & S_0 & S_0 \end{array} \right\} \right. \\ &\times [(S_{jk} + S_0 + S + 3/2)(-S + S_{jk} + S_0 + 1/2)(2S_0 - S_{jk})(S_{jk} + 1)]^{1/2} \\ &- \left. \left\{ \begin{array}{ccc} S_{ij} & S & (S_0 - 1/2) \\ (S_{jk} - 1/2) & S_0 & S_0 \end{array} \right\} \right. \\ &\times \left. [(-S_{jk} + S_0 + S + 1/2)(S + S_{jk} - S_0 + 1/2)(2S_0 + S_{jk} + 1)S_{jk}]^{1/2} \right) \end{aligned}$$

The above three trial kets $|I\rangle \equiv |A\bullet BC\rangle$ do not represent any physical state. Since they are threefold degenerate, the energy levels are obtained by solving the secular equation

$$\det\{H_{IJ} - \varepsilon_I \delta_{IJ}\} = 0$$

provided that the kets are orthogonal. The total number of states is $N = 3[2(S_A + 1/2) + 1](2S_B + 1)(2S_C + 1)$. The interaction (zero-field) operator

$$H_{IJ} = H_{IJ}^{\text{iso}} + H_{IJ}^{\text{tr}}$$

includes the usual bilinear isotropic exchange

$$H_{IJ}^{\text{iso}} = \left\langle I \left| [-J_{AB}(\vec{S}_A \cdot \vec{S}_B) - J_{AC}(\vec{S}_A \cdot \vec{S}_C) - J_{BC}(\vec{S}_B \cdot \vec{S}_C)] \hbar^{-2} \right| J \right\rangle$$

along with the transfer operator

$$H_{IJ}^{\text{tr}} = \left\langle I \left| \hat{H}^{\text{el}} \right| J \right\rangle = (-1)^\sigma p_{AB} R_\pm$$

The isotropic exchange operator does not contain the extra electron so that it projects only to the subspace of genuine spin functions $|I_0\rangle \equiv |S_A S_B S_C S_{AB} S_M\rangle$ with the usual matrix elements as listed in Table 11.4. In the case of an isosceles triangle the eigenvalues reduce to a simple formula

$$\varepsilon_I = -\frac{J}{2} S(S+1) - \frac{J}{2} \sum_{i=1}^3 S_i(S_i+1)$$

where the second term (constant within a cluster) can be omitted.

The transfer operator accounts for the degeneracy of the trial kets. It contains the recoupling coefficient R_+ or R_- (dimensionless) whereas the physical information is contained in the transfer parameter p_{AB} (in energy units). The content of the pair-interaction transfer parameter depends upon the number of electrons involved; it contains the usual one-electron integrals (transfer integrals) along with two- and three-centre electron repulsion integrals (in particular Coulomb and exchange integrals). The value of the transfer parameter is relatively high: $|p/J| \gg 1$. The sign factor σ in the matrix elements of the transfer operator accounts for the permutation symmetry of centres.

To exemplify the double exchange problem, let us consider the $d^1-d^1-d^2$ system. The number of kets is $N = 3[2(1/2 + 1/2) + 1][2(1/2) + 1][2(1/2) + 1] = 36$. One of the coupling schemes is

$$S_{As} = S_A + s = 1$$

$$S_{BC} = |S_B - S_C|, \dots, (S_B + S_C) = 0, 1$$

$$S = |S_{As} - S_{BC}|, \dots, (S_{As} + S_{BC}) = 1, 0, 1, 2$$

and each spin state is threefold (spatially) degenerate. For an isosceles triangle the interaction matrix can be factorised into blocks of lower dimension according to the total spin number, hence [9]

$$\mathbf{H}_{S=0} = \begin{pmatrix} 0 & * & * \\ -p/2 & 0 & * \\ -p/2 & -p/2 & 0 \end{pmatrix} \text{ for } \begin{bmatrix} S_{BC} = 1 & |A \bullet BC\rangle \\ & |AB \bullet C\rangle \\ & |ABC \bullet\rangle \end{bmatrix}$$

$$\mathbf{H}_{S=2} = \begin{pmatrix} -3J & * & * \\ p & -3J & * \\ p & p & -3J \end{pmatrix} \text{ for } \begin{bmatrix} S_{BC} = 1 & |A \bullet BC\rangle \\ & |AB \bullet C\rangle \\ & |ABC \bullet\rangle \end{bmatrix}$$

and

$$\mathbf{H}_{S=1} = \begin{pmatrix} -J & 0 & 0 & | & 0 & * & * \\ 0 & -J & 0 & | & * & 0 & * \\ 0 & 0 & -J & | & * & * & 0 \\ \hline 0 & -p/\sqrt{2} & +p/\sqrt{2} & | & -J & * & * \\ +p/\sqrt{2} & 0 & -p/\sqrt{2} & | & -p/2 & -J & * \\ -p/\sqrt{2} & +p/\sqrt{2} & 0 & | & -p/2 & -p/2 & -J \end{pmatrix}$$

$$\text{for } \begin{bmatrix} S_{BC} = 1 & |A \bullet BC\rangle \\ & |AB \bullet C\rangle \\ & |ABC \bullet\rangle \\ \hline S_{BC} = 0 & |A \bullet BC\rangle \\ & |AB \bullet C\rangle \\ & |ABC \bullet\rangle \end{bmatrix}$$

where the asterisk indicates a filled position determined by the symmetry property of the matrix.

The eigenvalues of the interaction matrix are collected in Table 11.16 along with other relevant data. In the absence of isotropic exchange:

TABLE 11.16

Zero-field energy levels for mixed-valence triads in the geometry of an isosceles triangle

System	S	State	Energy ^a
$d^0-d^0-d^1$	1/2	${}^2A_1''$	$2p$
		${}^2E''$	$-p$
$d^1-d^1-d^0$	0	${}^1A_1'$	$2p$
		${}^1E'$	$-p$
	1	${}^3A_2'$	$-J - 2p$
		${}^3E'$	$-J + p$
$d^1-d^1-d^2$	0	${}^1A_1''$	$-p$
	0	${}^1E''$	$(1/2)p$
	1	${}^3A_1''$	$-J$
		${}^3E''$	$-J + (3/2)p$
		${}^3A_2'', {}^3E''$	$-J - p$
	2	${}^5A_1''$	$-3J + 2p$
		${}^5E''$	$-3J - p$
$d^2-d^2-d^1$	1/2	${}^2A_1'', {}^2E''$	$-p$
		${}^2A_2''$	0
		${}^2E''$	$(3/2)p$
	3/2	${}^4A_2''$	$-(3/2)J + (3/2)p$
		${}^4E''$	$-(3/2)J - (3/2)p$
		${}^4A_1'', {}^4E''$	$-(3/2)J + (1/2)p$
	5/2	${}^6A_1''$	$-4J - 2p$
		${}^6E''$	$-4J + p$
$d^2-d^2-d^3$	1/2	${}^2A_2'', {}^2E'$	$(1/3)p$
		${}^2A_1'', {}^2E'$	$-p$
	3/2	${}^4A_2'', {}^4E'$	$-(3/2)J + (4/3)p$
		${}^4A_2'', {}^4E', {}^4A_1'$	$-(3/2)J - p, \#$
		${}^4E'$	$-(3/2)J$
	5/2	${}^6A_1'$	$-4J - (1/3)p$
		${}^6E'$	$-4J + (5/3)p$
		${}^6A_2'', {}^6E'$	$-4J - p$
	7/2	${}^8A_1'$	$-(15/2)J + 2p$
		${}^8E'$	$-(15/2)J - p$
$d^3-d^3-d^2$	0	${}^1A_2''$	$(4/3)p$
		${}^1E''$	$-(2/3)p$
	1	${}^3A_1'', {}^3A_2'', {}^3E''$	$-J - p$
		${}^3A_1'', {}^3E''$	$-J + (4/3)p$
		${}^3E''$	$-J$
	2	${}^5A_1'', {}^5A_2'', {}^5E''$	$-3J + (1/3)p$
		${}^5A_2'', {}^5E''$	$-3J - (4/3)p$
		${}^5E''$	$-3J + (4/3)p$
	3	${}^7A_2'', {}^7E''$	$-6J + (2/3)p$
		${}^7A_1''$	$-6J + (4/3)p$
		${}^7E''$	$-6J - (5/3)p$
	4	${}^9A_2''$	$-10J - 2p$
		${}^9E''$	$-10J + p$

TABLE 11.16

Zero-field energy levels for mixed-valence triads in the geometry of an isosceles triangle
(*contd.*)

System	<i>S</i>	State	Energy ^a
$d^3-d^3-d^4$	0	$^1A'_1$	$-p$
		$^1E'$	$(1/2)p$
	1	$^3A'_2, ^3E'$	$-J + p$
		$^3A'_1, ^3A'_2, ^3E'$	$-J - (1/4)p$
		$^3E'$	$-J - p$
	2	$^5A'_1, ^5A'_2, ^5E'$	$-3J + (5/4)p$
		$^5A'_1, ^5E', ^5E'$	$-3J - p$
		$^5A'_2, ^5E'$	$-3J$
	3	$^7A'_1, ^7A'_2, ^7E'$	$-6J - p$
		$^7A'_2, ^7E'$	$-6J + (3/2)p$
		$^7E'$	$-6J - (1/4)p$
	4	$^9A'_1, ^9E'$	$-10J - p, \#$
		$^9E'$	$-10J + (7/4)p$
		$^9A'_2$	$-10J - (1/2)p$
	5	$^{11}A'_2$	$-15J + 2p$
		$^{11}E'$	$-15J - p$
$d^4-d^4-d^3$	1/2	$^2A'_2, ^2E'$	$-(3/4)p$
		$^2A'_1$	$-(1/4)p$
		$^2E'$	$(5/4)p$
	3/2	$^4A'_1, ^4E', ^4E'$	$-(3/2)J - p$
		$^4A'_2, ^4E'$	$-(3/2)J$
	5/2	$^4A'_1, ^4A'_2, ^4E'$	$-(3/2)J + (5/4)p$
		$^6A'_1, ^6A'_2, ^6E'$	$-4J - (5/4)p$
		$^6A'_1, ^6E', ^6E'$	$-4J + (1/4)p$
	7/2	$^6A'_2, ^6E'$	$-4J + (5/4)p$
		$^8A'_1, ^8E'$	$-(15/2)J - (3/2)p$
		$^8A'_1, ^8A'_2, ^8E'$	$-(15/2)J + (1/4)p$
	9/2	$^8E'$	$-(15/2)J + (5/4)p$
		$^{10}E'$	$-12J - (7/4)p$
		$^{10}A'_1, ^{10}E'$	$-12J + (3/4)p$
	11/2	$^{10}A'_2$	$-12J + (5/4)p$
		$^{12}A'_1$	$-(35/2)J - 2p$
$d^4-d^4-d^5$	1/2	$^{12}E'$	$-(35/2)J + 2p$
		$^2A'_1$	$(4/5)p$
		$^2A'_2, ^2E'$	$(2/5)p$
	3/2	$^2E'$	$-p$
		$^4A'_2, ^4E'$	$-(3/2)J + p$
		$^4A'_1, ^4E', ^4E'$	$-(3/2)J + (1/5)p$
		$^4A'_1, ^4A'_2, ^4E'$	$-(3/2)J - p$
	5/2	$^6A'_1, ^6E', ^6E'$	$-4J + (6/5)p$
		$^6A'_1, ^6A'_2, ^6E'$	$-4J$
		$^6A'_1, ^6A'_2, ^6E', ^6E'$	$-4J - p$

(contd.)

TABLE 11.16

Zero-field energy levels for mixed-valence triads in the geometry of an isosceles triangle (contd.)

System	<i>S</i>	State	Energy ^a
$d^4-d^4-d^5$	7/2	${}^8A'_1, {}^8A'_2, {}^8E'$	$-(15/2)J + (7/5)p$
		${}^8A'_1, {}^8E'$	$-(15/2)J - (1/5)p$
		${}^8A'_2, {}^8E', {}^8E'$	$-(15/2)J - p$
	9/2	${}^{10}A'_1, {}^{10}E'$	$-12J + (8/5)p$
		${}^{10}E'$	$-12J - (2/5)p$
		${}^{10}A'_1, {}^{10}A'_2, {}^{10}E'$	$-12J - p$
	11/2	${}^{12}E'$	$-(35/2)J + (9/5)p$
		${}^{12}A'_1$	$-(35/2)J - (3/5)p$
		${}^{12}A'_2, {}^{12}E'$	$-(35/2)J - p$
	13/2	${}^{14}A'_1$	$-24J + 2p$
		${}^{14}E'$	$-24J - p$
$d^5-d^5-d^6$	0	${}^1E'$	$(3/5)p$
	1	${}^1A'_1$	$-(6/5)p$
		${}^3A'_1, {}^3A'_2, {}^3E'$	$-J + (4/5)p, \#$
		${}^3E'$	$-J + (1/5)p$
	2	${}^3A'_2, {}^3E'$	$-J - (6/5)p$
		${}^5A'_1, {}^5A'_2, {}^5E', {}^5E'$	$-3J + p$
		${}^5A'_1, {}^5A'_2, {}^5E'$	$-3J$
	3	${}^5A'_1, {}^5E', {}^5E'$	$-3J - (6/5)p$
		${}^7A'_1, {}^7E', {}^7E'$	$-6J + (6/5)p$
		${}^7A'_1, {}^7A'_2, {}^7E', {}^7E'$	$-6J - (1/5)p$
	4	${}^7A'_1, {}^7A'_2, {}^7E'$	$-6J - (6/5)p$
		${}^9A'_1, {}^9A'_2, {}^9E'$	$-10J + (7/5)p$
		${}^9A'_2, {}^9E', {}^9E'$	$-10J - (2/5)p$
	5	${}^9A'_1, {}^9E'$	$-10J - (6/5)p$
		${}^{11}A'_1, {}^{11}E'$	$-15J + (8/5)p$
		${}^{11}A'_1, {}^{11}A'_2, {}^{11}E'$	$-15J - (3/5)p$
	6	${}^{11}E'$	$-15J - (6/5)p$
		${}^{13}E'$	$-21J + (9/5)p$
		${}^{13}A'_2, {}^{13}E'$	$-21J - (4/5)p$
	7	${}^{13}A'_1$	$-21J - (6/5)p$
		${}^{15}A'_2$	$-28J + 2p$
		${}^{15}E'$	$-28J - p$

^a Rows marked by # have been corrected relative to the original reference [9]. Also, the multiplication factor within the isotropic bilinear exchange is different.

1. For the $d^n-d^n-d^{n+1}$ systems (with electron delocalisation) the energy levels are distributed within a band of width $\Delta = 3p$; the ground state involves all spin states ranging between $S_{\min}$ and $S_{\max}$ when $p > 0$ (except for $n \geq 5$ where the highest spin multiplicity level lies above the ground state).
2. For the $d^n-d^n-d^{n-1}$ systems with $p > 0$ the ground state is the highest spin multiplicity orbital singlet ${}^m A_{1(2)}$, with $m = 2S_{\max} + 1$.

While the isotropic exchange is on a crossover of the energy levels occurs, thus altering the ground state in a complicated manner. Even more complex situations exist when the magnetic field is on. The density of state function is exemplified in Fig. 11.10.

Considering the isotropic exchange and the geometry of an isosceles triangle, the magnetic susceptibility of mixed-valence (double exchange) systems can be evaluated according to the formula

$$\chi_{\text{mol}} = \frac{C_0 g_A^2}{3T} \frac{\sum_i d_i S_i (S_i + 1) (2S_i + 1) \exp(-\varepsilon_i/kT)}{\sum_i d_i (2S_i + 1) \exp(-\varepsilon_i/kT)}$$

(all the molecular-state g -factors, g_S , are equal to the local g -factors, g_A). The summation runs over all relevant rows in Table 11.16 with attached degeneracies d_i .

The magnetic behaviour of mixed-valence systems is exemplified in Fig. 11.11. It can be seen that for antiferromagnetic exchange ($J < 0$) the ground state varies from the lowest possible (singlet) to the highest possible, depending upon the value of the transfer integral. This means that with increasing electron delocalisation in the $d^n-d^n-d^{n+1}$ system the ferromagnetic ground state becomes stabilised despite the antiferromagnetic interaction within the $d^n-d^n-d^n$ pattern. For ferromagnetic exchange ($J > 0$), on the contrary, the ground state remains that of the highest spin multiplicity ($S_{\text{max}} = 5$) although the transfer parameter slightly tunes the temperature variation of the effective magnetic moment. The maximum spin-only effective magnetic moment is $\mu_{\text{eff}}/\mu_B = [2S_{\text{max}}(2S_{\text{max}} + 2)]^{1/2} = 10.95$.

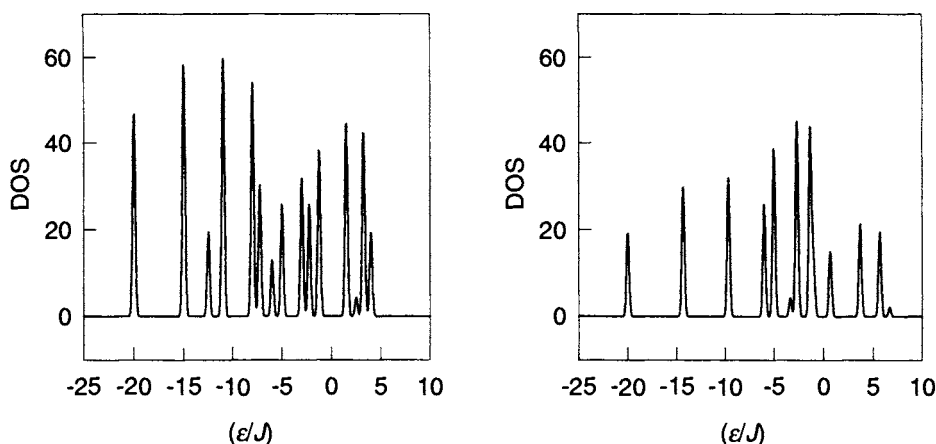


Fig. 11.10. Density of states for mixed-valence triads: left—electron delocalisation in $d^3-d^3-d^4$, $p/J = 5$; right—hole delocalisation in $d^3-d^3-d^2$, $p/J = 5$.

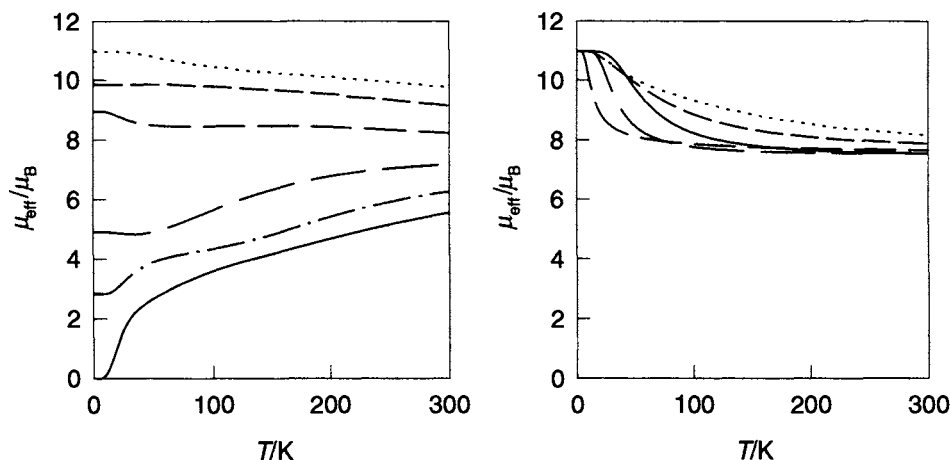


Fig. 11.11. Temperature variation of the effective magnetic moment for the mixed-valence triad $d^3-d^3-d^4$; left— $J/k = -100$ K, individual curves from bottom to top correspond to $p/k = 0, -500, -1000, -1500, -2000, -2500$ K; right— $J/k = +10$ K, solid— $p/k = -200$ K, long dashed— $p/k = -100$ K, medium dashed— $p/k = 0$, short dashed— $p/k = +100$ K, dotted— $p/k = +200$ K.

For hole delocalisation within the $d^3-d^3-d^2$ triad the maximum spin number is $S_{\max} = 4$ and the corresponding maximum spin-only effective magnetic moment is $\mu_{\text{eff}}/\mu_B = [2S_{\max}(2S_{\max} + 2)]^{1/2} = 8.94$. For ferromagnetic coupling the ground state is not necessarily that of the highest spin multiplicity, as seen from Fig. 11.12.

As seen from the density of states (Fig. 11.10), the energy levels in mixed-valence systems are highly degenerate when only the (bilinear) isotropic exchange and the double exchange are involved. Such a picture is in contradiction with the double-group theoretical analysis according to which the maximum degree of degeneracy is four for the irreducible representation Γ_8 within the cubic groups and only two within groups of lower orders. Thus there should exist some physical interactions which lead to a reduction of the degree of degeneracy and splitting of the energy levels. We already found that the spin-orbit coupling contributes to the A -tensor from which the magnetic parameters are derived: the magnetogyric ratio g -tensor, the spin-spin interaction D -tensor and the reduced magnetic susceptibility κ -tensor. The involvement of asymmetric exchange along with antisymmetric exchange means a more complete consideration of the D -tensor elements, not only its isotropic part (trace) covered by isotropic exchange. The splitting of energy levels is provided also by biquadratic exchange. The involvement of the orbital contribution along with the crystal-field splitting makes the model more realistic but at the same time the problem becomes much more complex.

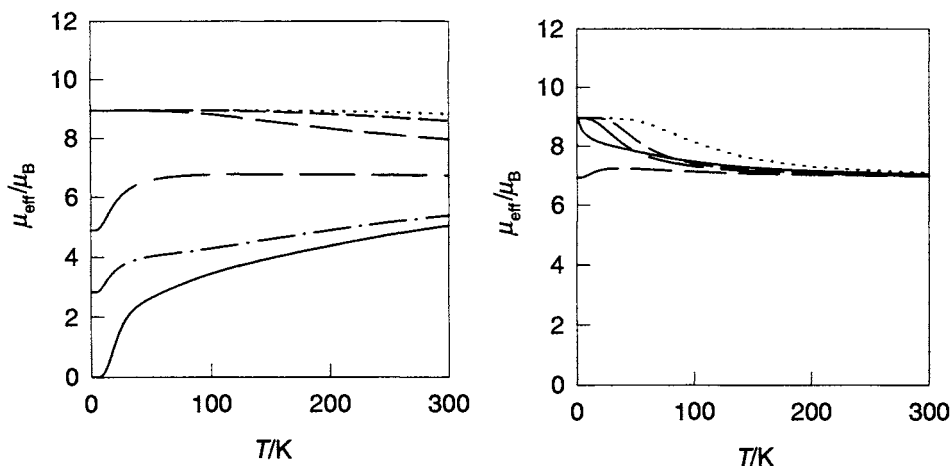


Fig. 11.12. Temperature variation of the effective magnetic moment for the mixed-valence triad $d^3-d^3-d^2$; left— $J/k = -100$ K, individual curves from bottom to top correspond to $p/k = 0, -500, -1000, -1500, -2000, -2500$ K; right— $J/k = +10$ K, solid— $p/k = -200$ K, long dashed— $p/k = -100$ K, medium dashed— $p/k = 0$, short dashed— $p/k = +100$ K, dotted— $p/k = +200$ K.

11.2.7 Jahn–Teller effect

The last but not the least aspect is associated with vibronic interactions and the Jahn–Teller effect. According to the Jahn–Teller theorem [10] the ground state of a non-linear molecule cannot be orbitally degenerate: for any point group there exists a nuclear displacement (coincident with a vibrational mode) along which the total energy function of the nuclear coordinates (the adiabatic potential) is lowered. In the new energy minimum the ground state is non-degenerate, except for Kramers degeneracy.

