Group Theory with Applications in Chemical Physics

PATRICK JACOBS

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Group theory is widely used in many branches of physics and chemistry, and today it may be considered as an essential component in the training of both chemists and physicists. This book provides a thorough, self-contained introduction to the fundamentals of group theory and its applications in chemistry and molecular and solid state physics. The first half of the book, with the exception of a few marked sections, focuses on elementary topics. The second half (Chapters 11–18) deals with more advanced topics which often do not receive much attention in introductory texts. These include the rotation group, projective representations, space groups, and magnetic crystals. The book includes numerous examples, exercises, and problems, and it will appeal to advanced undergraduates and graduate students in the physical sciences. It is well suited to form the basis of a two-semester course in group theory or for private study.

Professor P. W. M. Jacobs is Emeritus Professor of Physical Chemistry at the University of Western Ontario, where he taught widely in the area of physical chemistry, particularly group theory. He has lectured extensively on his research in North America, Europe, and the former USSR. He has authored more than 315 publications, mainly in solid state chemistry and physics, and he was awarded the Solid State Medal of the Royal Society of Chemistry.

Group Theory With Applications in Chemical Physics

P. W. M. JACOBS
The University of Western Ontario

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To MFM
and to all those who love group theory

Contents

Preface

Symmetry pervades many forms of art and science, and group theory provides a systematic way of thinking about symmetry. The mathematical concept of a group was invented in 1823 by Évariste Galois. Its applications in physical science developed rapidly during the twentieth century, and today it is considered as an indispensable aid in many branches of physics and chemistry. This book provides a thorough introduction to the subject and could form the basis of two successive one-semester courses at the advanced undergraduate and graduate levels. Some features not usually found in an introductory text are detailed discussions of induced representations, the Dirac characters, the rotation group, projective representations, space groups, magnetic crystals, and spinor bases. New concepts or applications are illustrated by worked examples and there are a number of exercises. Answers to exercises are given at the end of each section. Problems appear at the end of each chapter, but solutions to problems are not included, as that would preclude their use as problem assignments. No previous knowledge of group theory is necessary, but it is assumed that readers will have an elementary knowledge of calculus and linear algebra and will have had a first course in quantum mechanics. An advanced knowledge of chemistry is not assumed; diagrams are given of all molecules that might be unfamiliar to a physicist.

The book falls naturally into two parts. Chapters 1–10 (with the exception of a few marked sections) are elementary and could form the basis of a one-semester advanced undergraduate course. This material has been used as the basis of such a course at the University of Western Ontario for many years and, though offered as a chemistry course, it was taken also by some physicists and applied mathematicians. Chapters 11–18 are at a necessarily higher level; this material is suited to a one-semester graduate course.

Throughout, explanations of new concepts and developments are detailed and, for the most part, complete. In a few instances complete proofs have been omitted and detailed references to other sources substituted. It has not been my intention to give a complete bibliography, but essential references to core work in group theory have been given. Other references supply the sources of experimental data and references where further development of a particular topic may be followed up.

I am considerably indebted to Professor Boris Zapol who not only drew all the diagrams but also read the entire manuscript and made many useful comments. I thank him also for his translation of the line from Alexander Pushkin quoted below. I am also indebted to my colleague Professor Alan Allnatt for his comments on Chapters 15 and 16 and for several fruitful discussions. I am indebted to Dr. Peter Neumann and Dr. Gabrielle Stoy of Oxford

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Grateful acknowledgement is made to the following for permission to make use of previously published material:

The Chemical Society of Japan, for Figure 10.3;
Taylor and Francis Ltd (http://www.tandf.co.uk/journals) for Table 10.2;
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The American Physical Society and Dr. C. J. Bradley for Table 14.6.

"Сπуженъе муз не терпит суеты . . . " — А.С. Пушкин, "19 октября"

which might be translated as:
"Who serves the muses should keep away from fuss," or, more prosaically,
"Life interferes with Art."

I am greatly indebted to my wife Mary Mullin for shielding me effectively from the daily intrusions of "Life" and thus enabling me to concentrate on this particular work of "Art."