For example, the doubly degenerate electronic state implies that the proper molecular state function is a linear combination of the degenerate trial functions

$$|\Psi\rangle = C_1\Phi_1 + C_2\Phi_2$$

Introducing the matrix elements $H_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle$, the secular equation should be obeyed

$$\det \begin{pmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{pmatrix} = 0$$

having the roots ($H_{11} = H_{22}$)

$$E_{\pm} = H_{11} \pm |H_{12}|$$

If the off-diagonal matrix element is non-zero, the two roots are different: they correspond to a lower (upper) sheet of the adiabatic potential surface for which a crossover is excluded. In order to show that $H_{12} \neq 0$ let us apply the Taylor expansion of that matrix element with respect to symmetry coordinates Q_s (nuclear displacement coordinates) around a reference nuclear configuration Q_0 , hence

$$\begin{aligned} H_{IJ} = & E_0 \delta_{IJ} + \sum_s^{3N-6} \left\langle \Phi_I(r, Q_0) \left| \left(\frac{\partial \hat{H}(r, Q)}{\partial Q_s} \right)_0 \right| \Phi_J(r, Q_0) \right\rangle (Q_s - Q_0) \\ & + \frac{1}{2} \sum_s^{3N-6} \sum_t^{3N-6} \left\langle \Phi_I(r, Q_0) \left| \left(\frac{\partial^2 \hat{H}(r, Q)}{\partial Q_s \partial Q_t} \right)_0 \right| \Phi_J(r, Q_0) \right\rangle \\ & \times (Q_s - Q_0)(Q_t - Q_0) + \dots \end{aligned}$$

(r stands for the electronic coordinates). This expression can be rewritten in the form where the same diagonal (scalar) part, F_{II} , and the off-diagonal (tensor) part, V_{IJ} , occur

$$H_{IJ} = F_{II} \delta_{IJ} + V_{IJ}$$

Here the usual “force field”

$$F_{II} = E_0 + \sum_s^{3N-6} F_s \Delta Q_s + \frac{1}{2} \sum_s^{3N-6} \sum_t^{3N-6} F_{st} \Delta Q_s \Delta Q_t + \dots$$

contains the force constants

$$\begin{aligned} F_s & \equiv \left\langle \Phi_I(r, Q_0) \left| \left(\frac{\partial \hat{H}(r, Q)}{\partial Q_s} \right)_0 \right| \Phi_I(r, Q_0) \right\rangle \\ F_{st} & \equiv \left\langle \Phi_I(r, Q_0) \left| \left(\frac{\partial^2 \hat{H}(r, Q)}{\partial Q_s \partial Q_t} \right)_0 \right| \Phi_I(r, Q_0) \right\rangle \end{aligned}$$

where the linear term (gradient) vanishes at the apparent energy minimum in Q_0 . The vibronic term is

$$V_{IJ} = \sum_s^{3N-6} V_s \Delta Q_s + \frac{1}{2} \sum_s^{3N-6} \sum_t^{3N-6} V_{st} \Delta Q_s \Delta Q_t + \dots$$

and it contains the vibronic matrix elements introduced through derivatives of the electron–nuclear attraction

$$V_s \equiv \left\langle \Phi_I(r, Q_0) \left| \left(\frac{\partial V^{e-N}(r, Q)}{\partial Q_s} \right) \right| \Phi_J(r, Q_0) \right\rangle \neq 0$$

$$V_{st} \equiv \left\langle \Phi_I(r, Q_0) \left| \left(\frac{\partial^2 V^{e-N}(r, Q)}{\partial Q_s \partial Q_t} \right) \right| \Phi_J(r, Q_0) \right\rangle \neq 0$$

The linear vibronic matrix element is non-zero for any point group: the direct product of the irreducible representations of the trial wave functions is a reducible representation which necessarily contains the irreducible representation of a symmetry coordinate

$$\Gamma_I \otimes \Gamma_J = \Gamma_{\text{red}} = \Gamma_s + \dots$$

Stereochemical consequences of the Jahn–Teller theorem are straightforward: the higher symmetric polyhedra in electronic degenerate states should distort in order for their electronic ground state to become non-degenerate; this is the static Jahn–Teller effect. Some possible distortions are exemplified by:

- (a) isosceles triangle ($\mathbf{D}_{3h}$) $\rightarrow$ equilateral triangle ($\mathbf{C}_{2v}$)
- (b) octahedron ($\mathbf{O}_h$) $\rightarrow$ tetragonal bipyramid ($\mathbf{D}_{4h}$, $\mathbf{D}_{2h}$)
- (c) tetrahedron ($\mathbf{T}_d$) $\rightarrow$ bisphenoid ($\mathbf{D}_{2d}$) or trigonal pyramid ($\mathbf{C}_{3v}$).

As an effect of the linear and quadratic vibronic constants the adiabatic potential surface no longer stays paraboloid-shaped. It exhibits an additional warping with several local minima out of the reference high-symmetry configuration Q_0 .

We have not explicitly included the nuclear motions (molecular vibrations) so far, this fact being frequently misunderstood [11]. This is the second stage: the lowest sheet of the adiabatic potential surface, E_- , adopts the role of potential energy in solving the electron–nuclear Schrödinger equation containing explicitly the kinetic energy of nuclei

$$\left\{ \hat{T}_N(Q) + E_-(Q) - W \right\} \Phi_I^{\text{el}}(r, Q_0) \cdot \chi_{I,\mu}(Q) = 0$$

with the vibration functions $\chi_{I,\mu}(Q)$. The localisation of the system at one of the energy minima depends upon the distribution of thermally accessible vibration levels [12]. For small vibrational amplitudes well localised around one minimum the geometry of the system is localised at the moderate tem-

perature. For large vibrational amplitudes embracing several energy minima the geometry of the system is delocalised at the higher temperature; the system exhibits a dynamic Jahn–Teller effect.

Concerning trinuclear systems, the Jahn–Teller theorem predicts that the geometry of an isosceles triangle is unstable unless the ground electronic state is non-degenerate. In the geometry of D_{3h} the electronic wave functions are of either the A - or the E -type and there exist $3N - 6 = 3$ symmetry coordinates: (a) the breathing (stretching) coordinate Q_1 which is of a_1 -symmetry; (b) the doubly degenerate deformation coordinates Q_2 and Q_3 which are of e -symmetry.

The two sheets of the adiabatic potential (the roots of the secular equation) adopt the form of [11]

$$E_{\pm}(Q_1, Q_2, Q_3) = E(Q_0) + \frac{1}{2}F_{aa}Q_1^2 + \frac{1}{2}F_{ee}(Q_2^2 + Q_3^2) \\ \pm \left[(V_e + V_a Q_1)^2(Q_2^2 + Q_3^2) + V_{ee}^2(Q_2^2 + Q_3^2)^2 \right. \\ \left. + 2V_{ee}(V_e + V_a Q_1)Q_3(3Q_2^2 - Q_3^2) \right]^{1/2}$$

where the force constants and the vibronic constants of the given symmetry type occur. Restricting ourselves only to the linear approximation of the vibronic coupling E – e , we get the simplification

$$E_{\pm}([Q_1], Q_2, Q_3) = E(Q_0) + \left[\frac{1}{2}F_{aa}Q_1^2 \right] + \frac{1}{2}F_{ee}\rho^2 \pm V_e\rho$$

with the radial distortion parameter defined as

$$\rho \equiv (Q_2^2 + Q_3^2)^{1/2}$$

The energy minimum is determined by the condition

$$\left. \frac{\partial E}{\partial \rho} \right|_{\rho_0} = 0$$

whence the position of the energy minimum is

$$\rho_0 = \frac{V_e}{F_{ee}}$$

Then the lower sheet of the adiabatic potential is stabilised relative to the energy at the reference geometry Q_0 by the Jahn–Teller stabilisation energy

$$\Delta E_- = E(Q_0) - E_-(\rho_0) = -\frac{1}{2} \frac{V_e^2}{F_{ee}}$$

whereas the upper sheet of the adiabatic potential is destabilised by the amount

$$\Delta E_+ = E(Q_0) - E_+(\rho_0) = \frac{3}{2} \frac{V_e^2}{F_{ee}}$$

It can be concluded that any doubly degenerate energy level ^{2S+1}E is split due to the static Jahn–Teller effect, and the orbital degeneracy is removed. The sheets of the adiabatic potential are shown in Fig. 11.13.

Let us consider an $S_1 = S_2 = S_3 = 1/2$ system in the reference geometry of an isosceles triangle. We have already arrived at the result that the isotropic exchange yields the energy levels

$$\varepsilon(S_{12}, S) = -\frac{J}{2}[S(S+1) - 3S_1(S_1+1)]$$

which after an appropriate shift become

$$\varepsilon(1, 3/2) = -(3/2)J$$

$$\varepsilon(1, 1/2) = 0$$

$$\varepsilon(0, 1/2) = 0$$

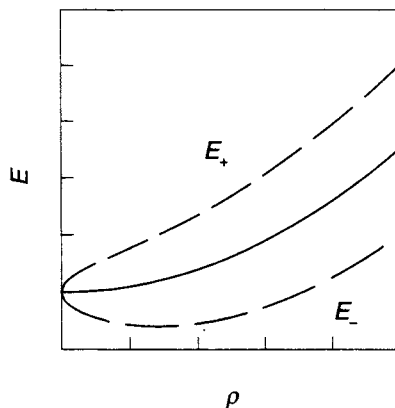


Fig. 11.13. Adiabatic potential in the presence of vibronic coupling: solid—a hypothetical parabolic force field ($V = 0$); long dashed—lower sheet with new minimum; medium dashed—upper sheet.

The first level spans the orbital singlet ${}^4A$ whereas the two remaining levels span the orbital doublet ${}^2E$. The latter is subject to Jahn–Teller splitting, yielding two Kramers doublets

$$\varepsilon_-(S = 1/2) = -(1/2)X$$

$$\varepsilon_+(S = 1/2) = +(3/2)X$$

with the vibronic coupling parameter

$$X \equiv \frac{V_e^2}{F_{ee}}$$

The magnetic susceptibility, resulting from the van Vleck formula, is

$$\begin{aligned} \bar{\chi}_{\text{mol}} = \frac{C_0 g_A^2}{T} \frac{1}{4} \{ & 2 \cdot 10 \exp[(3/2)J/kT] + 2 \exp[(1/2)X/kT] \\ & + 2 \exp[-(3/2)X/kT] \} / \{ 4 \exp[(3/2)J/kT] \\ & + 2 \exp[(1/2)X/kT] + 2 \exp[-(3/2)X/kT] \} \end{aligned}$$

and its plot is shown in Fig. 11.14. It can be seen that for ferromagnetic exchange the vibronic effect results in the reduction of the magnetic productivity and finally in a switch to the low-spin doublet ground state.

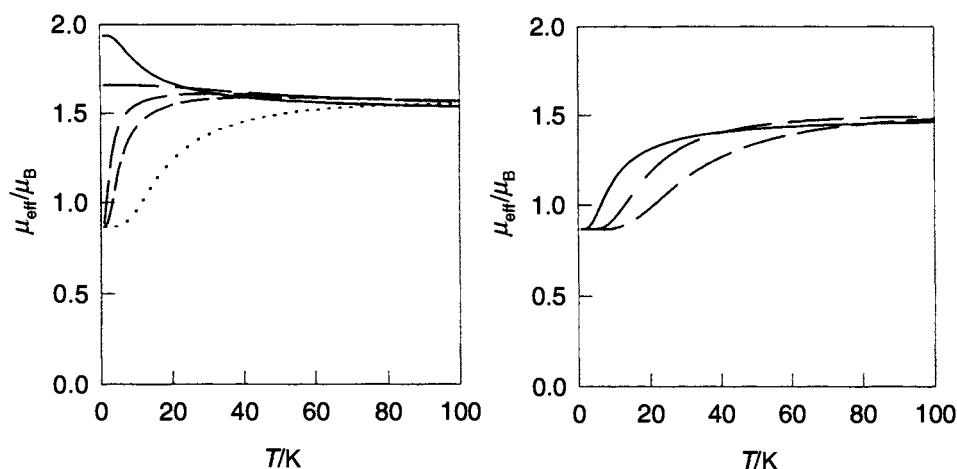


Fig. 11.14. Temperature variation of the effective magnetic moment for the $S_1 = S_2 = S_3 = 1/2$ system in a geometry of the isosceles triangle: left— $J/k = +10$ K, individual curves correspond to the vibronic parameter $X/k = 0$ (solid), 30 K (long dashed), 40 K (medium dashed), 50 K (short dashed) and 100 K (dotted); right— $J/k = -10$ K, $X/k = 0$ (solid), 50 K (long dashed) and 100 K (medium dashed).

For the mixed-valence $d^1-d^1-d^0$ system in a geometry of the isosceles triangle the energy levels are:

$$\varepsilon_-(^1A'_1) = 2p$$

$$\varepsilon_-(^1E') = -p - (1/2)X$$

$$\varepsilon_+(^1E') = -p + (3/2)X$$

$$\varepsilon_-(^3A'_2) = -J - 2p$$

$$\varepsilon_-(^3E') = -J + p - (1/2)X$$

$$\varepsilon_+(^3E') = -J + p + (3/2)X$$

The hole delocalisation (which increases with the value of the transfer parameter $p > 0$) is capable of switching the low-spin ground state to the high-spin one despite the antiferromagnetic coupling ($J < 0$). The vibronic coupling comes into competition with the double exchange, as seen from Fig. 11.15, which can result in a back switch to the low-spin ground state.

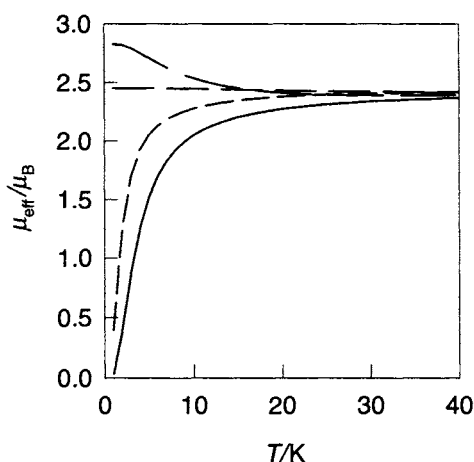


Fig. 11.15. Temperature variation of the effective magnetic moment for the mixed-valence $d^1-d^1-d^0$ system in a geometry of the isosceles triangle: $J/k = -10$, solid—low-spin ground state ($p = 0$, $X = 0$); long dashed—switch to the high-spin ground state ($p/k = 20$ K, $X = 0$); medium dashed—competition of double exchange and vibronic coupling ($p/k = 20$ K, $X/k = 20$ K); short dashed—return to the low-spin ground state ($p/k = 20$ K, $X/k = 30$ K).

11.3 TETRANUCLEAR CLUSTERS

The apparatus developed for trinuclear clusters is general enough to be successfully applied for clusters of higher nuclearity. Therefore only the key steps will be presented for tetranuclear and polynuclear systems.

11.3.1 Isotropic exchange

The bilinear isotropic exchange Hamiltonian for a tetranuclear cluster is written in the form

$$\hat{H}^{\text{iso}} = [-J_{12}(\vec{S}_1 \cdot \vec{S}_2) - J_{13}(\vec{S}_1 \cdot \vec{S}_3) - J_{14}(\vec{S}_1 \cdot \vec{S}_4) \\ - J_{23}(\vec{S}_2 \cdot \vec{S}_3) - J_{24}(\vec{S}_2 \cdot \vec{S}_4) - J_{34}(\vec{S}_3 \cdot \vec{S}_4)][\hbar^{-2}]$$

The applied coupling scheme is either

$$S_1 + S_2 = S_{12}$$

$$S_{12} + S_3 = S_{123}$$

$$S_{123} + S_4 = S$$

yielding the kets

$$|ISM\rangle = |S_1 S_2 S_{12} S_3 S_{123} S_4 SM\rangle$$

or alternatively

$$S_1 + S_2 = S_{12}$$

$$S_3 + S_4 = S_{34}$$

$$S_{12} + S_{34} = S$$

yielding

$$|ISM\rangle = |S_1 S_2 S_{12} S_3 S_4 S_{34} SM\rangle$$

In both coupling schemes we have the same reduction

$$\begin{aligned} & \langle I'S'M' | \vec{S}_i \cdot \vec{S}_j | ISM \rangle \\ &= -\sqrt{3}(-1)^{S-M} \begin{pmatrix} S & 0 & S' \\ -M & 0 & M' \end{pmatrix} \langle I'S || \{ \hat{T}_1(\vec{S}_i) \otimes \hat{T}_1(\vec{S}_j) \}_0 || IS \rangle \\ &= -[3/(2S+1)]^{1/2} \delta_{S,S'} \delta_{M,M'} \langle I'S || \{ \hat{T}_1(\vec{S}_i) \otimes \hat{T}_1(\vec{S}_j) \}_0 || IS \rangle \end{aligned}$$

The reduced matrix element of the compound operator is expressed as follows

$$\begin{aligned}
 & \langle S_1 S_2 S'_{12} S_3 S'_{123} S_4 S' \parallel \hat{X}_k \parallel S_1 S_2 S_{12} S_3 S_{123} S_4 S \rangle \\
 &= [(2S'_{12} + 1)(2S_{12} + 1)(2k_{12} + 1)]^{1/2} \left\{ \begin{matrix} S_1 & S_1 & k_1 \\ S_2 & S_2 & k_2 \\ S'_{12} & S_{12} & k_{12} \end{matrix} \right\} \\
 & \times \langle S_1 \parallel \hat{T}_{k_1}(\vec{S}_1) \parallel S_1 \rangle \langle S_2 \parallel \hat{T}_{k_2}(\vec{S}_2) \parallel S_2 \rangle \\
 & \times [(2S'_{123} + 1)(2S_{123} + 1)(2k_{123} + 1)]^{1/2} \left\{ \begin{matrix} S'_{12} & S_{12} & k_{12} \\ S_3 & S_3 & k_3 \\ S'_{123} & S_{123} & k_{123} \end{matrix} \right\} \\
 & \times \langle S_3 \parallel \hat{T}_{k_3}(\vec{S}_3) \parallel S_3 \rangle \\
 & \times [(2S' + 1)(2S + 1)(2k + 1)]^{1/2} \left\{ \begin{matrix} S'_{123} & S_{123} & k_{123} \\ S_4 & S_4 & k_4 \\ S' & S & k \end{matrix} \right\} \langle S_4 \parallel \hat{T}_{k_4}(\vec{S}_4) \parallel S_4 \rangle
 \end{aligned}$$

where the tensor ranks are assigned according to the scheme

Tensor operator	k_1	k_2	k_{12}	k_3	k_{123}	k_4	k
$\vec{S}_1 \cdot \vec{S}_2$	1	1	0	0	0	0	0
$\vec{S}_1 \cdot \vec{S}_3$	1	0	1	1	0	0	0
$\vec{S}_1 \cdot \vec{S}_4$	1	0	1	0	1	1	0
$\vec{S}_2 \cdot \vec{S}_3$	0	1	1	1	0	0	0
$\vec{S}_2 \cdot \vec{S}_4$	0	1	1	0	1	1	0
$\vec{S}_3 \cdot \vec{S}_4$	0	0	0	1	1	1	0

Alternatively there is

$$\begin{aligned}
 & \langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S' \parallel \hat{X}_k \parallel S_1 S_2 S_{12} S_3 S_4 S_{34} S \rangle \\
 &= [(2S'_{12} + 1)(2S_{12} + 1)(2k_{12} + 1)]^{1/2} \left\{ \begin{matrix} S_1 & S_1 & k_1 \\ S_2 & S_2 & k_2 \\ S'_{12} & S_{12} & k_{12} \end{matrix} \right\} \\
 & \times \langle S_1 \parallel \hat{T}_{k_1}(\vec{S}_1) \parallel S_1 \rangle \langle S_2 \parallel \hat{T}_{k_2}(\vec{S}_2) \parallel S_2 \rangle \\
 & \times [(2S'_{34} + 1)(2S_{34} + 1)(2k_{34} + 1)]^{1/2} \left\{ \begin{matrix} S_3 & S_3 & k_3 \\ S_4 & S_4 & k_4 \\ S'_{34} & S_{34} & k_{34} \end{matrix} \right\} \\
 & \times \langle S_3 \parallel \hat{T}_{k_3}(\vec{S}_3) \parallel S_3 \rangle \langle S_4 \parallel \hat{T}_{k_4}(\vec{S}_4) \parallel S_4 \rangle \\
 & \times [(2S' + 1)(2S + 1)(2k + 1)]^{1/2} \left\{ \begin{matrix} S'_{12} & S_{12} & k_{12} \\ S'_{34} & S_{34} & k_{34} \\ S' & S & k \end{matrix} \right\}
 \end{aligned}$$

with the tensor ranks according to the scheme

Tensor operator	k_1	k_2	k_{12}	k_3	k_4	k_{34}	k
$\vec{S}_1 \cdot \vec{S}_2$	1	1	0	0	0	0	0
$\vec{S}_1 \cdot \vec{S}_3$	1	0	1	1	0	1	0
$\vec{S}_1 \cdot \vec{S}_4$	1	0	1	0	1	1	0
$\vec{S}_2 \cdot \vec{S}_3$	0	1	1	1	0	1	0
$\vec{S}_2 \cdot \vec{S}_4$	0	1	1	0	1	1	0
$\vec{S}_3 \cdot \vec{S}_4$	0	0	0	1	1	0	0

Owing to one zero element, all $9j$ -symbols collapse into $6j$ -symbols. The tensor rank $k = 0$ implies a factor $\delta_{S,S}$ so that the isotropic exchange cannot mix states of different total spin. The simplified reduced matrix elements are collected in Table 11.17. These formulae can be simplified further by substituting the relevant $6j$ -symbols (Appendix 3).

The six terms of the isotropic exchange corresponding to the pair-interactions become simplified for some special cases:

(a) a regular tetrahedron when all pair interactions are equivalent

$$\hat{H}^{\text{iso}}(\mathbf{T}_d) = -J(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_4 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_4 + \vec{S}_3 \cdot \vec{S}_4)[\hbar^{-2}]$$

(b) a tetragonal distortion to $\mathbf{S}_4$ symmetry, leading in the limiting case to the square-planar arrangement of $\mathbf{D}_{4h}$ symmetry

$$\begin{aligned} \hat{H}^{\text{iso}}(\mathbf{S}_4) = & [-J_a(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_3 \cdot \vec{S}_4) \\ & - J_c(\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_4 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_4)][\hbar^{-2}] \end{aligned}$$

(c) a distortion to the $\mathbf{C}_{2v}$ symmetry, corresponding to unequal pairwise distortion

$$\begin{aligned} \hat{H}^{\text{iso}}(\mathbf{C}_{2v}) = & [-J_a(\vec{S}_1 \cdot \vec{S}_2) - J_b(\vec{S}_3 \cdot \vec{S}_4) \\ & - J_c(\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_4 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_4)][\hbar^{-2}] \end{aligned}$$

(d) a trigonal distortion to $\mathbf{C}_{3v}$ symmetry, leading in the limiting case to a regular triangle of $\mathbf{D}_{3h}$ symmetry

$$\begin{aligned} \hat{H}^{\text{iso}}(\mathbf{C}_{3v}) = & [-J_a(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3) \\ & - J_b(\vec{S}_1 \cdot \vec{S}_4 + \vec{S}_2 \cdot \vec{S}_4 + \vec{S}_3 \cdot \vec{S}_4)][\hbar^{-2}] \end{aligned}$$

TABLE 11.17

Reduced matrix elements of the isotropic exchange, $R_{ij}(S'_{12}, S'_{34}, S'; S_{12}, S_{34}, S)$, for a general tetrad with the $|S_1 S_2 S_{12} S_3 S_4 S_{34} SM\rangle$ coupling scheme

$$R_{12} = \delta_{S', S} \delta_{S'_{12}, S_{12}} \delta_{S'_{34}, S_{34}} [(2S+1)/3]^{1/2} (-1)^{S_1+S_2+1+S_{12}} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & S_{12} \end{Bmatrix} \\ \times [S_1(S_1+1)(2S_1+1)]^{1/2} [S_2(S_2+1)(2S_2+1)]^{1/2} [\hbar^2]$$

$$R_{13} = \delta_{S', S} [(2S+1)/3]^{1/2} [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'_{34}+1)(2S_{34}+1)]^{1/2} \\ \times (-1)^{2S_1+2S_2+S'_{12}+S_{12}} (-1)^{2S_3+2S_4+S'_{34}+S_{34}} (-1)^{S'_{12}+S_1+1+S_2} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_1 & S_1 & S_2 \end{Bmatrix} \\ \times (-1)^{S'_{34}+S_3+1+S_4} \begin{Bmatrix} S_{34} & S'_{34} & 1 \\ S_3 & S_3 & S_4 \end{Bmatrix} (-1)^{S_{12}+S'_{34}+1+S} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_{34} & S'_{34} & S \end{Bmatrix} \\ \times [S_1(S_1+1)(2S_1+1)]^{1/2} [S_3(S_3+1)(2S_3+1)]^{1/2} [\hbar^2]$$

$$R_{14} = \delta_{S', S} [(2S+1)/3]^{1/2} [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'_{34}+1)(2S_{34}+1)]^{1/2} \\ \times (-1)^{2S_1+2S_2+S'_{12}+S_{12}} (-1)^{S'_{12}+S_1+1+S_2} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_1 & S_1 & S_2 \end{Bmatrix} \\ \times (-1)^{S'_{34}+S_4+1+S_3} \begin{Bmatrix} S_{34} & S'_{34} & 1 \\ S_4 & S_4 & S_3 \end{Bmatrix} (-1)^{S_{12}+S'_{34}+1+S} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_{34} & S'_{34} & S \end{Bmatrix} \\ \times [S_1(S_1+1)(2S_1+1)]^{1/2} [S_4(S_4+1)(2S_4+1)]^{1/2} [\hbar^2]$$

$$R_{23} = \delta_{S', S} [(2S+1)/3]^{1/2} [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'_{34}+1)(2S_{34}+1)]^{1/2} \\ \times (-1)^{2S_3+2S_4+S'_{34}+S_{34}} (-1)^{S'_{12}+S_2+1+S_1} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} \\ \times (-1)^{S'_{34}+S_3+1+S_4} \begin{Bmatrix} S_{34} & S'_{34} & 1 \\ S_3 & S_3 & S_4 \end{Bmatrix} (-1)^{S_{12}+S'_{34}+1+S} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_{34} & S'_{34} & S \end{Bmatrix} \\ \times [S_2(S_2+1)(2S_2+1)]^{1/2} [S_3(S_3+1)(2S_3+1)]^{1/2} [\hbar^2]$$

$$R_{24} = \delta_{S', S} [(2S+1)/3]^{1/2} [(2S'_{12}+1)(2S_{12}+1)]^{1/2} [(2S'_{34}+1)(2S_{34}+1)]^{1/2} \\ \times (-1)^{S'_{12}+S_2+1+S_1} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} (-1)^{S'_{34}+S_4+1+S_3} \begin{Bmatrix} S_{34} & S'_{34} & 1 \\ S_4 & S_4 & S_3 \end{Bmatrix} \\ \times (-1)^{S_{12}+S'_{34}+1+S} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_{34} & S'_{34} & S \end{Bmatrix} \\ \times [S_2(S_2+1)(2S_2+1)]^{1/2} [S_4(S_4+1)(2S_4+1)]^{1/2} [\hbar^2]$$

$$R_{34} = \delta_{S', S} \delta_{S'_{12}, S_{12}} \delta_{S'_{34}, S_{34}} [(2S+1)/3]^{1/2} \\ \times (-1)^{S_3+S_4+1+S_{34}} \begin{Bmatrix} S_3 & S_3 & 1 \\ S_4 & S_4 & S_{34} \end{Bmatrix} [S_3(S_3+1)(2S_3+1)]^{1/2} [S_4(S_4+1)(2S_4+1)]^{1/2} [\hbar^2]$$

In these cases vector addition is successful leading, for example, to the simple formula

$$\begin{aligned}
 & \left\langle S_{12}S_{34}SM \left| \hat{H}^{\text{iso}}(\mathbf{C}_{2v}) \right| S_{12}S_{34}SM \right\rangle \\
 &= -\frac{J_c}{2} [S(S+1) - S_{12}(S_{12}+1) - S_{34}(S_{34}+1)] \\
 &\quad -\frac{J_a}{2} [S_{12}(S_{12}+1) - S_1(S_1+1) - S_2(S_2+1)] \\
 &\quad -\frac{J_b}{2} [S_{34}(S_{34}+1) - S_3(S_3+1) - S_4(S_4+1)]
 \end{aligned}$$

This formula even simplifies for the case of S_4 symmetry

$$\begin{aligned}
 & \left\langle S_{12}S_{34}SM \left| \hat{H}^{\text{iso}}(\mathbf{S}_4) \right| S_{12}S_{34}SM \right\rangle \\
 &= -\frac{J_c}{2} [S(S+1) - S_{12}(S_{12}+1) - S_{34}(S_{34}+1)] \\
 &\quad -\frac{J_a}{2} [S_{12}(S_{12}+1) - S_1(S_1+1) - S_2(S_2+1) + S_{34}(S_{34}+1) \\
 &\quad - S_3(S_3+1) - S_4(S_4+1)]
 \end{aligned}$$

and tetrahedral geometry

$$\begin{aligned}
 & \left\langle S_{12}S_{34}SM \left| \hat{H}^{\text{iso}}(\mathbf{T}_d) \right| S_{12}S_{34}SM \right\rangle \\
 &= +\frac{J}{2} S(S+1) - \frac{J}{2} [S_1(S_1+1) + S_2(S_2+1) + S_3(S_3+1) + S_4(S_4+1)]
 \end{aligned}$$

where the second term, constant within the cluster, can be omitted.

11.3.2 Zeeman interaction

In order to include the Zeeman term we need the reduced matrix elements for each spin, for example

$$\begin{aligned}
 R_1 &= \left\langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S' \left\| \hat{T}_1(\vec{S}_1) \right\| S_1 S_2 S_{12} S_3 S_4 S_{34} S \right\rangle \\
 &= [(2S'_{12}+1)(2S_{12}+1)(2 \cdot 1+1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 1 \end{Bmatrix} \\
 &\quad \times \left\langle S_1 \left\| \hat{T}_1(\vec{S}_1) \right\| S_1 \right\rangle \left\langle S_2 \left\| \hat{T}_0(\vec{S}_2) \right\| S_2 \right\rangle
 \end{aligned}$$

$$\begin{aligned}
& \times [(2S'_{34} + 1)(2S_{34} + 1)(2 \cdot 0 + 1)]^{1/2} \begin{Bmatrix} S_3 & S_3 & 0 \\ S_4 & S_4 & 0 \\ S'_{34} & S_{34} & 0 \end{Bmatrix} \\
& \times \langle S_3 \| \hat{T}_0(\vec{S}_3) \| S_3 \rangle \langle S_4 \| \hat{T}_0(\vec{S}_4) \| S_4 \rangle \\
& \times [(2S' + 1)(2S + 1)(2 \cdot 1 + 1)]^{1/2} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S'_{34} & S_{34} & 0 \\ S' & S & 1 \end{Bmatrix}
\end{aligned}$$

and again a simplification is obtained (Table 11.18). The matrix elements of the Zeeman operator are then

$$\begin{aligned}
H_{IJ}^Z & \equiv H_{S'_{12}S'_{34}S'M', S_{12}S_{34}SM}^Z \\
& = \langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S' M' | \hat{H}^Z | S_1 S_2 S_{12} S_3 S_4 S_{34} SM \rangle \\
& = \mu_B [\hbar^{-1}] \sum_{i=1}^4 \sum_{q=-1}^{+1} (-1)^q \gamma_{i,1,-q} \\
& \quad \times \langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S' M' | \hat{S}_{i,1,q} | S_1 S_2 S_{12} S_3 S_4 S_{34} SM \rangle
\end{aligned}$$

TABLE 11.18

Reduced matrix elements of the Zeeman term $R_{i(S'_{12}, S'_{34}, S'; S_{12}, S_{34}, S)}$ for a general tetrad

$$\begin{aligned}
R_1 & = \delta_{S'_{34}, S_{34}} [(2S'_{12} + 1)(2S_{12} + 1)]^{1/2} [(2S' + 1)(2S + 1)]^{1/2} \\
& \times (-1)^{S'_{12} + S_1 + 1 + S_2} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_1 & S_1 & S_2 \end{Bmatrix} (-1)^{S' + S_{12} + 1 + S_{34}} \begin{Bmatrix} S & S' & 1 \\ S'_{12} & S_{12} & S_{34} \end{Bmatrix} \\
& \times (-1)^{2S_1 + 2S_2 + S'_{12} + S_{12}} (-1)^{S'_{12} + S_{12} + 2S_{34} + S' + S} [S_1(S_1 + 1)(2S_1 + 1)]^{1/2} [\hbar] \\
R_2 & = \delta_{S'_{34}, S_{34}} [(2S'_{12} + 1)(2S_{12} + 1)]^{1/2} [(2S' + 1)(2S + 1)]^{1/2} \\
& \times (-1)^{S'_{12} + S_2 + 1 + S_1} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} (-1)^{S' + S_{12} + 1 + S_{34}} \begin{Bmatrix} S & S' & 1 \\ S'_{12} & S_{12} & S_{34} \end{Bmatrix} \\
& \times (-1)^{S'_{12} + S_{12} + 2S_{34} + S' + S} [S_2(S_2 + 1)(2S_2 + 1)]^{1/2} [\hbar] \\
R_3 & = \delta_{S'_{12}, S_{12}} [(2S'_{34} + 1)(2S_{34} + 1)]^{1/2} [(2S' + 1)(2S + 1)]^{1/2} \\
& \times (-1)^{S'_{34} + S_3 + 1 + S_4} \begin{Bmatrix} S_{34} & S'_{34} & 1 \\ S_3 & S_3 & S_4 \end{Bmatrix} (-1)^{S' + S_{34} + 1 + S_{12}} \begin{Bmatrix} S & S' & 1 \\ S'_{34} & S_{34} & S_{12} \end{Bmatrix} \\
& \times (-1)^{2S_3 + 2S_4 + S'_{34} + S_{34}} [S_3(S_3 + 1)(2S_3 + 1)]^{1/2} [\hbar] \\
R_4 & = \delta_{S'_{12}, S_{12}} [(2S'_{34} + 1)(2S_{34} + 1)]^{1/2} [(2S' + 1)(2S + 1)]^{1/2} \\
& \times (-1)^{S'_{34} + S_4 + 1 + S_3} \begin{Bmatrix} S_{34} & S'_{34} & 1 \\ S_4 & S_4 & S_3 \end{Bmatrix} (-1)^{S' + S_{34} + 1 + S_{12}} \begin{Bmatrix} S & S' & 1 \\ S'_{34} & S_{34} & S_{12} \end{Bmatrix} \\
& \times [S_4(S_4 + 1)(2S_4 + 1)]^{1/2} [\hbar]
\end{aligned}$$

and the application of the Wigner–Eckert theorem yields

$$\begin{aligned}
 H_{IJ}^Z &= \mu_B [\hbar^{-1}] \sum_{i=1}^4 \sum_{q=-1}^{+1} (-1)^q \gamma_{i,1,-q} \\
 &\quad \times \left\langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S' M' \left| \hat{S}_{i,1,q} \right| S_1 S_2 S_{12} S_3 S_4 S_{34} S M \right\rangle \\
 &= \mu_B [\hbar^{-1}] \sum_{i=1}^4 \sum_{q=-1}^{+1} (-1)^q \gamma_{i,1,-q} (-1)^{S'-M'} \\
 &\quad \times \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} R_{i(S'_{12}, S'_{34}, S'; S_{12}, S_{34}, S)}
 \end{aligned}$$

where the spherical transforms, as usual, are

$$\gamma_{i,1,+1} = -\frac{1}{\sqrt{2}}(B_x g_{i,x} + i B_y g_{i,y})$$

$$\gamma_{i,1,-1} = \frac{1}{\sqrt{2}}(B_x g_{i,x} - i B_y g_{i,y})$$

$$\gamma_{i,1,0} = B_z g_{i,z}$$

Notice that the matrix elements of the Zeeman operator mix states of different total spin. The structure of the Zeeman matrix follows the scheme

Total spin	Intermediate spins		Reduced matrix elements	
$S' = S$	$S'_{34} = S_{34}$	$S'_{12} = S_{12}$	a	b
		$S'_{12} = S_{12} - 1$	b	a
	$S'_{34} = S_{34} - 1$	$S'_{12} = S_{12}$	c	d
		$S'_{12} = S_{12} - 1$	d	c
$S' = S - 1$	$S'_{34} = S_{34}$	$S'_{12} = S_{12}$	e	f
		$S'_{12} = S_{12} - 1$	f	e
	$S'_{34} = S_{34} - 1$	$S'_{12} = S_{12}$	g	h
		$S'_{12} = S_{12} - 1$	h	g

The molecular-state g -tensor, g_S , is composed of the local g -tensors as follows

$$\bar{\bar{g}}_S = c_1 \bar{\bar{g}}_1 + c_2 \bar{\bar{g}}_2 + c_3 \bar{\bar{g}}_3 + c_4 \bar{\bar{g}}_4$$

where the combination coefficients are determined by the relationship

$$c_i = \delta_{S',S} \frac{R_{i(S'_{12}, S'_{34}, S'; S_{12}, S_{34}, S)}}{[S(S+1)(2S+1)]^{1/2} [\hbar]}$$

and depend upon all the intermediate spins. These coefficients can be generated by a recurrence scheme, as shown by Table 11.19.

The concept of the molecular-state g -tensor is a fast way of generating the matrix elements of the Zeeman operator within the given total spin

$$\begin{aligned}
 H_{S'_{12}S'_{34}SM', S_{12}S_{34}SM}^Z &= \mu_B [\hbar^{-1}] \vec{B} \cdot \vec{g}_S \\
 &\quad \cdot \left\langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S M' \right| \vec{S} \left| S_1 S_2 S_{12} S_3 S_4 S_{34} S M \right\rangle \\
 &= \mu_B [\hbar^{-1}] \sum_{q=-1}^{+1} (-1)^q G_{1,-q} \\
 &\quad \times \left\langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S M' \right| \hat{S}_q \left| S_1 S_2 S_{12} S_3 S_4 S_{34} S M \right\rangle \\
 &= \mu_B [\hbar^{-1}] \left\langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S \right\| \vec{S} \left\| S_1 S_2 S_{12} S_3 S_4 S_{34} S \right\rangle \\
 &\quad \times \left[(-1) G_{1,+1} (-1)^{S-M'} \begin{pmatrix} S & 1 & S \\ -M' & -1 & M \end{pmatrix} \right. \\
 &\quad + G_{1,0} (-1)^{S-M'} \begin{pmatrix} S & 1 & S \\ -M' & 0 & M \end{pmatrix} \\
 &\quad \left. + (-1) G_{1,-1} (-1)^{S-M'} \begin{pmatrix} S & 1 & S \\ -M' & +1 & M \end{pmatrix} \right]
 \end{aligned}$$

TABLE 11.19

Recurrence formulae for evaluating the combination coefficients of molecular-state g - and D -tensors for a general tetrad [1]^a

(a) Combination coefficients of the g -tensors

$$\begin{aligned}
 c_1(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= c_1(S_{12} S_{34} S) \cdot c_1(S_1 S_2 S_{12}) \\
 c_2(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= c_1(S_{12} S_{34} S) \cdot c_2(S_1 S_2 S_{12}) \\
 c_3(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= c_2(S_{12} S_{34} S) \cdot c_1(S_3 S_4 S_{34}) \\
 c_4(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= c_2(S_{12} S_{34} S) \cdot c_2(S_3 S_4 S_{34})
 \end{aligned}$$

(b) Combination coefficients of the local D -tensors

$$\begin{aligned}
 C_1(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_1(S_{12} S_{34} S) \cdot C_1(S_1 S_2 S_{12}) \\
 C_2(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_1(S_{12} S_{34} S) \cdot C_2(S_1 S_2 S_{12}) \\
 C_3(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_2(S_{12} S_{34} S) \cdot C_1(S_3 S_4 S_{34}) \\
 C_4(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_2(S_{12} S_{34} S) \cdot C_2(S_3 S_4 S_{34})
 \end{aligned}$$

(c) Combination coefficients of the pair-interaction D -tensors

$$\begin{aligned}
 C_{12}(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_1(S_{12} S_{34} S) \cdot C_{12}(S_1 S_2 S_{12}) \\
 C_{34}(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_2(S_{12} S_{34} S) \cdot C_{12}(S_3 S_4 S_{34}) \\
 C_{13}(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_{12}(S_{12} S_{34} S) \cdot c_1(S_1 S_2 S_{12}) \cdot c_1(S_3 S_4 S_{34}) \\
 C_{14}(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_{12}(S_{12} S_{34} S) \cdot c_1(S_1 S_2 S_{12}) \cdot c_2(S_3 S_4 S_{34}) \\
 C_{23}(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_{12}(S_{12} S_{34} S) \cdot c_2(S_1 S_2 S_{12}) \cdot c_1(S_3 S_4 S_{34}) \\
 C_{24}(S_1 S_2 S_{12} S_3 S_4 S_{34} S) &= C_{12}(S_{12} S_{34} S) \cdot c_2(S_1 S_2 S_{12}) \cdot c_2(S_3 S_4 S_{34})
 \end{aligned}$$

^aCombination coefficients for dinuclear systems are collected in Table 10.12.

with the spherical transform

$$\begin{aligned} G_{1,+1} &= -\frac{1}{\sqrt{2}}(B_x g_{S,x} + iB_y g_{S,y}) \\ G_{1,-1} &= \frac{1}{\sqrt{2}}(B_x g_{S,x} - iB_y g_{S,y}) \\ G_{1,0} &= B_z g_{S,z} \end{aligned}$$

or, in terms of Cartesian components

$$\begin{aligned} H_{S'_{12}S'_{34}SM', S_{12}S_{34}SM}^Z &= \mu_B [S(S+1)(2S+1)]^{1/2} \\ &\times \left[\frac{1}{\sqrt{2}}(B_x g_{S,x} + iB_y g_{S,y})(-1)^{S-M'} \right. \\ &\times \begin{pmatrix} S & 1 & S \\ -M' & -1 & M \end{pmatrix} \\ &+ B_z g_{S,z}(-1)^{S-M'} \begin{pmatrix} S & 1 & S \\ -M' & 0 & M \end{pmatrix} \\ &\left. - \frac{1}{\sqrt{2}}(B_x g_{S,x} - iB_y g_{S,y})(-1)^{S-M'} \right. \\ &\times \left. \begin{pmatrix} S & 1 & S \\ -M' & +1 & M \end{pmatrix} \right] \end{aligned}$$

The triangular condition for the non-zero $3j$ -symbols implies $M' = M, M \pm 1$. Thus the matrix elements fill the places at the diagonal ($g_{S,z}$ -component, $q = 0, M' = M$) and adjacent to the diagonal ($g_{S,x}$ - and $g_{S,y}$ -components, $q = \pm 1, M' = \pm 1$) for each block of $S' = S$.

For the case of $S' = S - 1$ a different treatment is required; the product involving the molecular-state g -tensor can be rewritten as follows

$$\begin{aligned} \bar{\bar{g}}_S \cdot \vec{S} &= \bar{\bar{g}}_4 \cdot (\vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \vec{S}_4) + (\bar{\bar{g}}_3 - \bar{\bar{g}}_4) \cdot (\vec{S}_1 + \vec{S}_2 + \vec{S}_3) \\ &+ (\bar{\bar{g}}_2 - \bar{\bar{g}}_3) \cdot (\vec{S}_1 + \vec{S}_2) + (\bar{\bar{g}}_1 - \bar{\bar{g}}_2) \cdot \vec{S}_1 \\ &= \bar{\bar{g}}_4 \cdot \vec{S} + (\bar{\bar{g}}_3 - \bar{\bar{g}}_4) \cdot \vec{S}_{123} + (\bar{\bar{g}}_2 - \bar{\bar{g}}_3) \cdot \vec{S}_{12} + (\bar{\bar{g}}_1 - \bar{\bar{g}}_2) \cdot \vec{S}_1 \end{aligned}$$

which is directly applicable within the coupling scheme $|S_1 S_2 S_{12} S_3 S_{123} S_4 SM\rangle$. The first term vanishes for the off-diagonal matrix elements ($S' \neq S$). The procedure outlined for trinuclear systems can be easily generalised.

Notice that when the local g -tensors are identical only the molecular-state g -tensor contributes and $\bar{\bar{g}}_S = \bar{\bar{g}}_A$ holds true.

Let us deal with the simplest tetrad $S_1 = S_2 = S_3 = S_4 = 1/2$ with the assumption that all local g -tensors are equal, $g_1 = g_2 = g_3 = g_4 \equiv g_A$. However, there exist several geometrical possibilities and we will consider the tetrahedral arrangement as a reference from which some distorted structures are derived: the trigonal pyramid (C_{3v}) and the bisphenoid (S_4). The zero-field energy levels can be easily generated along with the linear van Vleck coefficients. Then the magnetic properties can be expressed with the help of the true partition function (Table 11.20)

TABLE 11.20

Terms of the magnetic susceptibility for a tetranuclear cluster with $S_i = 1/2^a$

Z	$T_1/(\mu_B g)$	$T_2/(\mu_B g)^2$
(a) regular tetrahedron: $x = J/kT$		
$2 \cdot 1$	0	0
$+ 3 \cdot \exp(x + y)$	$+ 3 \cdot 1 \cdot \exp(x + y)$	$+ 3 \cdot 1^2 \cdot \exp(x + y)$
$+ 3 \cdot \exp(x)$	+ 0	+ 0
$+ 3 \cdot \exp(x - y)$	$- 3 \cdot 1 \cdot \exp(x - y)$	$+ 3 \cdot 1^2 \cdot \exp(x - y)$
$+ 1 \cdot \exp(3x + 2y)$	$+ 1 \cdot 2 \cdot \exp(3x + 2y)$	$+ 1 \cdot 2^2 \cdot \exp(3x + 2y)$
$+ 1 \cdot \exp(3x + y)$	$+ 1 \cdot 1 \cdot \exp(3x + y)$	$+ 1 \cdot 1^2 \cdot \exp(3x + y)$
$+ 1 \cdot \exp(3x)$	+ 0	+ 0
$+ 1 \cdot \exp(3x - y)$	$- 1 \cdot 1 \cdot \exp(3x - y)$	$+ 1 \cdot 1^2 \cdot \exp(3x - y)$
$+ 1 \cdot \exp(3x - 2y)$	$- 1 \cdot 2 \cdot \exp(3x - 2y)$	$+ 1 \cdot 2^2 \cdot \exp(3x - 2y)$
(b) trigonal distortion to C_{3v} symmetry: $x_1 = -3(J_a + J_b)/2kT$, $x_2 = -2J_b/kT$, $x_3 = -(3J_a + J_b)/2kT$		
$1 \cdot \exp(x_1)$	0	0
$+ 1 \cdot \exp(x_2 + y)$	$+ 1 \cdot 1 \cdot \exp(x_2 + y)$	$+ 1 \cdot 1^2 \cdot \exp(x_2 + y)$
$+ 1 \cdot \exp(x_2)$	+ 0	+ 0
$+ 1 \cdot \exp(x_2 - y)$	$- 1 \cdot \exp(x_2 - y)$	$+ 1 \cdot 1^2 \cdot \exp(x_2 - y)$
$+ 2 \cdot \exp(x_3 + y)$	$+ 2 \cdot 1 \cdot \exp(x_3 + y)$	$+ 2 \cdot 1^2 \cdot \exp(x_3 + y)$
$+ 2 \cdot \exp(x_3)$	+ 0	+ 0
$+ 2 \cdot \exp(x_3 - y)$	$- 2 \cdot 1 \cdot \exp(x_3 - y)$	$+ 2 \cdot 1^2 \cdot \exp(x_3 - y)$
$+ 1 \cdot \exp(2y)$	$+ 1 \cdot 2 \cdot \exp(2y)$	$+ 1 \cdot 2^2 \cdot \exp(2y)$
$+ 1 \cdot \exp(y)$	$+ 1 \cdot 1 \cdot \exp(y)$	$+ 1 \cdot 1^2 \cdot \exp(y)$
$+ 1 \cdot 1$	+ 0	+ 0
$+ 1 \cdot \exp(-y)$	$- 1 \cdot 1 \cdot \exp(-y)$	$+ 1 \cdot 1^2 \cdot \exp(-y)$
$+ 1 \cdot \exp(-2y)$	$- 1 \cdot 2 \cdot \exp(-2y)$	$+ 1 \cdot 2^2 \cdot \exp(-2y)$

(contd.)

TABLE 11.20

Terms of the magnetic susceptibility for a tetranuclear cluster with $S_i = 1/2^a$ (contd.)