Notation and conventions

General mathematical notation

$\equiv$	identically equal to
$\Rightarrow$	leads logically to; thus $p \Rightarrow q$ means if p is true, then q follows
$\sum$	sum of (no special notation is used when $\sum$ is applied to sets, since it will always be clear from the context when $\sum$ means a sum of sets)
$\forall$	all
iff	if and only if
$\exists$	there exists
$\overline{a}$	the negative of a (but note $\overline{\psi} = \Theta\psi$ in Chapter 13 and $\overline{R} = \overline{E}R$, an operator in the double group $\overline{\mathrm{G}}$, in Chapter 8)
C^n	n-dimensional space in which the components of vectors are complex numbers
c, s	$\cos\phi$, $\sin\phi$
c_2, s_2	$\cos 2\phi$, $\sin 2\phi$
$\mathrm{c}\,x$	$x\cos\phi$
c_n^m	$\cos(m\pi/n)$
i	imaginary unit, defined by $\mathrm{i}^2 = \sqrt{-1}$
$q_1\ q_2\ q_3$	quaternion units
$\Re^n$	n-dimensional space, in which the components of vectors are real numbers
$\Re^3$	configuration space, that is the three-dimensional space of real vectors in which symmetry operations are represented
$s\,x$	$x\sin\phi$
$T(n)$	tensor of rank n in Section 15.1

Sets and groups

$\{g_i\}$	the set of objects g_i, $i = 1, \ldots, g$, which are generally referred to as 'elements'
$\in$	belongs to, as in $g_i \in \mathrm{G}$
$\notin$	does not belong to
$\mathrm{A} \to \mathrm{B}$	map of set A onto set B
$a \to b$	map of element a (the pre-image of b) onto element b (the image of a)

$A \cap B$	intersection of A and B, that is the set of all the elements that belong to both A and B
$A \cup B$	the union of A and B, that is the set of all the elements that belong to A, or to B, or to both A and B
G	a group $G = \{g_i\}$, the elements g_i of which have specific properties (Section 1.1)
E, or g_1	the identity element in G
g	the order of G, that is the number of elements in G
H, A, B	groups of order h, a, and b, respectively, often subgroups of G
$H \subset G$	H is a subset of G; if $\{h_i\}$ have the group properties, H is a subgroup of G of order h
$A \sim B$	the groups A and B are isomorphous
C	a cyclic group of order c
$\mathscr{C}_k$	the class of g_k in G (Section 1.2) of order c_k
C_{ij}^k	class constants in the expansion $\Omega_i\Omega_j = \sum_{k=1}^{N_c} C_{ij}^k \Omega_{\overline{k}}$ (Section A2.2)
$g_i(\mathscr{C}_k)$	ith element of the kth class
$\underline{G}$	a group consisting of a unitary subgroup H and the coset AH, where A is an antiunitary operator (Section 13.2), such that $\underline{G} = \{H\} \oplus A\{H\}$
K	the kernel of G, of order k (Section 1.6)
l_i	dimension of ith irreducible representation
l_s	dimension of an irreducible spinor representation
l_v	dimension of an irreducible vector representation
N_c	number of classes in G
N_{rc}	number of regular classes
N_r	number of irreducible representations
N_s	number of irreducible spinor representations
N_v	number of irreducible vector representations
N(H|G)	the normalizer of H in G, of order n (Section 1.7)
t	index of a coset expansion of G on H, $G = \sum_{r=1}^{t} g_r H$, with $g_r \notin H$ except for $g_1 = E$; $\{g_r\}$ is the set of coset representatives in the coset expansion of G, and $\{g_r\}$ is not used for G itself.
$Z(h_j\|G)$	the centralizer of h_j in G, of order z (Section 1.7)
Z_i	an abbreviation for $Z(g_i\|G)$
Ω_k, $\Omega(\mathscr{C}_k)$	Dirac character of $\mathscr{C}_k$, equal to $\sum_{i=1}^{c_k} g_i(\mathscr{C}_k)$
$A \otimes B$	(outer) direct product of A and B, often abbreviated to DP
$A \boxtimes B$	inner direct product of A and B
$A \wedge B$	semidirect product of A and B
$A \overline{\otimes} B$	symmetric direct product of A and B (Section 5.3)
$A \underline{\otimes} B$	antisymmetric direct product of A and B (Section 5.3)