Z	$T_1/(\mu_B g)$	$T_2/(\mu_B g)^2$
(c) tetragonal distortion to S_4 symmetry: $z_1 = -(2J_a + J_b)/kT$, $z_2 = -3J_b/kT$, $z_3 = -(J_a + J_b)/kT$, $z_4 = -2J_b/kT$		
$1 \cdot \exp(z_1)$	0	0
$+ 1 \cdot \exp(z_2)$	+ 0	+ 0
$+ 2 \cdot \exp(z_3 + y)$	$+ 2 \cdot 1 \cdot \exp(z_3 + y)$	$+ 2 \cdot 1^2 \cdot \exp(z_3 + y)$
$+ 2 \cdot \exp(z_3)$	+ 0	+ 0
$+ 2 \cdot \exp(z_3 - y)$	$- 2 \cdot \exp(z_3 - y)$	$+ 2 \cdot 1^2 \exp(z_3 - y)$
$+ 1 \cdot \exp(z_4 + y)$	$+ 1 \cdot 1 \cdot \exp(z_4 + y)$	$+ 1 \cdot 1^2 \cdot \exp(z_4 + y)$
$+ 1 \cdot \exp(z_4)$	+ 0	+ 0
$+ 1 \cdot \exp(z_4 - y)$	$- 1 \cdot 1 \cdot \exp(z_4 - y)$	$+ 1 \cdot 1^2 \cdot \exp(z_4 - y)$
$+ 1 \cdot \exp(2y)$	$+ 1 \cdot 2 \cdot \exp(2y)$	$+ 1 \cdot 2^2 \cdot \exp(2y)$
$+ 1 \cdot \exp(y)$	$+ 1 \cdot 1 \cdot \exp(y)$	$+ 1 \cdot 1^2 \cdot \exp(y)$
$+ 1 \cdot 1$	+ 0	+ 0
$+ 1 \cdot \exp(-y)$	$- 1 \cdot 1 \cdot \exp(-y)$	$+ 1 \cdot 1^2 \cdot \exp(-y)$
$+ 1 \cdot \exp(-2y)$	$- 1 \cdot 2 \cdot \exp(-2y)$	$+ 1 \cdot 2^2 \cdot \exp(-2y)$

^aSubstitution: $y = B\mu_B g/kT$.

$$M_{\text{mol}} = N_A \frac{1}{Z} T_1$$

$$\tilde{\chi}_{\text{mol}} = \frac{N_A \mu_0}{kT} \frac{1}{Z^2} (T_2 Z - T_1^2)$$

The terms of the magnetisation and the differential magnetic susceptibility are

$$\begin{aligned}
 T_1 &= \sum_i \left(-\frac{\partial \varepsilon_i}{\partial B} \right) \exp(-\varepsilon_i/kT) \\
 &= \mu_B g \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S \exp[(n_S J - \mu_B g B M_S)/kT] \\
 T_2 &= \sum_i \left(\frac{\partial \varepsilon_i}{\partial B} \right)^2 \exp(-\varepsilon_i/kT) \\
 &= (\mu_B g)^2 \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S^2 \exp[(n_S J - \mu_B g B M_S)/kT]
 \end{aligned}$$

A modelling of the magnetisation, magnetic susceptibility and effective magnetic moment as two-dimensional functions of the applied field and temperature is presented in Figs. 11.16–18.

According to Fig. 11.16 the magnetisation per cluster, depending upon magnitude and sign of the exchange constant, exhibits different profiles with increasing field at low temperature. For ferromagnetic coupling ($J > 0$) the $M = f(B, [T])$ function has a concave profile whereas for anti-ferromagnetic coupling ($J < 0$) its profile is convex. When the temperature is

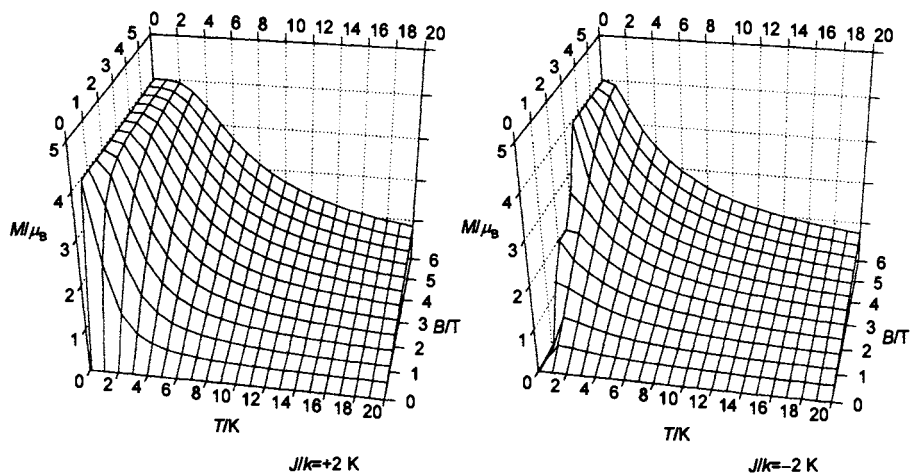


Fig. 11.16. Modelling of the magnetisation per cluster for a tetrahedral $S_1 = S_2 = S_3 = S_4 = 1/2$ system, $M = f(B, T)$.

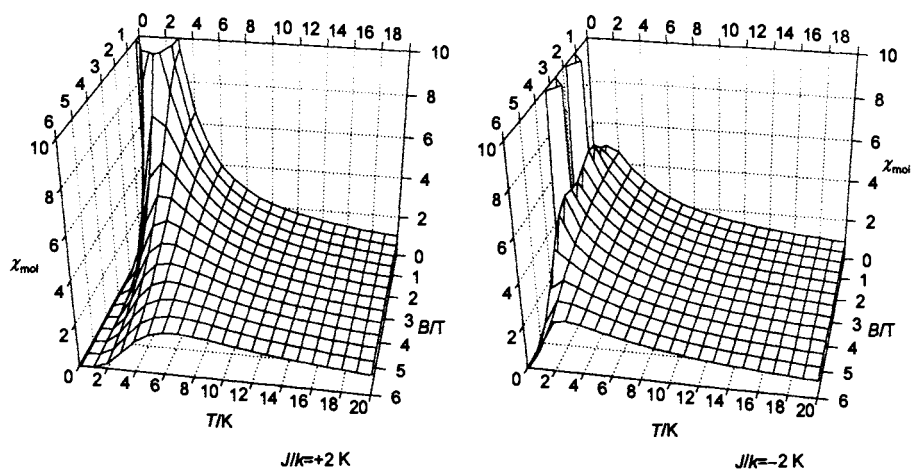


Fig. 11.17. Modelling of the molar differential magnetic susceptibility (in units of $10^{-6} \text{ m}^3 \text{ mol}^{-1}$) for a tetrahedral $S_1 = S_2 = S_3 = S_4 = 1/2$ system, $\bar{\chi}_{\text{mol}} = f(B, T)$.

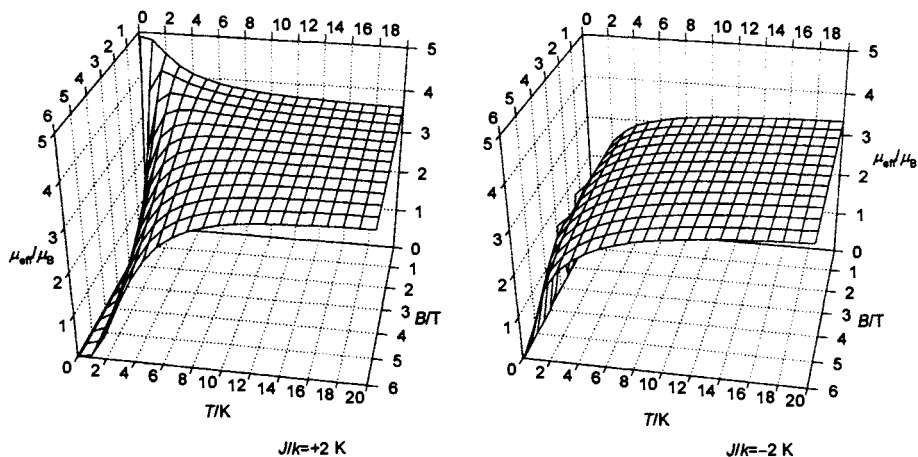


Fig. 11.18. Modelling of the effective magnetic moment per cluster for a tetrahedral $S_1 = S_2 = S_3 = S_4 = 1/2$ system, $\mu_{\text{eff}} = f(B, T)$.

low enough, two steps on the $M = f(B, [T])$ curve may appear for $J < 0$. These are associated with the switch of the ground singlet state to the triplet and eventually to the quintet.

The function $M = f(T, [B])$ decreases with increasing temperature. At a temperature high enough and at low field, the difference between $M(J > 0)$ and $M(J < 0)$ vanishes. At the same time $y \rightarrow 0$ and the van Vleck equation becomes operative.

Figure 11.17 displays the molar differential magnetic susceptibility as a function $\tilde{\chi}_{\text{mol}} = f(B, T)$. At zero (low) field the well-known behaviour is registered: with lowering temperature the function $\chi = f(T)$ increases for $J > 0$ whereas for $J < 0$ it passes through a maximum and then turns to zero. However, at the applied field of $B = 5$ T the function $\chi = f(T)$ exhibits a maximum even in the case of $J > 0$, i.e. ferromagnetic coupling. This property reflects nothing but saturation of the magnetisation at low temperature which results in the zero value of the differential susceptibility. Evidently the mean magnetic susceptibility is highly in error.

For $J < 0$ and temperature low enough the $\tilde{\chi}_{\text{mol}} = f(B, [T])$ dependence is no longer a monotonic but an oscillating function. Such two waves reflect the two steps on the magnetisation curve $M = f(B, [T])$.

Fig. 11.18 shows that, following the magnetic susceptibility behaviour, the $\mu_{\text{eff}} = f(B, [T])$ function reaches a saturation value at low temperature for $J > 0$ (full alignment of four $S = 1/2$ spins yields $\mu_{\text{eff}}/\mu_B = 4.9$). At higher field the $\mu_{\text{eff}} = f(B, [T])$ function decreases to zero on lowering the temperature. For $J < 0$ the $\mu_{\text{eff}} = f(B, [T])$ function decreases only on lowering the temperature.

11.3.3 Asymmetric, antisymmetric and biquadratic exchange

Let us consider the general expressions for the exchange operators as follows:

(a) for asymmetric exchange

$$\begin{aligned}\hat{H}^{\text{asym}} &= \sum_i^4 \sum_{j \leq i}^4 \vec{S}_i \cdot \vec{D}_{ij} \cdot \vec{S}_j \\ &= \sum_i^4 \sum_{j \leq i}^4 \sum_{q=-2}^{+2} (-1)^q D_{ij,2,-q} \left\{ \hat{T}_{2,q}(\vec{S}_i \otimes \vec{S}_j) \right\}\end{aligned}$$

(b) for antisymmetric exchange

$$\begin{aligned}\hat{H}^{\text{anti}} &= \sum_i^4 \sum_{j < i}^4 \vec{d}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) [\hbar^{-2}] \\ &= \sum_i^4 \sum_{j < i}^4 \sum_{q=-1}^{+1} (-1)^q d_{ij,1,-q} (-i\sqrt{2}) \left\{ \hat{T}_{1,q}(\vec{S}_i \otimes \vec{S}_j) \right\} [\hbar^{-2}]\end{aligned}$$

(c) for bilinear isotropic exchange

$$\begin{aligned}\hat{H}^{\text{iso}} &= \sum_i^4 \sum_{j < i}^4 (-J_{ij}) (\vec{S}_i \cdot \vec{S}_j) [\hbar^{-2}] \\ &= \sum_i^4 \sum_{j < i}^4 \sum_{q=0}^0 (-1)^q (-J_{ij}) (-\sqrt{3}) \left\{ \hat{T}_{0,q}(\vec{S}_i \otimes \vec{S}_j) \right\} [\hbar^{-2}] \\ &= \sum_i^4 \sum_{j < i}^4 (-J_{ij}) (-\sqrt{3}) \left\{ \hat{T}_{0,0}(\vec{S}_i \otimes \vec{S}_j) \right\} [\hbar^{-2}]\end{aligned}$$

(d) for pair-interaction biquadratic exchange

$$\begin{aligned}\hat{H}^{\text{biqu}} &= \sum_i^4 \sum_{j < i}^4 (-j_{ijij}) (\vec{S}_i \cdot \vec{S}_j)^2 [\hbar^{-4}] \\ &= \sum_i^4 \sum_{j < i}^4 (-j_{ijij}) \left[\sqrt{5} \left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_i \otimes \vec{S}_i) \} \otimes \{ \hat{T}_2(\vec{S}_j \otimes \vec{S}_j) \} \right\} \right. \\ &\quad \left. + \frac{1}{3} (\vec{S}_i \cdot \vec{S}_i) (\vec{S}_j \cdot \vec{S}_j) \right] [\hbar^{-4}]\end{aligned}$$

(e) for triad- and tetrad-interaction biquadratic exchange

$$\begin{aligned}\hat{H}^{\text{biqu}} &= \sum_i^4 \sum_{j<i}^4 \sum_{k<j}^4 \sum_{l<k}^4 (-j_{ijkl}) \frac{1}{2} \left[(\vec{S}_i \cdot \vec{S}_j)(\vec{S}_k \cdot \vec{S}_l) + (\vec{S}_i \cdot \vec{S}_l)(\vec{S}_j \cdot \vec{S}_k) \right] [\hbar^{-4}] \\ &= \sum_i^4 \sum_{j<i}^4 \sum_{k<j}^4 \sum_{l<k}^4 (-j_{ijkl}) \left[\sqrt{5} \left\{ \hat{T}_0 \{ \hat{T}_2(\vec{S}_i \otimes \vec{S}_k) \} \otimes \{ \hat{T}_2(\vec{S}_j \otimes \vec{S}_l) \} \right\} \right. \\ &\quad \left. + \frac{1}{3} (\vec{S}_i \cdot \vec{S}_k)(\vec{S}_j \cdot \vec{S}_l) \right] [\hbar^{-4}]\end{aligned}$$

(f) along with the Zeeman operator

$$\begin{aligned}\hat{H}^Z &= \mu_B [\hbar^{-1}] \sum_{i=1}^4 \vec{B} \cdot \vec{g}_i \cdot \vec{S}_i \\ &= \mu_B \sum_{i=1}^4 \sum_{q=-1}^{+1} (-1)^q (\vec{B} \cdot \vec{g}_i)_{1,-q} \left\{ \hat{T}_{1,q}(\vec{S}_i) \right\} [\hbar^{-1}]\end{aligned}$$

The above pair-interaction operators can be written in the general form

$$\hat{H}^{\text{ex}} = \sum_i^4 \sum_j^4 \sum_{q=-k}^{+k} (-1)^q P_{ij,k,-q} \left\{ \hat{T}_{k,q}(\vec{S}_i \otimes \vec{S}_j) \right\}$$

where $P_{ij,k,-q}$ stands for the spherical transform of the pair-interaction parameters (e.g. $\vec{D}_{ij} \rightarrow D_{ij,2,q}$, $\vec{d}_{ij} \rightarrow d_{ij,1,q}$, $(\vec{B} \cdot \vec{g}_i) \rightarrow (\vec{B} \cdot \vec{g}_i)_{1,q}$, etc.) including all necessary units factors. The second sum should be properly restricted according to the actual case. The matrix elements of the corresponding tensor operator are evaluated by applying the Wigner–Eckart theorem

$$\begin{aligned}H_{S'_{12}S'_{34}S'M', S_{12}S_{34}SM} &= \sum_i^4 \sum_j^4 \sum_{q=-k}^{+k} (-1)^q P_{ij,k,-q} (-1)^{S'-M'} \\ &\quad \times \begin{pmatrix} S' & k & S \\ -M' & q & M \end{pmatrix} R_{ij(S'_{12}, S'_{34}, S'; S_{12}, S_{34}, S)}^{(k)}\end{aligned}$$

with the reduced matrix elements of the compound operator

$$R_{ij(S'_{12}, S'_{34}, S'; S_{12}, S_{34}, S)}^{(k)} \equiv \left\langle S_1 S_2 S'_{12} S_3 S_4 S'_{34} S' \left\| \hat{T}_k(\vec{S}_i \otimes \vec{S}_j) \right\| S_1 S_2 S_{12} S_3 S_4 S_{34} S \right\rangle$$

expressed through a decoupling formula over the uncoupled spins

$$\begin{aligned}
 & R_{ij(S'_{12}, S'_{34}, S'; S_{12}, S_{34}, S)}^{(k)} \\
 &= \langle S_1 \| \hat{T}_{k1}(\vec{S}_1) \| S_1 \rangle \langle S_2 \| \hat{T}_{k2}(\vec{S}_2) \| S_2 \rangle \langle S_3 \| \hat{T}_{k3}(\vec{S}_3) \| S_3 \rangle \langle S_4 \| \hat{T}_{k4}(\vec{S}_4) \| S_4 \rangle \\
 &\quad \times [(2S'_{12} + 1)(2S_{12} + 1)(2k_{12} + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & k_1 \\ S_2 & S_2 & k_2 \\ S'_{12} & S_{12} & k_{12} \end{Bmatrix} \\
 &\quad \times [(2S'_{34} + 1)(2S_{34} + 1)(2k_{34} + 1)]^{1/2} \begin{Bmatrix} S_3 & S_3 & k_3 \\ S_4 & S_4 & k_4 \\ S'_{34} & S_{34} & k_{34} \end{Bmatrix} \\
 &\quad \times [(2S' + 1)(2S + 1)(2k + 1)]^{1/2} \begin{Bmatrix} S'_{12} & S_{12} & k_{12} \\ S'_{34} & S_{34} & k_{34} \\ S' & S & k \end{Bmatrix}
 \end{aligned}$$

The generalisation of these expressions for clusters of higher nuclearity is straightforward: only the number of terms increases ($N > 4$). However, one should work with a selected coupling scheme consistently; otherwise a recoupling has to be applied.

Useful recurrence relationships exist for the combination coefficients of the molecular-state D -tensor. These are collected in Table 11.19.

11.4 CHAIN SYSTEMS

A good approximation to the problem of an N -member chain is that only the interactions of the adjacent pairs contribute, hence

$$\hat{H}^{\text{iso}} = \sum_{i=2}^N (-J_{i-1,i}) (\vec{S}_{i-1} \cdot \vec{S}_i) [\hbar^2]$$

An appropriate coupling scheme for the recurrence procedure is

$$|I_{12}SM\rangle = |S_1 S_2 SM\rangle$$

$$|I_{123}SM\rangle = |S_1 S_2 S_{12} S_3 SM\rangle$$

$$|I_{1234}SM\rangle = |S_1 S_2 S_{12} S_3 S_{123} S_4 SM\rangle$$

etc.,

$$|I_{1\dots N}SM\rangle = |S_1S_2S_{12}S_3S_{123}\dots S_{\dots N-2,N-1}SM\rangle$$

i.e., the states of the N -centre cluster result from addition of the spin $\vec{S}_N$ to the $(N-1)$ -centre cluster.

The matrix elements, according to the Wigner–Eckart theorem, are

$$\begin{aligned} & \langle I'S'M' | \vec{S}_{i-1} \cdot \vec{S}_i | ISM \rangle \\ &= -\sqrt{3}(-1)^{S-M} \begin{pmatrix} S & 0 & S' \\ -M & 0 & M' \end{pmatrix} \langle I'S | \{ \hat{T}_1(\vec{S}_{i-1}) \otimes \hat{T}_1(\vec{S}_i) \}_0 | IS \rangle \\ &= -[3/(2S+1)]^{1/2} \delta_{S,S'} \delta_{M,M'} R_{i-1,i(I',S;I,S)} \end{aligned}$$

so that we need to evaluate the reduced matrix elements

$$R_{i-1,i(I',S;I,S)} \equiv \langle I'S | \{ \hat{T}_1(\vec{S}_{i-1}) \otimes \hat{T}_1(\vec{S}_i) \}_0 | IS \rangle$$

with the help of the decoupling formula. For example

$$\begin{aligned} & \langle S_1S_2S'_{12}S_3S'_{123}S_4S | \hat{T}_k | S_1S_2S_{12}S_3S_{123}S_4S \rangle = \langle S_1 | \hat{T}_{k1}(\vec{S}_1) | S_1 \rangle \\ & \times [(2S'_{12}+1)(2S_{12}+1)(2k_{12}+1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & k_1 \\ S_2 & S_2 & k_2 \\ S'_{12} & S_{12} & k_{12} \end{Bmatrix} \langle S_2 | \hat{T}_{k2}(\vec{S}_2) | S_2 \rangle \\ & \times [(2S'_{123}+1)(2S_{123}+1)(2k_{123}+1)]^{1/2} \begin{Bmatrix} S'_{12} & S_{12} & k_{12} \\ S_3 & S_3 & k_3 \\ S'_{123} & S_{123} & k_{123} \end{Bmatrix} \langle S_3 | \hat{T}_{k3}(\vec{S}_3) | S_3 \rangle \\ & \times [(2S+1)(2S+1)(2 \cdot 0 + 1)]^{1/2} \begin{Bmatrix} S'_{123} & S_{123} & k_{123} \\ S_4 & S_4 & k_4 \\ S & S & 0 \end{Bmatrix} \langle S_4 | \hat{T}_{k4}(\vec{S}_4) | S_4 \rangle \end{aligned}$$

The last element to be added is

$$\begin{aligned}
R_{N-1,N(I',S;I,S)} &= \left\langle S_1 \dots S'_{1\dots N-2} S_{N-1} S'_{1\dots N-1} S_N S \left\| \hat{T}_k(\vec{S}_{N-1} \otimes \vec{S}_N) \right\| \right. \\
&\quad \left. S_1 \dots S_{1\dots N-2} S_{N-1} S_{1\dots N-1} S_N S \right\rangle \\
&= [(2S'_{12} + 1)(2S_{12} + 1)(2 \cdot 0 + 1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & 0 \\ S_2 & S_2 & 0 \\ S'_{12} & S_{12} & 0 \end{Bmatrix} \\
&\quad \times \left\langle S_1 \left\| \hat{T}_0(\vec{S}_1) \right\| S_1 \right\rangle \left\langle S_2 \left\| \hat{T}_0(\vec{S}_2) \right\| S_2 \right\rangle \\
&\quad \dots \\
&\quad \times [(2S'_{1\dots(N-2)} + 1)(2S_{1\dots(N-2)} + 1)(2 \cdot 0 + 1)]^{1/2} \\
&\quad \times \begin{Bmatrix} S'_{1\dots(N-3)} & S_{1\dots(N-3)} & 0 \\ S_{N-2} & S_{N-2} & 0 \\ S'_{1\dots(N-2)} & S_{1\dots(N-2)} & 0 \end{Bmatrix} \left\langle S_{N-2} \left\| \hat{T}_0(\vec{S}_{N-2}) \right\| S_{N-2} \right\rangle \\
&\quad \times [(2S'_{1\dots(N-1)} + 1)(2S_{1\dots(N-1)} + 1)(2 \cdot 1 + 1)]^{1/2} \\
&\quad \times \begin{Bmatrix} S'_{1\dots(N-2)} & S_{1\dots(N-2)} & 0 \\ S_{N-1} & S_{N-1} & 1 \\ S'_{1\dots(N-1)} & S_{1\dots(N-1)} & 1 \end{Bmatrix} \left\langle S_{N-1} \left\| \hat{T}_1(\vec{S}_{N-1}) \right\| S_{N-1} \right\rangle \\
&\quad \times [(2S' + 1)(2S + 1)(2 \cdot 0 + 1)]^{1/2} \\
&\quad \times \begin{Bmatrix} S'_{1\dots(N-1)} & S_{1\dots(N-1)} & 1 \\ S_N & S_N & 1 \\ S' & S & 0 \end{Bmatrix} \left\langle S_N \left\| \hat{T}_1(\vec{S}_N) \right\| S_N \right\rangle
\end{aligned}$$

and it can be simplified owing to the presence of one or three zeroes in the 9j-symbols (Appendix 3). This expression can be used to generate the matrix element of the isotropic exchange for chain compounds of an arbitrary length. The reduced matrix elements for finite chains are collected in Table 11.21.

For a homospin system, and using the substitutions for the intermediate spins

$$S_N = S_{N-1} \equiv S_1$$

$$a \equiv S_{1\dots(N-1)}$$

$$b \equiv S_{1\dots(N-2)}$$

TABLE 11.21

Reduced matrix elements of isotropic exchange for finite chains

N	$R_{N-1,N(I',S';I,S)}$
2	$R_{12} = [(2S+1)/3]^{1/2} (-1)^{S_1+S_2+1+S_{12}} \begin{Bmatrix} S_1 & S_1 & 1 \\ S_2 & S_2 & S_{12} \end{Bmatrix}$ $\times [S_1(S_1+1)(2S_1+1)]^{1/2} [S_2(S_2+1)(2S_2+1)]^{1/2} [\hbar^2]$
3	$R_{23} = [(2S+1)/3]^{1/2} [(2S'_{12}+1)(2S_{12}+1)]^{1/2}$ $\times (-1)^{S'_{12}+S_2+1+S_1} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_2 & S_2 & S_1 \end{Bmatrix} (-1)^{S_{12}+S_3+1+S} \begin{Bmatrix} S'_{12} & S_{12} & 1 \\ S_3 & S_3 & S \end{Bmatrix}$ $\times [S_2(S_2+1)(2S_2+1)]^{1/2} [S_3(S_3+1)(2S_3+1)]^{1/2} [\hbar^2]$
4	$R_{34} = \delta_{S'_{12},S_{12}} [(2S+1)/3]^{1/2} [(2S'_{123}+1)(2S_{123}+1)]^{1/2}$ $\times (-1)^{S'_{123}+S_3+1+S_{12}} \begin{Bmatrix} S_{123} & S'_{123} & 1 \\ S_3 & S_3 & S_{12} \end{Bmatrix} (-1)^{S_{123}+S_4+1+S} \begin{Bmatrix} S'_{123} & S_{123} & 1 \\ S_4 & S_4 & S \end{Bmatrix}$ $\times [S_3(S_3+1)(2S_3+1)]^{1/2} [S_4(S_4+1)(2S_4+1)]^{1/2} [\hbar^2]$
5	$R_{45} = \delta_{S'_{12},S_{12}} \delta_{S'_{123},S_{123}} [(2S+1)/3]^{1/2} [(2S'_{1234}+1)(2S_{1234}+1)]^{1/2}$ $\times (-1)^{S'_{1234}+S_4+1+S_{123}} \begin{Bmatrix} S_{1234} & S'_{1234} & 1 \\ S_4 & S_4 & S_{123} \end{Bmatrix} (-1)^{S_{1234}+S_5+1+S} \begin{Bmatrix} S'_{1234} & S_{1234} & 1 \\ S_5 & S_5 & S \end{Bmatrix}$ $\times [S_4(S_4+1)(2S_4+1)]^{1/2} [S_5(S_5+1)(2S_5+1)]^{1/2} [\hbar^2]$
N	$R_{N-1,N(I',S';I,S)} = \delta_{S'_{12},S_{12}} \dots \delta_{S'_{1...(N-2)},S_{1...(N-2)}} [(2S+1)/3]^{1/2} [(2S'_{1...(N-1)}+1)(2S_{1...(N-1)}+1)]^{1/2}$ $\times (-1)^{S'_{1...(N-1)}+S_{N-1}+1+S_{1...(N-2)}} \begin{Bmatrix} S_{1...(N-1)} & S'_{1...(N-1)} & 1 \\ S_{N-1} & S_{N-1} & S_{1...(N-2)} \end{Bmatrix}$ $\times (-1)^{S_{1...(N-1)}+S_N+1+S} \begin{Bmatrix} S'_{1...(N-1)} & S_{1...(N-1)} & 1 \\ S_N & S_N & S \end{Bmatrix}$ $\times [S_{N-1}(S_{N-1}+1)(2S_{N-1}+1)]^{1/2} [S_N(S_N+1)(2S_N+1)]^{1/2} [\hbar^2]$

two types of reduced matrix elements result:

(a) the diagonal element

$$R_{N-1,N(b,a,S_1,S;b,a,S_1,S)} = \{[(2S+1)/3]^{1/2}$$

$$\times [-a(a+1) + b(b+1) - S_1(S_1+1)]$$

$$\times [-a(a+1) + S(S+1) - S_1(S_1+1)]$$

$$/[4a(a+1)(2a+1)S_1(S_1+1)(2S_1+1)]\}[\hbar^2]$$

(b) the off-diagonal element (for $S'_{1...(N-1)} = S'_{1...(N-1)} - 1$)

$$\begin{aligned}
 R_{N-1,N(b,a-1,S_1,S;b,a,S_1,S)} &= \{-(2S+1)/3\}^{1/2} \\
 &\times [(a+b-S_1)(a+S-S_1)(a-b+S_1)(1-a+b+S_1)]^{1/2} \\
 &\times [(1+a+b+S_1)(a-S+S_1)(1-a+S+S_1)(1+a+S+S_1)]^{1/2} \\
 &/[4a(2a-1)(2a+1)S_1(S_1+1)(2S_1+1)]\hbar^2
 \end{aligned}$$

Owing to the factor $\delta_{M',M}$ it is possible to restrict ourselves to only the subspace of any (say maximum) spin projection in order to treat the isotropic exchange.

Let us deal with the chain system of equal spins $S_1 = 1/2$. The interaction matrices adopt the following form.

(a) For $N = 2$ the trivial result is

$$\mathbf{H}_{12}^{\text{int}} = \left(\begin{array}{c|c} 1/4 & \\ \hline 0 & -3/4 \end{array} \right) \text{ for } \left[\begin{array}{c} S=1 \\ S=0 \end{array} \right]$$

(b) For $N = 3$ we have two interaction matrices. The first one contains exactly those matrix elements which were contained in the result for $N = 2$

$$\mathbf{H}_{12}^{\text{int}} = \left(\begin{array}{c|cc} 1/4 & & \\ \hline 0 & 1/4 & \\ 0 & 0 & -3/4 \end{array} \right) \text{ for kets } \left[\begin{array}{c} S=3/2, a=1 \\ S=1/2, a=1 \\ S=1/2, a=0 \end{array} \right]$$

Here the intermediate spins for the N -centre system are substituted for the total spins of the $(N-1)$ -centre system, so that $a_{(N)} \rightarrow S_{(N-1)}$. The new term, evaluated according to the formula listed in Table 11.21, is

$$\mathbf{H}_{23}^{\text{int}} = \left(\begin{array}{c|cc} 1/4 & & \\ \hline 0 & -1/2 & \\ 0 & \sqrt{3}/4 & 0 \end{array} \right) \text{ for kets } \left[\begin{array}{c} S=3/2, a=1 \\ S=1/2, a=1 \\ S=1/2, a=0 \end{array} \right]$$

The total interaction matrix is the sum of the adjacent-pair interactions

$$\mathbf{H}^{\text{iso}} = -J_{12}\mathbf{H}_{12}^{\text{int}} - J_{23}\mathbf{H}_{23}^{\text{int}}$$

and this result is necessarily equivalent to that obtained with the help of Table 11.3 or 11.4 for $J_{13} = 0$.

(c) For $N = 4$ two interaction terms are constructed with the help of the result for $N < 4$, i.e.

$$\mathbf{H}_{12}^{\text{int}} = \left(\begin{array}{c|cc|c} 1/4 & & & \\ \hline & 1/4 & & \\ & 0 & 1/4 & \\ & 0 & 0 & -3/4 \\ \hline & & & 1/4 \\ & & & 0 & -3/4 \end{array} \right) \text{ for } \left[\begin{array}{l} S = 2, a = 3/2, b = 1 \\ S = 1, a = 3/2, b = 1 \\ \hline S = 1, a = 1/2, b = 1 \\ S = 1, a = 1/2, b = 0 \\ \hline S = 0, a = 1/2, b = 1 \\ S = 0, a = 1/2, b = 0 \end{array} \right]$$

$$\mathbf{H}_{23}^{\text{int}} = \left(\begin{array}{c|cc|c} 1/4 & & & \\ \hline & 1/4 & & \\ & 0 & -1/2 & \\ & 0 & 0 & 0 \\ \hline & & & -1/2 \\ & & & 0 & 0 \end{array} \right) \text{ for } \left[\begin{array}{l} S = 2, a = 3/2, b = 1 \\ S = 1, a = 3/2, b = 1 \\ \hline S = 1, a = 1/2, b = 1 \\ S = 1, a = 1/2, b = 0 \\ \hline S = 0, a = 1/2, b = 1 \\ S = 0, a = 1/2, b = 0 \end{array} \right]$$

and the only new term is

$$\mathbf{H}_{34}^{\text{int}} = \left(\begin{array}{c|cc|c} 1/4 & & & \\ \hline & -5/12 & & \\ & \sqrt{2}/3 & -1/12 & \\ & 0 & 0 & 1/4 \\ \hline & & & 1/4 \\ & & & 0 & -3/4 \end{array} \right) \text{ for } \left[\begin{array}{l} S = 2, a = 3/2, b = 1 \\ S = 1, a = 3/2, b = 1 \\ \hline S = 1, a = 1/2, b = 1 \\ S = 1, a = 1/2, b = 0 \\ \hline S = 0, a = 1/2, b = 1 \\ S = 0, a = 1/2, b = 0 \end{array} \right]$$

The total interaction matrix is the sum of three contributions

$$\mathbf{H}^{\text{iso}} = -J_{12}\mathbf{H}_{12}^{\text{int}} - J_{23}\mathbf{H}_{23}^{\text{int}} - J_{34}\mathbf{H}_{34}^{\text{int}}$$

(d) For $N = 5$ let the kets be ordered as follows

$$\left[\begin{array}{l} S = 5/2, a = 2, b = 3/2 \\ \hline S = 3/2, a = 2, b = 3/2 \\ S = 3/2, a = 1, b = 3/2 \\ S = 3/2, a = 1, b = 1/2 \\ \hline S = 3/2, a = 1, b = 1/2 \\ S = 1/2, a = 1, b = 3/2 \\ S = 1/2, a = 1, b = 1/2 \\ S = 1/2, a = 0, b = 1/2 \\ S = 1/2, a = 1, b = 1/2 \\ S = 1/2, a = 0, b = 1/2 \end{array} \right]$$

Then the last matrix term is

$$\mathbf{H}_{45}^{\text{int}} = \left(\begin{array}{c|cccc|ccccc} 1/4 & & & & & & & & & \\ \hline & -3/8 & & & & & & & & \\ & \sqrt{15}/8 & -1/8 & & & & & & & \\ & 0 & 0 & 1/4 & & & & & & \\ & 0 & 0 & 0 & 1/4 & & & & & \\ \hline & & & & & 1/4 & & & & \\ & & & & & 0 & -1/2 & & & \\ & & & & & 0 & \sqrt{3}/4 & 0 & & \\ & & & & & 0 & 0 & 0 & -1/2 & \\ & & & & & 0 & 0 & 0 & \sqrt{3}/4 & 0 \end{array} \right)$$

whereas the remaining three terms are constructed with the help of the results for $N < 5$. Finally it holds true

$$\mathbf{H}^{\text{iso}} = -J_{12}\mathbf{H}_{12}^{\text{int}} - J_{23}\mathbf{H}_{23}^{\text{int}} - J_{34}\mathbf{H}_{34}^{\text{int}} - J_{45}\mathbf{H}_{45}^{\text{int}}$$

Assuming now that all the coupling constants are equal, the energy levels are easily obtained: the blocks to be diagonalised have maximum dimension 2×2 .

For ring compounds we need to add the interaction $-J_{N1}\mathbf{H}_{N1}^{\text{int}}$ based on the reduced matrix element $R_{1,N(I',S;I,S)}$.

The chain compounds include several special cases [13]:

(a) ring compounds with the periodic boundary $\vec{S}_{N+1} = \vec{S}_1$;

- (b) regular chains;
- (c) alternating chains;
- (d) regular ferrimagnetic chains;
- (e) alternating ferrimagnetic chains;
- (f) double chains (ladder-type structures).

A few numerical solutions for the magnetic susceptibility of regular chains in the form of

$$\chi_{\text{mol}} = \frac{C_0 g^2 N}{T D}$$

are presented in Table 11.22. A high-temperature expansion is also known in the form

$$\chi_{\text{mol}} = \frac{C_0 g^2}{4T} \left[\frac{N}{D} \right]^{2/3}$$

A frequent approach to one-dimensional extended systems is the *Ising model* based on the assumption

$$\hat{H} = \sum_{i=1}^N \hat{H}_i = (-J)[\hbar^{-2}] \sum_{i=1}^N \hat{\sigma}_i \hat{\sigma}_{i+1} + \mu_B [\hbar^{-1}] g B \sum_{i=1}^N \frac{1}{2} (\hat{\sigma}_i + \hat{\sigma}_{i+1})$$

Here $\hat{\sigma}_i$ is the formal spin operator with eigenvalues $\pm 1[\hbar]$ and it resembles the *z*-component of the true spin operator; the applied magnetic field is long-

TABLE 11.22

Numerical solutions for magnetic susceptibility of regular chain compounds

<i>S</i>	Restriction	Numerator/denominator ^b
1/2	$J < 0^a$	$N = 0.25 + 0.074975x + 0.075235x^2$ $D = 1 + 0.9931x + 0.172135x^2 + 0.757825x^3$
1	$J < 0$	$N = 2 + 0.0194x + 0.777x^2$ $D = 3 + 4.346x + 3.232x^2 + 5.834x^3$
1/2	$y \ll 1$	$N = 1 + 5.7979916y + 16.902653y^2 + 29.376885y^3$ $\quad + 29.832959y^4 + 14.036918y^5$ $D = 1 + 2.7979916y + 7.0086780y^2 + 8.6538644y^3$ $\quad + 4.5743114y^4$

^aBonner–Fischer equation [14].

^bArguments: $x = |J|/kT$ and $y = J/2kT$.

itudinal, parallel to the z -direction. The *transfer operator* is introduced as a Boltzmann factor

$$\begin{aligned}\hat{T}_i &= \exp\{-\hat{H}_i/kT\} \\ &= \exp\{[J[\hbar^{-2}]\hat{\sigma}_i\hat{\sigma}_{i+1} - \mu_B[\hbar^{-1}]gB\frac{1}{2}(\hat{\sigma}_i + \hat{\sigma}_{i+1})]/kT\}\end{aligned}$$

Its representation in the basis set of uncoupled spins is the *transfer matrix*

$$T_{i,\sigma_i,\sigma_{i+1}} \equiv \langle \sigma_i | \hat{T}_i | \sigma_{i+1} \rangle$$

which in our case is the $k = 2 \times 2$ matrix

$$\mathbf{T}_i = \begin{pmatrix} \langle \sigma_i = +1 | \hat{T}_i | \sigma_{i+1} = +1 \rangle & \langle \sigma_i = +1 | \hat{T}_i | \sigma_{i+1} = -1 \rangle \\ \langle \sigma_i = -1 | \hat{T}_i | \sigma_{i+1} = +1 \rangle & \langle \sigma_i = -1 | \hat{T}_i | \sigma_{i+1} = -1 \rangle \end{pmatrix}$$

adopting the form of

$$\mathbf{T}_i = \begin{pmatrix} \exp[(J - \mu_B g B/kT)] & \exp[-J/kT] \\ \exp[-J/kT] & \exp[(J + \mu_B g B/kT)] \end{pmatrix} = e^x \begin{pmatrix} e^{-y} & e^{-2x} \\ e^{-2x} & e^y \end{pmatrix}$$

where we have used the substitutions of

$$x = J/kT$$

$$y = \mu_B g B/kT$$

When the eigenvalues of the spin operators are $\pm 1/2[\hbar]$, then the first argument is $x' = x/4$ and the second one $y' = y/2$. The transfer matrix has two eigenvalues

$$\varepsilon_{\pm} = \frac{1}{2}e^x \{ (e^y + e^{-y}) \pm [(e^y + e^{-y})^2 - 4(1 - e^{-4x})]^{1/2} \}$$

Now the partition function is given by the expression

$$Z = \sum_{\sigma_1=\pm 1} \dots \sum_{\sigma_N=\pm 1} \exp \left\{ \sum_{i=1}^N -\hat{H}_i/kT \right\} = \sum_{\sigma_1=\pm 1} \dots \sum_{\sigma_N=\pm 1} (\hat{T}_1 \dots \hat{T}_N)$$

which can be rearranged with the help of the transfer matrices as follows

$$Z = \text{Tr}\{\mathbf{T}_1 \dots \mathbf{T}_N\}$$

The trace is a sum of the diagonal matrix elements of the product matrix. Since the transfer matrices have been diagonalised, only their eigenvalues are to be multiplied and, for equivalent transfer matrices (a ring, $\mathbf{T}_1 = \mathbf{T}_N$), one gets

$$Z = \text{Tr}\{(\mathbf{T}_1)^N\} = \varepsilon_1^N + \dots + \varepsilon_k^N = \varepsilon_+^N + \varepsilon_-^N$$

In our case we can rearrange

$$Z = \varepsilon_+^N [1 + (\varepsilon_-^N / \varepsilon_+^N)] \xrightarrow{\lim N \rightarrow \infty} \varepsilon_+^N$$

and for large N (in a “thermodynamic limit”) only the greatest eigenvalue really contributes. The standard equation of statistical thermodynamics gives the molar Helmholtz energy in the form ($N = N_A$)

$$F = -kT \ln Z = -kT \ln \varepsilon_+^N = -N_A kT \ln \varepsilon_+$$

and the molar magnetisation becomes

$$\begin{aligned} M(B, T) &= -\left(\frac{\partial F}{\partial B}\right) = N_A kT \left(\frac{\partial \ln \varepsilon_+}{\partial B}\right) \\ &= N_A \mu_B g \frac{e^{2y} - 1}{e^y [4e^{-4x} + e^{2y} + e^{-2y} - 2]^{1/2}} \end{aligned}$$

Finally, the molar differential magnetic susceptibility is an analytic function

$$\tilde{\chi}(B, T) = \mu_0 \left(\frac{\partial M}{\partial B}\right)$$

The Ising model, in the limit of the vanishing field ($B \rightarrow 0$), yields the result [15]

$$\chi_z = \frac{C_0 g_z^2}{T} \exp(2x) + O(y^2)$$

which, when rescaled to $S_1 = 1/2$ local spins, becomes

$$\chi_z = \frac{C_0 g_z^2}{4T} \exp(J/2kT)$$

According to Fig. 11.19, the product function $\chi_z T$ diverges at $T \rightarrow 0$ for ferromagnetic coupling ($J > 0$) and vanishes exponentially for antiferromag-

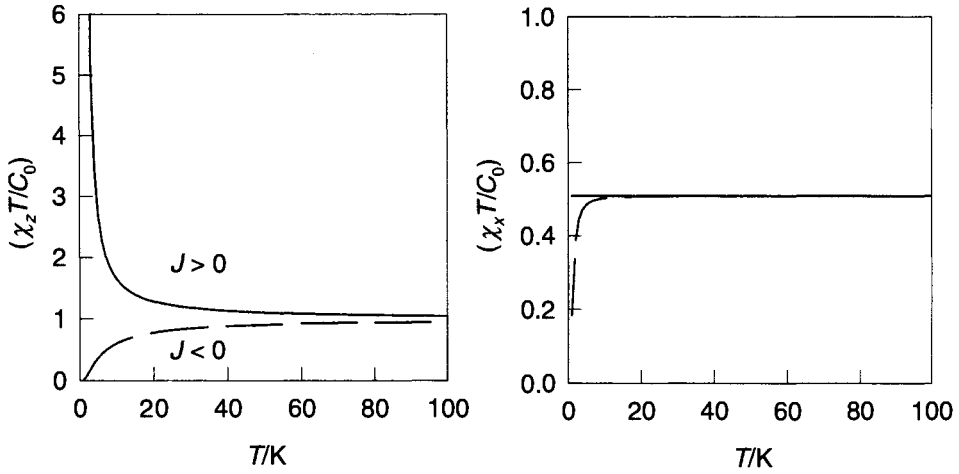


Fig. 11.19. Parallel and perpendicular product functions for an $S_1 = 1/2$ Ising chain: left— $J/k = \pm 10$ K; right— $|J/k| = 10$ K (solid), $|J/k| = 1000$ K (dashed).

netic coupling ($J < 0$). The perpendicular susceptibility for $S_1 = 1/2$ local spins was originally calculated as

$$\chi_x = \frac{C_0 g_x^2}{(2J/k)} \left[\frac{\sinh(J/2kT)}{\cosh(J/2kT)} + \frac{J}{4kT} \frac{1}{\cosh^2(J/4kT)} \right]$$

but a later reinvestigation [16] yielded a slightly modified formula having only a single argument.

When the Ising chain (S_1 spins) interacts substantially with another one (S'_1 spins), forming thus a ladder-type structure, the model Hamiltonian is extended for an interchain coupling parameter. In the simplest case of the $S_1 = S'_1 = 1/2$ system the representation of the transfer matrix has the dimension $k = 4 \times 4$. Its eigenvalues are then obtained only numerically and thus the magnetisation and the magnetic susceptibility cannot be represented by an analytic function. However, numerical solution is accessible using computers [17].

The model exchange Hamiltonian can be written in a more general form

$$\hat{H} = -J[\hbar^{-2}] \sum_{i=1}^{N-1} [\alpha \hat{S}_{i,z} \hat{S}_{i+1,z} + \beta (\hat{S}_{i,x} \hat{S}_{i+1,x} + \hat{S}_{i,y} \hat{S}_{i+1,y})]$$

where $\alpha = 1$ and $\beta = 0$ are valid for the Ising model, $\alpha = 0$ and $\beta = 1$ for the XY model and $\alpha = 1$ and $\beta = 1$ for the Heisenberg model. Some more information about the Ising and XY models can be found elsewhere [16].

11.5 DOUBLE EXCHANGE

The generalisation of the double exchange concept to tetranuclear and polynuclear systems represents a difficult problem for several reasons:

- (a) the number of centres, N , is high;
- (b) the number of shared (delocalised, itinerant) electrons, P , can be higher than one;
- (c) a great variety in the topology of high-nuclearity clusters exists;
- (d) the Hamiltonian of the mixed-valence system cannot be replaced by a simple spin Hamiltonian and the model Hamiltonian involves double-exchange parameters which contain one-electron and two-electron integrals over the (spatial) orbitals.

Let us recapitulate the approach applied for trinuclear systems where each ket is constructed by means of its own coupling scheme depending on the localisation of the extra electron (hole). Any pair of kets is related through a recoupling formula which, for the four spins, contains the $9j$ -symbol, e.g.

$$|A\bullet BC\rangle = [(2S_{AB} + 1)(2S_{BC} + 1)(2S_A + 2s + 1)(2S_C + 2s + 1)]^{1/2} \\ \times \left\{ \begin{array}{ccc} S_A & S_B & S_{AB} \\ s & S_C & (S_C + s) \\ (S_A + s) & S_{BC} & S \end{array} \right\} |ABC\bullet\rangle$$

($s = 1/2$ is the spin number of the extra electron). For a tetranuclear system the recoupling will require $12j$ -symbols, and higher nj -symbols are needed for the recoupling in higher-nuclearity systems. Such an approach is not tractable owing to the limited knowledge about the properties of the higher nj -symbols.

The second possibility is to work in the basis set of uncoupled spins. The corresponding kets have the form of

$$|i\bullet\rangle \equiv |S_1 M_1, \dots, (S_i = S_0 + s) M_i, \dots, (S_k = S_0) M_k, \dots, S_N M_N\rangle$$

and the $i \rightarrow k$ electron transfer counterpart

$$|k\bullet\rangle \equiv |S_1 M_1, \dots, (S_i = S_0) M_i, \dots, (S_k = S_0 + s) M_k, \dots, S_N M_N\rangle$$

The model Hamiltonian appropriate to the problem consists of several contributions [18]

$$\hat{H} = \hat{H}_0 + \hat{H}^{\text{iso}} + \hat{H}_1^{\text{et}} + \hat{H}_2^{\text{et}} + \hat{H}^{\text{ex-et}}$$

where the individual terms represent the usual electronic Hamiltonian, isotropic exchange, one-electron transfer, two-electron transfer and potential exchange-electron transfer, respectively. The one-electron transfer operator is split into two parts

$$\hat{H}_1^{\text{et}} = \sum_i \sum_{k \neq i} (\hat{T}_i^k + \hat{F}_i^k)$$

and the matrix elements in the uncoupled basis set are obtained, with the help of the Slater rules, as follows

$$\begin{aligned} \langle (k\bullet) | \hat{T}_i^k + \hat{F}_i^k | i\bullet \rangle &= t_{ik} (-1)^{2(S_0 + S_{i+1} + \dots + S_{k-1})} \prod_{n=1, n \neq i, k}^N \delta_{S_n, S'_n} \delta_{M_n, M'_n} \\ &\times \sum_{m=\pm 1/2} \langle S_0, M'_i, s, m | (S_0 + s), M_i \rangle \cdot \langle S_0, M_k, s, m | (S_0 + s), M'_k \rangle \end{aligned}$$

where the Clebsch–Gordan coefficients occur and t_{ik} is the double exchange parameter that includes one-electron and two-electron integrals over the spatial orbitals

$$\begin{aligned} t_{ik} &= \langle k | \hat{h}_1 | i \rangle + \sum_j^{(\text{all centres})} \sum_v^{(\text{all core-orbitals})} \langle kj_v | \hat{g}_{12} | ij_v \rangle \\ &+ \sum_{j \neq i, k}^{(\text{excess centres})} \langle kj | \hat{g}_{12} | ij \rangle - \sum_{j=i, k} \sum_v \langle kj_v | \hat{g}_{12} | j_v i \rangle \end{aligned}$$

Except for the transferred electron, the remaining ones are inert and the moving electron keeps its spin projection m . The above matrix element represents the dominant part of the double exchange.

There are

$$K = \frac{N!}{P!(N-P)!}$$

possibilities for the distribution of P extra electrons among N sites and the number of states becomes evaluated as

$$n = 2^P (S_0 + 1)^P (2S_0 + 1)^{N-P} \frac{N!}{P!(N-P)!}$$

For example, for the $d^2-d^2-d^3-d^3$ system with $N = 4$, $P = 2$ and $S_0 = 1$ the number of states is as high as $n = 864$. In such a case, however, we arrive at the problem of high-dimensional matrices which is difficult to treat even with the help of contemporary computers.

The third possibility is to evaluate the matrix elements in the coupled-spin representation. The procedure utilises a successive (chain-like) spin addition scheme

$$S_1 + S_2 = \tilde{S}_2; \tilde{S}_2 + S_3 = \tilde{S}_3; \dots, \tilde{S}_{N-1} + S_N = \tilde{S}_N \equiv S$$

with the intermediate spins denoted as $S_{1,\dots,n} \equiv \tilde{S}_n$ and having the projections $\tilde{M}_n$. The coupled-spin kets are denoted hereafter as follows

$$\begin{aligned} & |S_1, S_2, \tilde{S}_2, \dots, (S_i = S_0 + s), \tilde{S}_i, \dots, S_k, \tilde{S}_k, \dots, \tilde{S}_{N-1}, S_N, S, M\rangle \\ & \equiv |i \bullet (\tilde{S}) SM\rangle \end{aligned}$$

where $(\tilde{S})$ stands for the full set of intermediate spins. Now the recurrence coupling is performed with the help of the Clebsch–Gordan coefficients

$$\begin{aligned} |i \bullet (\tilde{S}) SM\rangle &= \sum_{\text{all } M} \sum_{\text{all } \tilde{M}} \langle S_1 M_1 S_2 M_2 | \tilde{S}_2 \tilde{M}_2 \rangle \\ &\times \dots \langle \tilde{S}_{i-1} \tilde{M}_{i-1} (S_i = S_0 + s) M_i | \tilde{S}_i \tilde{M}_i \rangle \\ &\times \dots \langle \tilde{S}_{N-1} \tilde{M}_{N-1} S_N M_N | \tilde{S} \tilde{M} \rangle \cdot |S_1 M_1, \dots, (S_i = S_0 + s) M_i, \dots, S_N M_N\rangle \end{aligned}$$

Using the properties of the Clebsch–Gordan coefficients and the $6j$ -symbols, it is possible to rearrange the matrix elements of the one-electron transfer operator into the form

$$\begin{aligned} & \langle (k \bullet)' (\tilde{S}') SM | \hat{T}_i^k + \hat{F}_i^k | i \bullet (\tilde{S}) SM \rangle \\ &= t_{ik} (-1)^{2S_0} Z_i^k [S_i = S_0 + s, S'_i = S_0, S_k = S_0, S'_k = S_0 + s; (\tilde{S}), (\tilde{S}'), S] \end{aligned}$$

with the spin-only function defined as follows:

(a) for $i < k$

$$\begin{aligned}
& Z_i^k[S_i, S'_i, S_k, S'_k; (\tilde{S}), (\tilde{S}'), S] \\
&= (-1)^{1+2S_i+2S_k+S'_i+S'_k+(1/2)(k-i)-\tilde{S}_{i-1}-\tilde{S}_i-\tilde{S}'_{k-1}-\tilde{S}_k} \\
&\quad \times \delta_{\tilde{S}_2\tilde{S}'_2} \cdots \delta_{\tilde{S}_{i-1}\tilde{S}'_{i-1}} \delta_{\tilde{S}_k\tilde{S}'_k} \delta_{\tilde{S}_{k+1}\tilde{S}'_{k+1}} \cdots \delta_{\tilde{S}_{N-1}\tilde{S}'_{N-1}} \\
&\quad \times [(2S_i+1)(2\tilde{S}'_i+1)]^{1/2} \begin{Bmatrix} S'_i & s & S_i \\ \tilde{S}_i & \tilde{S}_{i-1} & \tilde{S}'_i \end{Bmatrix} \\
&\quad \times [(2S'_k+1)(2\tilde{S}_{k-1}+1)]^{1/2} \begin{Bmatrix} S_k & s & S'_k \\ \tilde{S}'_{k-1} & \tilde{S}_k & \tilde{S}'_{k-1} \end{Bmatrix} \\
&\quad \times \prod_{n=1}^{k-i-1} (-1)^{-S_{i+n}+\tilde{S}'_{i+n}+\tilde{S}_{i+n-1}} [(2\tilde{S}_{i+n-1}+1)(2\tilde{S}'_{i+n}+1)]^{1/2} \\
&\quad \times \begin{Bmatrix} \tilde{S}'_{i+n-1} & s & \tilde{S}_{i+n-1} \\ \tilde{S}_{i+n} & S_{i+n} & \tilde{S}'_{i+n} \end{Bmatrix}
\end{aligned}$$

(b) for $i > k$

$$\begin{aligned}
& Z_i^k[S_i, S'_i, S_k, S'_k; (\tilde{S}), (\tilde{S}'), S] \\
&= (-1)^{1+2S_i+2S_k+S'_i+S'_k-(1/2)(k-i)-\tilde{S}_{k-1}-\tilde{S}_k-\tilde{S}'_{i-1}-\tilde{S}_i} \\
&\quad \times \delta_{\tilde{S}_2\tilde{S}'_2} \cdots \delta_{\tilde{S}_{k-1}\tilde{S}'_{k-1}} \delta_{\tilde{S}_i\tilde{S}'_i} \delta_{\tilde{S}_{i+1}\tilde{S}'_{i+1}} \cdots \delta_{\tilde{S}_{N-1}\tilde{S}'_{N-1}} \\
&\quad \times [(2S_i+1)(2\tilde{S}_{i-1}+1)]^{1/2} \begin{Bmatrix} S_i & s & S'_i \\ \tilde{S}'_{i-1} & \tilde{S}_i & \tilde{S}'_{i-1} \end{Bmatrix} \\
&\quad \times [(2S'_k+1)(2\tilde{S}'_k+1)]^{1/2} \begin{Bmatrix} S'_k & s & S_k \\ \tilde{S}_k & \tilde{S}_{k-1} & \tilde{S}'_k \end{Bmatrix} \\
&\quad \times \prod_{n=1}^{k-i-1} (-1)^{-S_{k+n}+\tilde{S}'_{k+n}+\tilde{S}_{k+n-1}} [(2\tilde{S}_{k+n-1}+1)(2\tilde{S}'_{k+n}+1)]^{1/2} \\
&\quad \times \begin{Bmatrix} \tilde{S}'_{k+n-1} & s & \tilde{S}_{k+n-1} \\ \tilde{S}_{k+n} & S_{k+n} & \tilde{S}'_{k+n} \end{Bmatrix}
\end{aligned}$$

The one-electron transfer matrix adopts a block-diagonal form according to the value of the total spin.

The operator of the two-electron transfer has the form of

$$\hat{H}_2^{\text{et}} = \sum_i \sum_{k \neq i} \sum_{j \neq k} \sum_{l \neq j} \hat{G}_{i,j}^{k,l}$$

and its matrix elements become

$$\begin{aligned}
 & \left\langle (k \bullet l \bullet)'(\tilde{S}')SM \left| \hat{G}_{ij}^{k,l} \right| i \bullet j \bullet (\tilde{S})SM \right\rangle = \langle kl | \hat{g}_{12} | ij \rangle \\
 & \times \sum_{(\tilde{S}'')} \{ Z_j^l [(S''_i = S'_i = S_0, S''_k = S'_k = S_0 + s), \\
 & \quad (S''_j = S_0 + s, S'_j = S_0, S''_l = S_0, S'_l = S_0 + s), (\tilde{S}''), (\tilde{S}'), S] \\
 & \times Z_i^k [(S_j = S''_j = S_0 + s, S_l = S''_l = S_0), \\
 & \quad (S_i = S_0 + s, S''_i = S_0, S_k = S_0, S''_k = S_0 + s), (\tilde{S}), (\tilde{S}''), S] \}
 \end{aligned}$$

Finally, the potential exchange-electron transfer operator can be expressed as follows

$$\hat{H}^{\text{ex-et}} = \sum_i \sum_{k \neq i} \hat{P}_i^k$$

with matrix elements

$$\begin{aligned}
 & \left\langle (k \bullet)'(\tilde{S}')SM \left| \hat{P}_i^k \right| i \bullet (\tilde{S})SM \right\rangle = \sum_{j \neq i, k} \theta_{ij}(S_i) \theta_{kj}(S_j) A_{ijk} \\
 & \times \sum_{(\tilde{S}'')} \{ Z_i^j [(S''_k = S'_k = S_0 + s), \\
 & \quad (S''_i = S_0 + s, S'_i = S_0, S''_j = S_j - s, S'_j = S_j), (\tilde{S}''), (\tilde{S}'), S] \\
 & \times Z_k^j [(S_i = S''_i = S_0 + s), \\
 & \quad (S''_k = S_0 + s, S_k = S_0, S''_j = S_j - s, S'_j = S_j), (\tilde{S}), (\tilde{S}''), S] \}
 \end{aligned}$$

where the electron interaction enters the parameters

$$A_{ijk} = \begin{cases} \langle kj | \hat{g}_{12} | ji \rangle + \sum_v \langle kj_v | \hat{g}_{12} | j_v i \rangle, & \text{for } d_j^{n+1} - \text{ions} \\ \sum_v \langle kj_v | \hat{g}_{12} | j_v i \rangle, & \text{for } d_j^n - \text{ions} \end{cases}$$

and the sign factor is

$$\theta_{ij}(S_j) = \begin{cases} -1, & \text{for } i < j \\ (-1)^{2S_0 + 2S_j}, & \text{for } i > j \end{cases}$$

SUMMARY

1. The exchange interactions which operate in polynuclear systems are compared in Table 11.23. With increasing number of non-equivalent centres the number of magnetic parameters becomes quite large. In addition to the pair-interaction parameters, triad- and tetrad-interaction parameters can occur. The inclusion of orbital interaction is not well developed for polynuclear systems so far.
2. Clusters of higher nuclearity can be treated by three approaches. The representation of uncoupled spins requires a diagonalisation of the full-size interaction matrix that includes all the relevant interactions: the bilinear isotropic exchange, Zeeman term, the asymmetric exchange, the antisymmetric exchange and eventually the biquadratic exchange. Its dimension is $K = \prod_{i=1}^N (2S_i + 1)$. The resulting eigenvalues represent the energy levels from which the partition function, $Z(B, T)$, and consequently the magnetic thermodynamic functions, e.g. $F(B, T)$, $M(B, T)$, $C_M(B, T)$, $\tilde{\chi}$, can be constructed.
3. A transformation matrix that relates the uncoupled-spin and the coupled-spin kets can be generated by a recurrence procedure utilising only the Clebsch–Gordan coefficients. This can be applied to the uncoupled-spin interaction matrix in order to factorise the secular equation into blocks of lower dimension.
4. The matrix elements of the Zeeman interaction and any exchange-coupling term can be directly generated by utilising the irreducible tensor approach without explicit knowledge of the coupled-spin kets. The matrix elements of a spherical tensor operator are expressed via the Wigner–Eckart theorem through a $3j$ -symbol and a reduced matrix ele-

TABLE 11.23

Comparison of magnetic interactions for various nuclearity systems

Interaction term	Magnetic parameter	Tensor rank	Mononuclear	Dinuclear	Trinuclear
Zeeman	$\bar{g}_A$	1	✓	✓	✓
zero-field splitting	D, E	2	✓	✓	✓
orbital contribution	$\xi_d, (\lambda), \kappa$	0	✓	✓	✓
isotropic exchange	J_{AB}	0	—	✓	✓
asymmetric exchange	$\bar{D}_{AB}$	2	—	✓	✓
antisymmetric exchange	$\bar{d}_{AB}$	1	—	✓	✓
biquadratic exchange	J_{ABBB}	0	—	✓	✓
	J_{ABBC}	0	—	—	✓
double exchange	p_{AB}	0	—	✓	✓
Jahn–Teller effect	X_e, X_{ee}	0	—	—	✓

- ment over the coupled spins. The latter is subjected to a decoupling formula requiring 9j-symbols which in most cases collapse into 6j-symbols evaluable by analytic formulae. This approach also gives selection rules determining the position of the reduced matrix element in the interaction matrix that adopts a multi-band structure along its main diagonal.
5. The local magnetic parameters can be combined to yield the molecular-state parameters, particularly the g_S -tensors and D_S -tensors. These are useful when one works in the limit of strong exchange coupling.
 6. Spin (hole) localisation and/or delocalisation leads to the concept of double exchange in mixed-valence systems. This has a close relationship to the Jahn–Teller effect in polynuclear systems, occurring when the (hypothetical) ground state is orbitally degenerate and disappearing when the nuclear distortion removes the orbital degeneracy.

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Appendix 1

Units and Important Definitions

Fundamental physical constants

Constant	Symbol	SI units
Avogadro constant	N_A	$6.022045 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	k_B, k	$1.380662 \times 10^{-23} \text{ J K}^{-1}$
elementary charge	e	$1.6021892 \times 10^{-19} \text{ C}$
rest mass of electron	m_e	$9.109534 \times 10^{-31} \text{ kg}$
rest mass of proton	m_p	$1.6726485 \times 10^{-27} \text{ kg}$
absolute velocity	c	$2.99792458 \times 10^8 \text{ m s}^{-1}$
permittivity of vacuum	ϵ_0	$8.854187818 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
permeability of vacuum	μ_0	$4\pi \times 10^{-7} \text{ J A}^{-2} \text{ m}^{-1}$
Planck constant	h	$6.626176 \times 10^{-34} \text{ J s}$
reduced Planck constant	$\hbar = h/2\pi$	$1.0545887 \times 10^{-34} \text{ J s}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274078 \times 10^{-24} \text{ J T}^{-1}$
nuclear magneton	$\mu_p = e\hbar/2m_p$	$5.050824 \times 10^{-27} \text{ J T}^{-1}$
fine structure constant	$\alpha = e^2/(4\pi\epsilon_0\hbar c)$	7.29735×10^{-3}
electronic g -factor (Zeeman)	g	2.00231929
—(spin-orbital)	g'	2.00463858
reduced Curie constant	$C_0 = N_A\mu_0\mu_B^2/k$	$4.7141997 \times 10^{-6} \text{ K m}^3 \text{ mol}^{-1}$

Conversion factors

	$(E/k), \text{ K}$	$(E/hc), \text{ cm}^{-1}$
temperature (E/k)	—	0.69503877
wavenumber (E/hc)	1.43876866	—

Selected magnetic quantities

Quantity		Relationship ^a	Unit
magnetic induction (physical vector)		$\vec{B} = \mu_0 \vec{H}$	T = J A ⁻¹ m ⁻²
magnetisation (physical vector)	(volume)	$\vec{M}$	A m ⁻¹
	mass	$M_\rho = M/\rho$	A m ² kg ⁻¹
	molar	$M_{\text{mol}} = M_r M_\rho = M_r M/\rho$	A m ² mol ⁻¹
Magnetic susceptibility (second-rank tensor)	volume, —differential	$\tilde{\chi}_{ab} = \chi_{ab} = (\partial M_a / \partial H_b)$ $= \mu_0 (\partial M_a / \partial B_b)$ $= (\mu_0 / V) \kappa_{ab}$	dimensionless
	—mean	$\bar{\chi} = M/H = \mu_0 M/B$	
	mass	$\chi_\rho = \chi/\rho$	m ³ kg ⁻¹
	molar	$\chi_{\text{mol}} = M_r \chi_\rho = M_r \chi/\rho$	m ³ mol ⁻¹
	reduced	$\kappa_{ab} = -(\partial^2 E / \partial B_a \partial B_b)$	J T ⁻²

^a M_r —molar mass [kg mol⁻¹], ρ —density [kg m⁻³], V —volume.

Spin-only values^a

S	Curie constant, C (10 ⁻⁶ K m ³ mol ⁻¹)	Product factor ($\chi_{\text{mol}} T / C_0$), dimensionless	Effective magnetic moment, μ_{eff} / μ_B
1/2	4.71	1	1.73
1	12.6	8/3	2.83
3/2	23.6	5	3.87
2	37.7	8	4.90
5/2	55.0	35/3	5.91
3	75.4	16	6.93
7/2	99.0	21	7.94

^a Curie constant: $C = C_0 g^2 S(S+1)/3$; product factor: $P = C/C_0$; effective magnetic moment: $\mu_{\text{eff}}/\mu_B = 2[S(S+1)]^{1/2}$.

Sign conventions:

- (a) Condon–Shortley phase convention for spherical harmonics;
 (b) constant factor in front of exchange coupling constants: $-J(\vec{S}_A \cdot \vec{S}_B)$.

Appendix 2

Angular Momentum Matrices

Three principal angular momenta correspond to the operators $\hat{J}_z$, $\hat{J}_+$ and $\hat{J}_-$. Their matrix elements are generated through the formulae

$$\hat{J}_z|j, m\rangle = m|j, m\rangle[\hbar]$$

$$\hat{J}_+|j, m\rangle = \sqrt{(j-m)(j+m+1)}|j, m+1\rangle[\hbar]$$

$$\hat{J}_-|j, m\rangle = \sqrt{(j+m)(j-m+1)}|j, m-1\rangle[\hbar]$$

They can be used to construct other matrices of interest:

$$\hat{J}_x = \frac{1}{2}(\hat{J}_+ + \hat{J}_-)$$

$$\hat{J}_y = \frac{1}{2i}(\hat{J}_+ - \hat{J}_-) = -i\frac{1}{2}(\hat{J}_+ - \hat{J}_-)$$

and the operator equivalents, which are compounds of angular momentum matrices.

The matrix of the $\hat{J}_z$ operator is diagonal. The shift operator matrices are interrelated through a transposition

$$(\mathbf{J}_-) = (\mathbf{J}_+)^T$$

and have non-zero matrix elements adjacent to the diagonal and possess values obtained from the following triangle:

Angular momentum J	Matrix elements $(\hat{J}_+)_{m,m+1}$ and $(\hat{J}_-)_{m-1,m}$
1/2	$\sqrt{1 \cdot 1}$
1	$\sqrt{2 \cdot 1} \sqrt{1 \cdot 2}$
3/2	$\sqrt{3 \cdot 1} \sqrt{2 \cdot 2} \sqrt{1 \cdot 3}$
2	$\sqrt{4 \cdot 1} \sqrt{3 \cdot 2} \sqrt{2 \cdot 3} \sqrt{1 \cdot 4}$
5/2	$\sqrt{5 \cdot 1} \sqrt{4 \cdot 2} \sqrt{3 \cdot 3} \sqrt{2 \cdot 4} \sqrt{1 \cdot 5}$
3	$\sqrt{6 \cdot 1} \sqrt{5 \cdot 2} \sqrt{4 \cdot 3} \sqrt{3 \cdot 4} \sqrt{2 \cdot 5} \sqrt{1 \cdot 6}$
7/2	$\sqrt{7 \cdot 1} \sqrt{6 \cdot 2} \sqrt{5 \cdot 3} \sqrt{4 \cdot 4} \sqrt{3 \cdot 5} \sqrt{2 \cdot 6} \sqrt{1 \cdot 7}$

The angular momentum matrices follow:

$$J = 1/2 \quad \mathbf{J}_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}$$

$$\mathbf{J}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$J = 1 \quad \mathbf{J}_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\mathbf{J}_+ = \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}$$

$$J = 3/2 \quad \mathbf{J}_z = \begin{pmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{pmatrix}$$

$$\mathbf{J}_+ = \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & \sqrt{4} & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\begin{aligned}
 J=2 \quad \mathbf{J}_z &= \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -2 \end{pmatrix} \\
 \mathbf{J}_+ &= \begin{pmatrix} 0 & \sqrt{4} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{6} & 0 \\ 0 & 0 & 0 & 0 & \sqrt{4} \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\
 J=5/2 \quad \mathbf{J}_z &= \begin{pmatrix} 5/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5/2 \end{pmatrix} \\
 \mathbf{J}_+ &= \begin{pmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{8} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{9} & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{8} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\
 J=3 \quad \mathbf{J}_z &= \begin{pmatrix} 3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3 \end{pmatrix}
 \end{aligned}$$

Special Formulae

There exist several sources where special formulae for the nj -symbols are presented. One reference compilation is represented by the Landolt–Börnstein series [1]. Of great advantage is the computer system *Mathematica* which is capable of deriving $3j$ - and $6j$ -symbols in both symbolic and numerical forms [2]. Another source using the FORTRAN computer program is available [3].

Special formulae for $3j$ -symbols

1. The $3j$ -symbol is invariant under the even permutations of the columns; in odd permutations of the columns the sign factor is $(-1)^s$, where s is the sum of the upper symbols; for example

$$\begin{pmatrix} j' & j & J \\ m' & m & M \end{pmatrix} = (-1)^{j'+j+J} \begin{pmatrix} j & j' & J \\ m & m' & M \end{pmatrix}$$

2. The $3j$ -symbol $\begin{pmatrix} S' & k & S \\ -M' & q & M \end{pmatrix}$ is non-zero only when $M' = M + q$.
3. Some formulae follow:

$$\begin{pmatrix} S' & 0 & S \\ -M' & 0 & M \end{pmatrix} = (-1)^{S-M} (2S+1)^{-1/2} \delta_{S,S'} \delta_{M,M'}$$

$$\begin{pmatrix} S & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} = -(-1)^{-M+S} \left[\frac{(S-M+1)(S+M)}{2S(S+1)(2S+1)} \right]^{1/2}$$

$$\begin{pmatrix} S & 1 & S \\ -M & 0 & M \end{pmatrix} = (-1)^{M-S} \frac{M}{[S(S+1)(2S+1)]^{1/2}}$$

$$\begin{pmatrix} S & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} = (-1)^{M-S} \left[\frac{(S-M)(S+M+1)}{2S(S+1)(2S+1)} \right]^{1/2}$$

$$\begin{pmatrix} (S-1) & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} = (-1)^{-M+S} \left[\frac{(S+M-1)(S+M)}{2S(2S-1)(2S+1)} \right]^{1/2}$$

$$\begin{pmatrix} (S-1) & 1 & S \\ -M & 0 & M \end{pmatrix} = (-1)^{-M+S} \left[\frac{(S-M)(S+M)}{S(2S-1)(2S+1)} \right]^{1/2}$$

$$\begin{pmatrix} (S-1) & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} = (-1)^{-M+S} \left[\frac{(S-M-1)(S-M)}{2S(2S-1)(2S+1)} \right]^{1/2}$$

$$\begin{pmatrix} (S+1) & 1 & S \\ -(M-1) & -1 & M \end{pmatrix} = (-1)^{M-S} \left[\frac{(S-M+1)(S-M+2)}{2(S+1)(2S+1)(2S+3)} \right]^{1/2}$$

$$\begin{pmatrix} (S+1) & 1 & S \\ -M & 0 & M \end{pmatrix} = -(-1)^{M-S} \left[\frac{(S-M+1)(S+M+1)}{(S+1)(2S+1)(2S+3)} \right]^{1/2}$$

$$\begin{pmatrix} (S+1) & 1 & S \\ -(M+1) & +1 & M \end{pmatrix} = (-1)^{M-S} \left[\frac{(S+M+1)(S+M+2)}{2(S+1)(2S+1)(2S+3)} \right]^{1/2}$$

Special formulae for 6j-symbols

1. The 6j-symbol is invariant by interchange of any two columns

$$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix} = \begin{Bmatrix} b & a & c \\ e & d & f \end{Bmatrix} = \dots$$

2. It is invariant by switching the upper and lower members of any two columns

$$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix} = \begin{Bmatrix} d & e & c \\ a & b & f \end{Bmatrix} = \dots$$

3. The 6j-symbol $\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix}$ is non-zero only when the elements of each of the four triads $(j_i, j_k, j_l) = (j_1, j_2, j_3), (j_1, j_5, j_6), (j_4, j_2, j_6)$ and (j_4, j_5, j_3) satisfy the triangular condition $|j_i - j_k| \leq j_l \leq j_i + j_k$ and have an integral sum.

4. Some formulae follow:

$$\left\{ \begin{matrix} a & b & 0 \\ c & d & e \end{matrix} \right\} = (-1)^{a+c+e} [(2a+1)(2c+1)]^{-1/2} \delta_{a,b} \delta_{c,d}$$

$$\left\{ \begin{matrix} c & c & 1 \\ b & b & a \end{matrix} \right\} = (-1)^{-(a+b+c)} \frac{1}{2} \frac{a(a+1) - b(b+1) - c(c+1)}{[b(b+1)(2b+1)c(c+1)(2c+1)]^{1/2}}$$

$$\left\{ \begin{matrix} c & (c-1) & 1 \\ b & b & a \end{matrix} \right\} = (-1)^{-(a+b+c)} \\ \times \frac{1}{2} \left[\frac{(1+a+b-c)(a-b+c)(-a+b+c)(1+a+b+c)}{b(b+1)(2b+1)c(2c-1)(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} c & (c-1) & 1 \\ (b-1) & b & a \end{matrix} \right\} = (-1)^{-(a+b+c)} \\ \times \frac{1}{2} \left[\frac{(-1-a+b+c)(-a+b+c)(a+b+c)(1+a+b+c)}{b(2b-1)(2b+1)c(2c-1)(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} c & (c-2) & 2 \\ (b-2) & b & a \end{matrix} \right\} = (-1)^{-(a+b+c)} \frac{1}{4} \\ \times \left[\frac{(-3-a+b+c)(-2-a+b+c)(-1-a+b+c)(-a+b+c)}{(b-1)b(2b-3)(2b-1)(2b+1)} \right]^{1/2} \\ \times \left[\frac{(-2+a+b+c)(-1+a+b+c)(a+b+c)(1+a+b+c)}{(c-1)c(2c-3)(2c-1)(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} c & (c-2) & 2 \\ (b-1) & b & a \end{matrix} \right\} = (-1)^{-(a+b+c)} \frac{1}{2} \\ \times \left[\frac{(1+a+b-c)(a-b+c)(-2-a+b+c)(-1-a+b+c)}{2(b-1)b(b+1)(2b-1)(2b+1)} \right]^{1/2} \\ \times \left[\frac{(-a+b+c)(-1+a+b+c)(a+b+c)(1+a+b+c)}{(c-1)c(2c-3)(2c-1)(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{array}{ccc} c & (c-2) & 2 \\ b & b & a \end{array} \right\} = (-1)^{-(a+b+c)} \frac{1}{2} \\ \times \left[\frac{3(1+a+b-c)(2+a+b-c)(-1+a-b+c)(a-b+c)}{2b(b+1)(2b-1)(2b+1)(2b+3)} \right]^{1/2} \\ \times \left[\frac{(-1-a+b+c)(-a+b+c)(a+b+c)(1+a+b+c)}{(c-1)c(2c-3)(2c-1)(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{array}{ccc} c & (c-1) & 2 \\ (b-1) & b & a \end{array} \right\} = (-1)^{-(a+b+c)} \\ \times \left[\frac{(-1-a+b+c)(-a+b+c)(a+b+c)(1+a+b+c)}{2(b-1)b(b+1)(2b-1)(2b+1)} \right]^{1/2} \\ \times \left[\frac{1+a(a+1)-b^2+bc-c^2}{2(c-1)c(c+1)(2c-1)(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{array}{ccc} c & (c-1) & 2 \\ b & b & a \end{array} \right\} = (-1)^{-(a+b+c)} \left[\frac{3}{2} \right]^{1/2} \\ \times \left[\frac{(1+a+b-c)(a-b+c)(-a+b+c)(1+a+b+c)}{b(b+1)(2b-1)(2b+1)(2b+3)} \right]^{1/2} \\ \times \left[\frac{1+a(a+1)-b(b+1)-c^2}{2(c-1)c(c+1)(2c-1)(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{array}{ccc} c & c & 2 \\ b & b & a \end{array} \right\} = (-1)^{-(c+b+a)} \\ \times 2\{3[c(c+1)+b(b+1)-a(a+1)] \\ \times [c(c+1)+b(b+1)-a(a+1)-1]-4c(c+1)b(b+1)\} / \\ \{[(2c-1)(2c)(2c+1)(2c+2)(2c+3)]^{1/2} \\ [(2b-1)(2b)(2b+1)(2b+2)(2b+3)]^{1/2}\}$$

Special formulae for 9j-symbols

1. The 9j-symbol is invariant in even permutations of rows and columns; it has to be multiplied by the factor of $(-1)^s$ in odd permutations of rows and columns, where s is equal to the sum of all nine symbols. An example is

$$\{9j\} \equiv \begin{Bmatrix} A & A & 1 \\ B & B & 1 \\ C & C' & 2 \end{Bmatrix} = (-1)^{2A+2B+C+C'+4} \begin{Bmatrix} C & C' & 2 \\ B & B & 1 \\ A & A & 1 \end{Bmatrix}$$

2. The 9j-symbol containing one zero collapses to the 6j-symbol

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & 0 \end{Bmatrix} = \delta_{cf} \delta_{g,h} \frac{(-1)^{b+d+c+g}}{[(2c+1)(2g+1)]^{1/2}} \begin{Bmatrix} a & b & c \\ e & d & g \end{Bmatrix}$$

or [1]

$$\begin{Bmatrix} f & f & 0 \\ d & c & e \\ b & a & e \end{Bmatrix} = \begin{Bmatrix} a & b & e \\ c & d & e \\ f & f & 0 \end{Bmatrix} = \frac{(-1)^{b+c+e+f}}{[(2e+1)(2f+1)]^{1/2}} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix}$$

3. The 9j-symbol containing 1 becomes expressed as follows

$$\begin{Bmatrix} f & f & 1 \\ d & c & e \\ b & a & e \end{Bmatrix} = \begin{Bmatrix} f & f & 0 \\ d & c & e \\ b & a & e \end{Bmatrix} \times \frac{d(d+1) + a(a+1) - b(b+1) - c(c+1)}{2[f(f+1)e(e+1)]^{1/2}}$$

4. An orthogonality relation is applicable for higher 9j-symbols [1]

$$(-1)^{2k} \begin{Bmatrix} c & d & e \\ b & k & g \end{Bmatrix} \begin{Bmatrix} f & g & h \\ k & a & c \end{Bmatrix} = \sum_{x=0} (2x+1) \begin{Bmatrix} a & b & x \\ c & d & e \\ f & g & h \end{Bmatrix} \times \begin{Bmatrix} a & b & x \\ e & h & k \end{Bmatrix}$$

5. In a special case of

$$(-1)^{2k} \begin{Bmatrix} B' & B & 1 \\ C & k & A \end{Bmatrix} \begin{Bmatrix} A' & A & 1 \\ k & C' & B' \end{Bmatrix} = \sum_{x=0}^2 (2x+1) \begin{Bmatrix} C' & C & x \\ B' & B & 1 \\ A' & A & 1 \end{Bmatrix} \\ \times \begin{Bmatrix} C' & C & x \\ 1 & 1 & k \end{Bmatrix}$$

and for $k = C$ the following equation holds true

$$(-1)^{2C} \begin{Bmatrix} B' & B & 1 \\ C & C & A \end{Bmatrix} \begin{Bmatrix} A' & A & 1 \\ C & C' & B' \end{Bmatrix} \\ = 1 \cdot \begin{Bmatrix} C' & C & 0 \\ B' & B & 1 \\ A' & A & 1 \end{Bmatrix} \begin{Bmatrix} C' & C & 0 \\ 1 & 1 & C \end{Bmatrix} + 3 \cdot \begin{Bmatrix} C' & C & 1 \\ B' & B & 1 \\ A' & A & 1 \end{Bmatrix} \begin{Bmatrix} C' & C & 1 \\ 1 & 1 & C \end{Bmatrix} \\ + 5 \cdot \begin{Bmatrix} C' & C & 2 \\ B' & B & 1 \\ A' & A & 1 \end{Bmatrix} \begin{Bmatrix} C' & C & 2 \\ 1 & 1 & C \end{Bmatrix}$$

which allows us to evaluate a more complex $9j$ -symbol with the help of the simpler symbols

$$\begin{Bmatrix} C' & C & 2 \\ B' & B & 1 \\ A' & A & 1 \end{Bmatrix} = \frac{1}{5 \cdot \begin{Bmatrix} C' & C & 2 \\ 1 & 1 & C \end{Bmatrix}} \left[(-1)^{2C} \begin{Bmatrix} B' & B & 1 \\ C & C & A \end{Bmatrix} \right. \\ \times \begin{Bmatrix} A' & A & 1 \\ C & C' & B' \end{Bmatrix} - 1 \cdot \begin{Bmatrix} C' & C & 0 \\ B' & B & 1 \\ A' & A & 1 \end{Bmatrix} \begin{Bmatrix} C' & C & 0 \\ 1 & 1 & C \end{Bmatrix} \\ \left. - 3 \cdot \begin{Bmatrix} C' & C & 1 \\ B' & B & 1 \\ A' & A & 1 \end{Bmatrix} \begin{Bmatrix} C' & C & 1 \\ 1 & 1 & C \end{Bmatrix} \right]$$

For $B' = B$ it holds true that

$$\begin{aligned}
 \begin{Bmatrix} C' & C & 1 \\ B & B & 1 \\ A' & A & 1 \end{Bmatrix} &= (-1)^{A'+A+2B+C'+C+3} \begin{Bmatrix} B & B & 1 \\ C' & C & 1 \\ A' & A & 1 \end{Bmatrix} \\
 &= (-1)^{A'+A+2B+C'+C+3} \begin{Bmatrix} B & B & 0 \\ C' & C & 1 \\ A' & A & 1 \end{Bmatrix} \\
 &\quad \times \frac{[C'(C'+1) - C(C+1)] + [A(A+1) - A'(A'+1)]}{2[B(B+1)2]^{1/2}} \\
 &= (-1)^{A'+A+2B+C'+C+3} \frac{(-1)^{A'+B+C+1}}{[(2 \cdot 1 + 1)(2B+1)]^{1/2}} \begin{Bmatrix} A & A' & 1 \\ C' & C & B \end{Bmatrix} \\
 &\quad \times \frac{[C'(C'+1) - C(C+1)] + [A(A+1) - A'(A'+1)]}{2[B(B+1)2]^{1/2}}
 \end{aligned}$$

and then

$$\begin{aligned}
 \begin{Bmatrix} C' & C & 2 \\ B & B & 1 \\ A' & A & 1 \end{Bmatrix} &= \frac{1}{5 \cdot \begin{Bmatrix} C' & C & 2 \\ 1 & 1 & C \end{Bmatrix}} \left[(-1)^{2C} \begin{Bmatrix} B & B & 1 \\ C & C & A \end{Bmatrix} \right. \\
 &\quad \times \begin{Bmatrix} A' & A & 1 \\ C & C' & B \end{Bmatrix} + (-1)^{A'+B+3C+1} \delta_{C',C} \frac{1}{3(2C+1)} \begin{Bmatrix} A & A' & 1 \\ B & B & C \end{Bmatrix} \\
 &\quad + (-1)^{2A'+A+3B+C'+2C+1} \\
 &\quad \times 3 \frac{C'(C'+1) - C(C+1) + A(A+1) - A'(A'+1)}{2[6B(B+1)(2B+1)]^{1/2}} \\
 &\quad \left. \times \begin{Bmatrix} C' & C & 1 \\ 1 & 1 & C \end{Bmatrix} \begin{Bmatrix} A & A' & 1 \\ C' & C & B \end{Bmatrix} \right]
 \end{aligned}$$

For the special case of $A' = A$ and $C' = C$ the last term disappears and a simplification is obtained

$$\begin{aligned}
 \begin{Bmatrix} C & C & 2 \\ B & B & 1 \\ A & A & 1 \end{Bmatrix} &= \frac{(-1)^{2C}}{5 \cdot \begin{Bmatrix} C & C & 2 \\ 1 & 1 & C \end{Bmatrix}} \left[\begin{Bmatrix} B & B & 1 \\ C & C & A \end{Bmatrix} \begin{Bmatrix} A & A & 1 \\ C & C & B \end{Bmatrix} \right. \\
 &\quad \left. + (-1)^{A+B+C+1} \frac{1}{3(2C+1)} \begin{Bmatrix} A & A & 1 \\ B & B & C \end{Bmatrix} \right]
 \end{aligned}$$

Appendix 4

Pascal Constants for Diamagnetic Susceptibility

Several sources are available for the Pascal constants [4–8]. One of them [4] is used below.

(a) Pascal constants for elements

Atom	$\chi_A (10^{-12} \text{ m}^3 \text{ mol}^{-1})$	Ion	$\chi_A (10^{-12} \text{ m}^3 \text{ mol}^{-1})$
H	−36.8	Li ⁺	−52.8
B	−90.5	Na ⁺	−115.6
C	−75.4	Mg ²⁺	−126.9
N, open chain	−70.0	Al ³⁺	−75.4
N, ring	−57.9	K ⁺	−232.5
N, monoamide	−19.4	Ca ²⁺	−199.8
N, diamide, imide	−26.5	Zn ²⁺	−169.6
O, ether, alcohol	−57.9	Ge ⁴⁺	−326.7
O, ketone, aldehyde	+21.7	As ³⁺	−262.6
O, carboxyl	−42.2	As ⁵⁺	−540.3
F	−79.2	Rb ⁺	−339.3
Si	−163.4	Sr ²⁺	−307.9
P	−330.5	Ag ⁺	−389.6
S	−150.8	Cd ²⁺	−251.3
Cl	−252.6	Sn ⁴⁺	−377.0
As	−262.6	Sb ³⁺	−929.9
Se	−289.0	Cs ⁺	−515.2
Br	−384.5	Ba ²⁺	−480.0
Te	−468.7	Hg ²⁺	−521.5
I	−560.5	Tl ⁺	−503.9
		Pb ²⁺	−575.5
		Pb ⁴⁺	−370.7

(b) Closed-shell anions

Group	$\chi_X (10^{-12} \text{ m}^3 \text{ mol}^{-1})$	Group	$\chi_X (10^{-12} \text{ m}^3 \text{ mol}^{-1})$
F ⁻	-138	SeO ₄ ²⁻	-641
Cl ⁻	-327	Te ²⁻	-880
Br ⁻	-452	TeO ₃ ²⁻	-792
I ⁻	-653	TeO ₄ ²⁻	-691
ClO ₃ ⁻	-402	NO ₂ ⁻	-126
ClO ₄ ⁻	-427	NO ₃ ⁻	-251
BrO ₃ ⁻	-503	PO ₃ ⁻	-377
IO ₃ ⁻	-628	PO ₃ ³⁻	-528
IO ₄ ⁻	-679	PO ₄ ³⁻	-591
O ²⁻	-151	AsO ₃ ³⁻	-641
OH ⁻	-151	AsO ₄ ³⁻	-754
S ²⁻	-478	CO ₃ ²⁻	-427
SO ₃ ²⁻	-478	CN ⁻	-226
S ₂ O ₃ ²⁻	-615	CNO ⁻	-264
SO ₄ ²⁻	-503	CNS ⁻	-440
S ₂ O ₈ ²⁻	-980	NCS ⁻	-390
Se ²⁻	-603	SiO ₃ ²⁻	-452
SeO ₃ ²⁻	-553	BF ₄ ⁻	-490
		BO ₃ ³⁻	-440

(c) Closed-shell cations

Group	$\chi_X (10^{-12} \text{ m}^3 \text{ mol}^{-1})$	Group	$\chi_X (10^{-12} \text{ m}^3 \text{ mol}^{-1})$
H ⁺	0	Sn ⁴⁺	-201
Li ⁺	-7.5	Pb ²⁺	-352
Na ⁺	-63	Pb ⁴⁺	-327
K ⁺	-163	N ⁵⁺	-1.3
Rb ⁺	-251	P ³⁺	-50
Cs ⁺	-390	P ⁵⁺	-13
NH ₄ ⁺	-145	As ³⁺	-113
Be ²⁺	-5.0	As ⁵⁺	-75
Mg ²⁺	-38	Sb ³⁺	-214
Ca ²⁺	-101	Sb ⁵⁺	-176
Sr ²⁺	-188	Bi ³⁺	-314
Ba ²⁺	-302	Bi ⁵⁺	-289
B ³⁺	-2.5	S ⁴⁺	-38
Al ³⁺	-25	S ⁶⁺	-13
Ga ³⁺	-101	Se ⁴⁺	-101
In ³⁺	-239	Se ⁶⁺	-63
Tl ⁺	-427	Te ⁴⁺	-176
Tl ³⁺	-390	Te ⁶⁺	-151
C ⁴⁺	-1.3	Cl ⁵⁺	-25
Si ⁴⁺	-19	Br ⁵⁺	-75
Ge ⁴⁺	-88	I ⁵⁺	-151
Sn ²⁺	-251	I ⁷⁺	-126

(d) Closed-shell transition metal cations

Group	$\chi_X (10^{-12} \text{ m}^3 \text{ mol}^{-1})$	Group	$\chi_X (10^{-12} \text{ m}^3 \text{ mol}^{-1})$
Cu ⁺	-151	V ⁵⁺	-50
Ag ⁺	-302	Nb ⁵⁺	-113
Au ⁺	-503	Ta ⁵⁺	-176
Au ³⁺	-402	Cr ⁶⁺	-38
Zn ²⁺	-126	Mo ⁶⁺	-94
Cd ²⁺	-276	W ⁶⁺	-163
Hg ²⁺	-465	U ⁶⁺	-239
Y ³⁺	-151	Mn ⁷⁺	-38
Ti ⁴⁺	-63	Re ⁷⁺	-151
Zr ⁴⁺	-126	Os ⁸⁺	-138
Hf ⁴⁺	-201	Rare earth M ³⁺	-251

(e) Transition metals with partially filled 3d-shells ($10^{-12} \text{ m}^3 \text{ mol}^{-1}$)

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
M ²⁻	-1056	-754	-578	-465				
M ⁻	-679	-528	-427	-364	-276			
M ⁰	-453	-377	-327	-289	-251	-226		
M ⁺	-289	-264	-239	-226	-201	-188	-176	
M ²⁺	-188	-188	-176	-176	-163	-151	-138	-138
M ³⁺	-116	-126	-138	-138	-126	-126	-121	-114
M ⁴⁺		-87	-98	-102	-103	-102	-101	-98
M ⁵⁺			-69	-77	-82	-83	-83	-82
M ⁶⁺				-57	-63	-67	-69	-69

(f) Transition metals with partially filled 4d-shells ($10^{-12} \text{ m}^3 \text{ mol}^{-1}$)

	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
M ²⁻	-2262	-1621	-1244	-1018				
M ⁻	-1483	-1143	-943	-792	-691			
M ⁰	-968	-817	-704	-616	-553	-503		
M ⁺	-641	-591	-540	-490	-452	-402	-377	
M ²⁺	-415	-415	-402	-390	-364	-339	-314	-302
M ³⁺	-263	-302	-302	-302	-289	-276	-276	-264
M ⁴⁺		-201	-226	-239	-238	-226	-226	-226
M ⁵⁺			-163	-176	-188	-188	-188	-188
M ⁶⁺				-138	-151	-151	-163	-163
M ⁷⁺					-114	-124	-126	
M ⁸⁺						-99	-108	

(g) Transition metals with partially filled 5d-shells ($10^{-12} \text{ m}^3 \text{ mol}^{-1}$)

	Hf	Ta	W	Re	Os	Ir	Pt	Au
M^{2-}	-3393	-2413	-1872	-1521				
M^-	-2187	-1709	-1395	-1181	-1030			
M^0	-1432	-1219	-1056	-930	-829	-779		
M^+	-943	-867	-792	-729	-679	-628	-578	
M^{2+}	-603	-616	-603	-578	-540	-515	-490	-465
M^{3+}	-364	-427	-452	-452	-440	-427	-415	-402
M^{4+}		-289	-327	-352	-352	-352	-352	-339
M^{5+}			-239	-264	-289	-289	-289	-289
M^{6+}				-201	-226	-239	-251	-251
M^{7+}					-176	-188	-201	
M^{8+}						-151	-176	

(h) Constitutive corrections

Group	χ_λ ($10^{-12} \text{ m}^3 \text{ mol}^{-1}$)	Group	χ_λ ($10^{-12} \text{ m}^3 \text{ mol}^{-1}$)
C, mononuclear ^a	-3.0	C—Cl	+39.0
C, binuclear ^a	-39.0	C—Br	+51.5
C, trinuclear ^a	-50.3	C—I	+51.5
C=C	+69.1	Cl—C—C—Cl	+54.0
C=C—C=C	+133.2	Br—C—C—Br	+77.9
C≡C	+10.1	CCl ₂	+17.6
CH ₂ =CH—CH ₂	+56.5	N=N	+22.6
cyclopentane	+90.5	C=N—R, Schiff base	+103.0
cyclohexane	+37.7	RC≡N, nitrile	+10.1
cyclohexene, C ₆ H ₁₀	+86.7	RN≡C, carbylamine	0
dicyclohexyl	+98.0	>C=N—R, urea	+20.1
cyclohexadiene	+133.2	C=N—N=C, azine	+128.2
		N=O	+21.4

^aMononuclear as in benzene, binuclear as in naphthalene, trinuclear as in pyrene.

(i) Group susceptibilities^a

Group	χ_G ($10^{-12} \text{ m}^3 \text{ mol}^{-1}$)	Group	χ_G ($10^{-12} \text{ m}^3 \text{ mol}^{-1}$)
H ₂ O	-163 (-165)	C ₃ H ₄ N ₂ , imidazole	-498
NH ₃	-226 (-239)	C ₄ H ₄ N ₂ , pyrazine	-628 (-564)
CO, carbonyl	-126 (-148)	C ₅ H ₅ N, pyridine	-616 (-621)
CH ₃ COO ⁻ , acetato	-377 (-400)	C ₁₀ H ₈ N ₂ , bipyridine	-1319
C ₂ O ₄ ²⁻ , oxalato	-314 (-447)	C ₁₆ H ₁₄ N ₂ O ₂ ²⁻ , salen	-2287 (-2048)
C ₅ H ₅ ⁻ , cyclopentadienyl	-817 (-564)	C ₁₂ H ₈ N ₂ , phenanthroline	-1608
C ₅ H ₇ O ₂ ⁻ , acetylacetonato	-653 (-690)	C ₂ H ₈ N ₂ , ethylenediamine	-578 (-589)

^aValues in parentheses are experimental data (hydrogen atoms added to anions).

Appendix 5

Program for 3j-, 6j- and 9j-Symbols

```
PROGRAM NjSymbol
C=====
C   Calculates Clebsch-Gordan, 3j, 6j, 9j coefficients of any variables.
C   [H.Appel, in Landolt-Bornstein, Neue Serie, Band 3. Springer, Berlin, 1968]
C   by Roman Boca, Slovak Technical University, Bratislava (SK), 1999.
C=====
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /C1/ FAC1(51)
      DATA ZERO, ONE, ONEM /0.0D0, 1.0D0, -1.0D0/
      FAC1(1)=ONE
      DO 10 I=2, 51
      II=I-1
10  FAC1(I)=DFLOAT(II)*FAC1(II)
      OPEN(1, file='njc.1', form='formatted', status='unknown')
      WRITE(*, 20)
20  FORMAT(' Set switcher 3, 6 or 9; then real symbols (6, 6 or 9)')
      READ (*, *) KS
      KS3=KS/3
      GO TO (100, 200, 300), KS3
C-----3j-symbols-----
100 WRITE(1, 197)
197 FORMAT('   j1   j2   j3   m1   m2   m3   Clebsh-G   C3J')
110 READ (*, *) A, B, C, AL, BE, GA
      XXX=F3j(A, B, C, AL, BE, GA)
      IF (XXX.EQ.ZERO) GO TO 120
      CGC=XXX*DSQRT(C+C+ONE)
      C3J=XXX*(ONEM** (A-B-GA))
      GO TO 130
120 CGC=ZERO
      C3J=ZERO
130 WRITE(*, 198) CGC, C3J
198 FORMAT(' CGC=', E12.6, ' 3j=', E12.6)
      WRITE(1, 199) A, B, C, AL, BE, GA, CGC, C3J
199 FORMAT(6F6.1, 2(2X, E15.9))
      GO TO 110
C-----6j-symbols-----
200 WRITE(1, 297)
297 FORMAT('   j1   j2   j3   j4   j5   j6   C6J')
210 READ (*, *) A, B, C, AL, BE, GA
      C6J=F6j(A, B, C, AL, BE, GA)
      WRITE(*, 298) C6J
298 FORMAT(' 6j = ', E12.6)
      WRITE(1, 299) A, B, C, AL, BE, GA, C6J
299 FORMAT(6F6.1, 2X, E15.9)
      GO TO 210
C-----9j-symbols-----
300 WRITE(1, 397)
397 FORMAT('j1   j2   j3   j4   j5   j6   j7   j8   j9   C9J')
310 READ (*, *) A11, A12, A13, A21, A22, A23, A31, A32, A33
      C9J=ZERO
```

```

T1=DMIN1 (DABS (A11-A33), DABS (A32-A21), DABS (A12-A23))
T2=DMAX1 (A11+A33, A32+A21, A12+A23)
N1=IDINT (T1)+1
N2=IDINT (T2)+1
A=T1-ONE
DO 320 N=N1,N2
A=A+ONE
X1=F6j (A11, A21, A31, A32, A33, A)
X2=F6j (A12, A32, A22, A21, A23, A)
X3=F6j (A33, A23, A13, A12, A11, A)
A2=A+A
C9J=C9J+ (ONEM**A2) * (A2+ONE) *X1*X2*X3
320 CONTINUE
WRITE (*, 398) C9J, N
398 FORMAT (' 9j=', E12.6, ' sum of=', I2)
WRITE (1, 399) A11, A12, A13, A21, A22, A23, A31, A32, A33, C9J
399 FORMAT (9F6.1, 2X, E15.9)
GO TO 310
C ... Program is corrupted by setting a character...
END
DOUBLE PRECISION FUNCTION F3j (A, B, C, AL, BE, GA)
IMPLICIT REAL*8 (A-H, O-Z)
COMMON /C1/ FAC1 (51)
DATA ZERO, ONEM /0.0D0, -1.0D0/
F3j=ZERO
IF (NTRI (A, B, C).EQ.0) RETURN
IF (IABS (IDINT (A-B-GA) -IDNINT (A-B-GA)).NE.0) RETURN
I1=IDINT (A+B-C)+1
I2=IDINT (B+C-A)+1
I3=IDINT (C+A-B)+1
I4=IDINT (A+B+C)+1+1
I5=IDINT (A+AL)+1
I6=IDINT (A-AL)+1
I7=IDINT (B+BE)+1
I8=IDINT (B-BE)+1
I9=IDINT (C+GA)+1
I10=IDINT (C-GA)+1
X1=DSQRT (FAC1 (I1)*FAC1 (I2)*FAC1 (I3)/FAC1 (I4)*
$FAC1 (I5)*FAC1 (I6)*FAC1 (I7)*FAC1 (I8)*FAC1 (I9)*FAC1 (I10))
C Number of terms
T1=DMAX1 (ZERO, -C+B-AL, -C+A+BE)
N1=IDINT (T1)+1
T2=DMIN1 (A+B-C, A-AL, B+BE)
N2=IDINT (T2)+1
C The number of terms was increased by 1 because of the DO cycle
X2=ZERO
DO 20 KK=N1,N2
C Decrease by -1 to go back to 0!
K=KK-1
T=DFLOAT (K)
J1=IDINT (C-B+AL)+K+1
J2=IDINT (C-A-BE)+K+1
J3=IDINT (A+B-C)-K+1
J4=IDINT (A-AL)-K+1
J5=IDINT (B+BE)-K+1
IF (J1.LT.1) GO TO 20
IF (J2.LT.1) GO TO 20
IF (J3.LT.1) GO TO 20
IF (J4.LT.1) GO TO 20
IF (J5.LT.1) GO TO 20
X2=X2+
$ (ONEM**T) / (FAC1 (K+1) *FAC1 (J1) *FAC1 (J2) *FAC1 (J3) *FAC1 (J4) *FAC1 (J5))

```



```

20 CONTINUE
F3j=X1*X2
RETURN
END
DOUBLE PRECISION FUNCTION F6j(A,B,C,AL,BE,GA)
IMPLICIT REAL*8(A-H,O-Z)
COMMON /C1/ FAC1(51)
DATA ZERO,ONEM /0.0D0,-1.0D0/
F6j=ZERO
IF (NTRI(A,B,C).EQ.0) RETURN
IF (NTRI(AL,BE,C).EQ.0) RETURN
IF (NTRI(A,BE,GA).EQ.0) RETURN
IF (NTRI(AL,B,GA).EQ.0) RETURN
IF (NTRI(A,B,C).EQ.0) RETURN
IF (IABS(IDINT(A+B+AL+BE)-IDNINT(A+B+AL+BE)).NE.0) RETURN
I1=IDINT(A+B-C) +1
I2=IDINT(A-B+C) +1
I3=IDINT(-A+B+C) +1
I4=IDINT(A+B+C)+1 +1
F1=FAC1(I1)*FAC1(I2)*FAC1(I3)/FAC1(I4)
I1=IDINT(AL+BE-C) +1
I2=IDINT(AL-BE+C) +1
I3=IDINT(-AL+BE+C) +1
I4=IDINT(AL+BE+C)+1 +1
F2=FAC1(I1)*FAC1(I2)*FAC1(I3)/FAC1(I4)
I1=IDINT(AL+B-GA) +1
I2=IDINT(AL-B+GA) +1
I3=IDINT(-AL+B+GA) +1
I4=IDINT(AL+B+GA)+1 +1
F3=FAC1(I1)*FAC1(I2)*FAC1(I3)/FAC1(I4)
I1=IDINT(A+BE-GA) +1
I2=IDINT(A-BE+GA) +1
I3=IDINT(-A+BE+GA) +1
I4=IDINT(A+BE+GA)+1 +1
F4=FAC1(I1)*FAC1(I2)*FAC1(I3)/FAC1(I4)
X1=DSQRT(F1*F2*F3*F4)
C Number of all terms for non-negative factorials
T1=DMAX1(ZERO,A+AL-C-GA,B+BE-C-GA)
N1=IDINT(T1)+1
T2=DMIN1(A+B+AL+BE+1,A+B-C,AL+BE-C,A+BE-GA,AL+B-GA)
N2=IDINT(T2)+1
C The term index NN was increased by 1 because of the DO cycle
X2=ZERO
DO 20 NN=N1,N2
C Decrease by -1 to go back to 0!
N=NN-1
T=DFLOAT(N)
J1=IDINT(A+B+AL+BE)+1-N +1
J2=N +1
J3=IDINT(A+B-C)-N +1
J4=IDINT(AL+BE-C)-N +1
J5=IDINT(A+BE-GA)-N +1
J6=IDINT(AL+B-GA)-N +1
J7=IDINT(-A-AL+C+GA)+N +1
J8=IDINT(-B-BE+C+GA)+N +1
IF (J1.LT.1) GO TO 20
IF (J2.LT.1) GO TO 20
IF (J3.LT.1) GO TO 20
IF (J4.LT.1) GO TO 20
IF (J5.LT.1) GO TO 20
IF (J6.LT.1) GO TO 20
IF (J7.LT.1) GO TO 20

```

```

      IF (J8.LT.1) GO TO 20
      X2=X2+(ONEM**T)*FAC1(J1)/
$ (FAC1(J2)*FAC1(J3)*FAC1(J4)*FAC1(J5)*FAC1(J6)*FAC1(J7)*FAC1(J8))
20 CONTINUE
      L=IDINT(A+B+AL+BE)
      F6j=X1*X2*(ONEM**L)
      RETURN
      END
      FUNCTION NTRI(A,B,C)
      IMPLICIT REAL*8(A-H,O-Z)
      DATA ZERO /0.0D0/
      NTRI=0
      IF ((A+B-C).LT.ZERO) RETURN
      IF ((A-B+C).LT.ZERO) RETURN
      IF ((-A+B+C).LT.ZERO) RETURN
      IF (IABS(IDINT(A+B+C)-IDNINT(A+B+C)).EQ.0) NTRI=1
      RETURN
      END

```

Appendix 6

Program for Low-Spin to High-Spin Conversion

```
PROGRAM SpinX
C=====
C   Iterative solution of equations for spin crossover models
C   using Ising-like Hamiltonian with molecular vibrations.
C   by Roman Boca, Slovak Technical University, Bratislava (SK), 1999.
C=====
C --- Hamiltonian parameters for two sublattices (A and B):
C   DA, DB - energy difference (HS-LS);
C   GH, GL - electronic degeneracy ratio, Rel=GH/GL=5.0;
C   JA, JB, JAB - coupling constants (inter-lattice, intra-lattice),
C   Important: positive = ferromagnetic, negative = antiferromagnetic;
C   vHA, vHB, vLA, vLB - averaged vibration frequencies.
C --- There are several relevant physical cases (ICASE = 1, 2, 3, 4, 5)
C   1. One-step mononuclear, no vibrations
C       DA>0, DB=0, GH>5, GL=1, JA>0, JB=JAB=0, vHA=vHB=vLA=vLB=0
C   2. One-step mononuclear, including vibrations
C       DA>0, DB=0, GH=5, GL=1, JA>0, JB=JAB=0, vHA<vLA, vHB=vLB=0
C   3. Two-step mononuclear, no vibrations
C       DA,DB>0, GH>5, GL=1, JA,JB>0, JAB, vHA=vHB=vLA=vLB=0
C   4. Two-step mononuclear, including vibrations
C       DA>0, DB>0, GH=5, GL=1, JA,JB>0, JAB, vHA<vLA, vHB<vLB
C   5. Two-step binuclear, no vibrations
C       DA>0, DB=0, GH>5, GL=1, JA=J'>0, JB=J'>0, JAB<0, vHA=vHB=vLA=vLB=0
C   IMPLICIT REAL*8 (A-H,O-Z)
C   DATA ONE,TWO,FOUR,ZERO6 /1.0D0,2.0D0,4.0D0,1.D-6/
C   DATA ITMAX /1000/, XMODES /15.0/
C   WRITE(*,1)
C   1 FORMAT(' Set temperature range: Tmin, Tmax, dT(step)')
C   READ(*,*) Tmin,Tmax,dT
C   WRITE(*,2)
C   2 FORMAT(' Set Hamiltonian parameters:',/,
C           ' DA,DB,GH,GL,JA,JB,JAB,vHA,vHB,vLA,vLB (in K)')
C   READ(*,*) DA,DB,GH,GL,AJ,BJ,ABJ,vHA,vHB,vLA,vLB
C   WRITE(*,3)
C   3 FORMAT(' Set proper case: 1, 2, 3, 4, 5')
C   READ(*,*) ICASE
C   WRITE(*,4)
C   4 FORMAT(' Set initial averaged spins: SA,SB; -1(heat) or +1(cool)')
C   READ(*,*) SA0,SB0
C --- Final results on unit '1 = fort.1'
C   OPEN(1,file='1',form='formatted', status='unknown')
C   WRITE(1,5)
C   5 FORMAT(' T      X(HS)      XA      XB      Gr/R
C   $ 1/T      ln(K)      E1/k      E2/k      E3/k      E4/k')
C --- Temporary results of iterations on unit '2 = fort.2'
C   OPEN(2,file='2',form='formatted', status='unknown')
C   WRITE(2,6)
C   6 FORMAT
C   $ (' T      ITER      Sold      Snew      SA      SB')
```

```

C --- Start temperature drift (dT can be positive or negative)
  T=Tmin-dT
  10 CONTINUE
  T=T+dT
C --- Effective degeneracy ratio
  Rel=GH/GL
  GO TO (19,12,19,14,19), ICASE
  12 RA=Rel* ((ONE-DEXP(-vLA/T)) / (ONE-DEXP(-vHA/T))) **XMODES
  EVA=XMODES/TWO*(vHA-vLA)
  GO TO 19
  14 RAA= ((ONE-DEXP(-vLA/T)) / (ONE-DEXP(-vHA/T))) **XMODES
  RBB= ((ONE-DEXP(-vLB/T)) / (ONE-DEXP(-vHB/T))) **XMODES
  RA=DSQRT(Rel*RAA)
  RB=DSQRT(Rel*RBB)
  EVA=XMODES/FOUR*(vHA-vLA)
  EVB=XMODES/FOUR*(vHB-vLB)
C --- Start iterations
  19 SA=SA0
  SB=SB0
  ITER=0
  20 CONTINUE
  ITER=ITER+1
  GO TO (100,200,300,400,500), ICASE
100 SOLD=SA
  EA=DA-TWO*AJ*SA
  A=Rel*DEXP(-EA/T)
  SA=(-ONE+A) / (ONE+A)
  SNEW=SA
  GO TO 900
200 SOLD=SA
  EA=DA-TWO*AJ*SA
  A=RA*DEXP(-(EA+EVA)/T)
  SA=(-ONE+A) / (ONE+A)
  SNEW=SA
  GO TO 900
300 SOLD=SA+SB
  EA=DA-AJ*SA-ABJ*SB
  A=Rel*DEXP(-EA/T)
  SA=(-ONE+A) / (ONE+A)
  EB=DB-BJ*SB-ABJ*SA
  B=Rel*DEXP(-EB/T)
  SB=(-ONE+B) / (ONE+B)
  SNEW=SA+SB
  GO TO 900
400 SOLD=SA+SB
  EA=DA-AJ*SA-ABJ*SB
  A=RA*DEXP(-(EA+EVA)/T)
  SA=(-ONE+A) / (ONE+A)
  EB=DB-BJ*SB-ABJ*SA
  B=RB*DEXP(-(EB+EVB)/T)
  SB=(-ONE+B) / (ONE+B)
  SNEW=SA+SB
  GO TO 900
500 SOLD=SA+SB
  XJP=AJ+BJ
  XJM=AJ-BJ
  XM=SA+SB
  XN=SA-SB
  EA=-DA+XM*XJP-ABJ
  EB= XN*XJM+ABJ
  EC= -XN*XJM+ABJ
  ED= DA-XM*XJP-ABJ
  E1= DEXP(-EA/T)
  E2=Rel* DEXP(-EB/T)
  E3=Rel* DEXP(-EC/T)

```

```

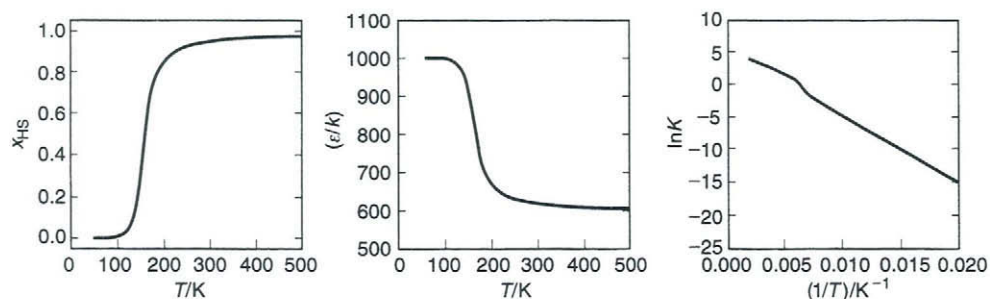
E4=Rel*Rel*DEXP(-ED/T)
Z=E1+E2+E3+E4
SA=(-E1-E2+E3+E4)/Z
XM=SA+SB
XN=SA-SB
EA=-DA+XM*XJP-ABJ
EB=  XN*XJM+ABJ
EC= -XN*XJM+ABJ
ED= DA-XM*XJP-ABJ
E1=      DEXP(-EA/T)
E2=Rel*  DEXP(-EB/T)
E3=Rel*  DEXP(-EC/T)
E4=Rel*Rel*DEXP(-ED/T)
Z=E1+E2+E3+E4
SB=(-E1+E2-E3+E4)/Z
SNEW=SA+SB
900 WRITE(2,7) T,ITER,SOLD,SNEW,SA,SB
    7 FORMAT(F5.1,1X,I6,4(1X,E13.5))
C   No solution up to the limit of iterations:
    IF (ITER.EQ.ITMAX) STOP00001
    IF (DABS(SOLD-SNEW).GT.ZERO6) GO TO 20
    go to (901,901,903,903,905),ICASE
901 XA=(SA+ONE)/TWO
    XB=XA
    X=XA
    EB=EA
    EC=EA
    ED=EA
    go to 910
903 XA=(SA+ONE)/TWO
    XB=(SB+ONE)/TWO
    X=(XA+XB)/TWO
    EC=EA
    ED=EB
    go to 910
905 XA=(TWO+SA+SB)/FOUR
    XB=XA
    X=XA
910 XlnK=DLOG(X/(ONE-X))
    Gr=-T*XlnK
    Tinv=ONE/T
    WRITE(1,8) T,X,XA,XB,Gr,Tinv,XlnK,EA,EB,EC,ED
    8 FORMAT(F5.1,1X,10(E12.5))
    IF (dT.GT.0.and.T.LT.Tmax) go to 10
    IF (dT.LT.0.and.T.GT.Tmax) go to 10
    stop
C-----Typical input 1 (mononuclear without vibrations, heating)
C   20 500 1
C   800 0 150 1 100 0 0 0 0 0
C   1
C   -1 0
C-----Typical input 2 (mononuclear with vibrations, heating)
C   20 500 1
C   800 0 5 1 100 0 0 150 150 240 240
C   2
C   -1 0
C-----Typical input 3 (two-step mononuclear without vibrations, heating)
C   50 500 1
C   800 800 150 1 300 100 -50 0 0 0 0
C   3
C   -1 -1
C-----Typical input 4 (two-step mononuclear with vibrations, heating)
C   50 500 1

```

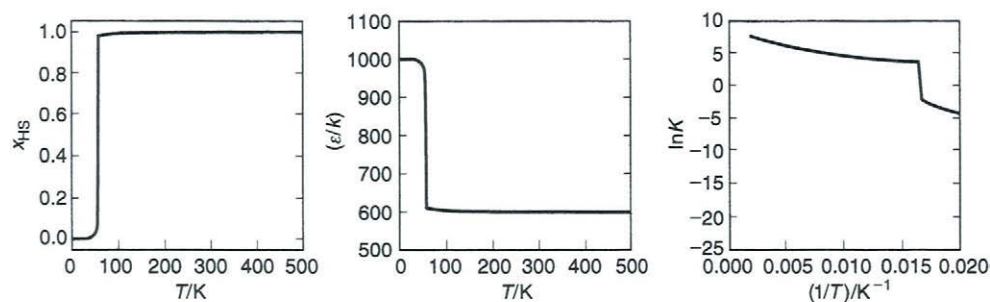
```
C      800 800 5 1 300 100 -50 150 150 240 240
C      4
C      -1 -1
C-----Typical input 5 (binuclear without vibrations, heating)
C      50 500 1
C      800 800 150 1 100 50 -100 0 0 0 0
C      5
C      -1 -1
C-----Typical input 6 (mononuclear, cooling direction)
C      500 50 -1
C      800 0 150 1 300 0 0 0 0 0 0
C      1
C      1 1
C      end
```

Results of the program SpinX

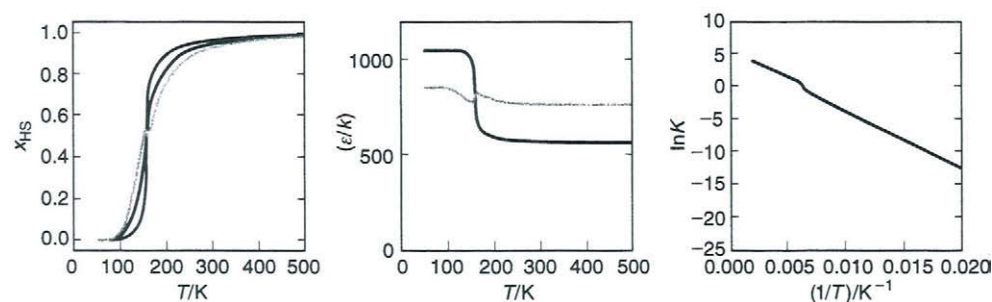
Input 1:



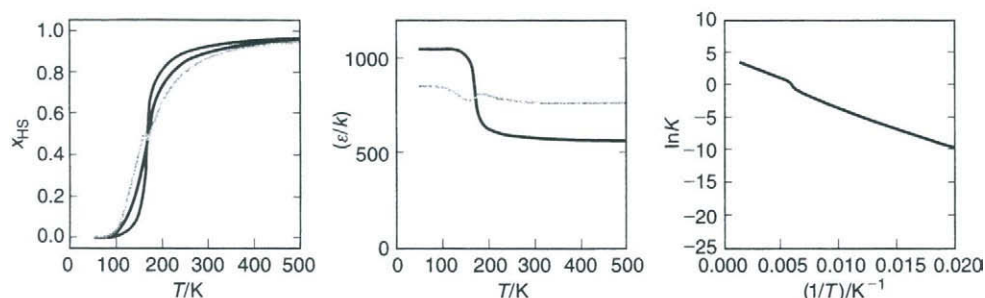
Input 2:



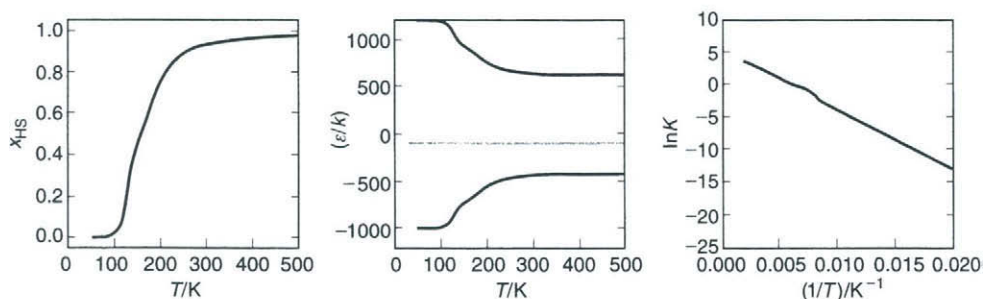
Input 3:



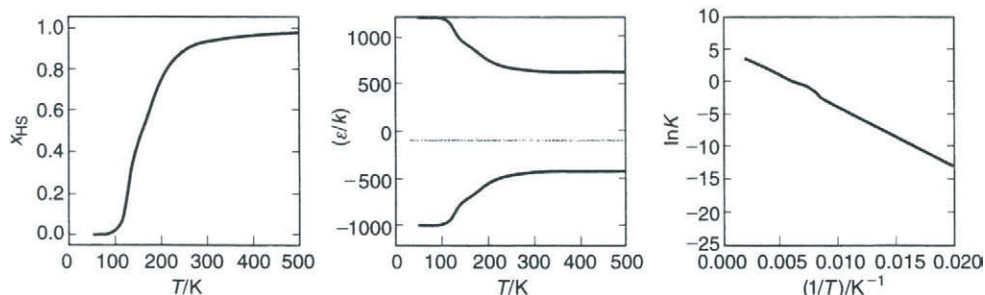
Input 4:



Input 5:



Input 6:



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