Vectors and matrices

$\mathbf{r}$	a polar vector (often just a vector) which changes sign under inversion; $\mathbf{r}$ may be represented by the directed line segment OP, where O is the origin of the coordinate system
$x\ y\ z$	coordinates of the point P and therefore the components of a vector $\mathbf{r} = \mathrm{OP}$; independent variables in the function $f(x, y, z)$.
$\mathbf{x}\ \mathbf{y}\ \mathbf{z}$	space-fixed right-handed orthonormal axes, collinear with OX, OY, OZ
$\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3$	unit vectors, initially coincident with $\mathbf{x}\ \mathbf{y}\ \mathbf{z}$, but firmly embedded in configuration space (see $R(\phi\ \ \mathbf{n})$ below). Note that $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ behave like polar vectors under rotation but are invariant under inversion and therefore they are *pseudovectors*. Since, in configuration space the vector $\mathbf{r} = \mathbf{e}_1 x + \mathbf{e}_2 y + \mathbf{e}_3 z$ changes sign on inversion, the components of $\mathbf{r}$, $\{x\ y\ z\}$, must change sign on inversion and are therefore *pseudoscalars*
$\{\mathbf{e}_i\}$	unit vectors in a space of n dimensions, $i = 1, \ldots, n$
$\{v_i\}$	components of the vector $\mathbf{v} = \sum_i \mathbf{e}_i v_i$
$\mathbb{A}$	the matrix $\mathbb{A} = [a_{rs}]$, with m rows and n columns so that $r = 1, \ldots, m$ and $s = 1, \ldots, n$. See Table A1.1 for definitions of some special matrices
$\mathbb{A}_{rs}$, a_{rs}	element of matrix $\mathbb{A}$ common to the rth row and sth column
$\mathbb{E}_n$	unit matrix of dimensions $n \times n$, in which all the elements are zero except those on the principal diagonal, which are all unity; often abbreviated to $\mathbb{E}$ when the dimensions of $\mathbb{E}$ may be understood from the context
$\det \mathbb{A}$ or $\|a_{rs}\|$	determinant of the square matrix $\mathbb{A}$
$\mathbb{A} \otimes \mathbb{B}$	direct product of the matrices $\mathbb{A}$ and $\mathbb{B}$
$\mathbb{C}_{pr,qs}$	element $a_{pq} b_{rs}$ in $\mathbb{C} = \mathbb{A} \otimes \mathbb{B}$
$\mathbb{A}_{[ij]}$	ijth element (which is itself a matrix) of the supermatrix $\mathbb{A}$
$\langle a_1\ \ a_2 \ldots a_n\|$	a matrix of one row containing the set of elements $\{a_i\}$
$\langle a\|$	an abbreviation for $\langle a_1\ a_2 \ldots a_n\|$. The set of elements $\{a_i\}$ may be basis vectors, for example $\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\|$, or basis functions $\langle \phi_1\ \ \phi_2 \ldots \phi_n\|$.
$\|b_1\ \ b_2 \ldots b_n\rangle$	a matrix of one column containing the set of elements $\{b_i\}$, often abbreviated to $\|b\rangle$; $\langle b\|$ is the transpose of $\|b\rangle$
$\langle a'\|$	the transform of $\langle a\|$ under some stated operation
$\langle \mathbf{e}\|r\rangle$	an abbreviation for the matrix representative of a vector $\mathbf{r}$; often given fully as $\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3 \mid x\ y\ z\rangle$

Brackets

$\langle\ \|, \|\ \rangle$	Dirac bra and ket, respectively; no special notation is used to distinguish the bra and ket from row and column matrices, since which objects are intended will always be clear from the context

$[A,\ B]$	commutator of A and B equal to $AB - BA$
$[a,\ A]$	complex number $a + \mathrm{i}A$
$[a\ ;\ \mathbf{A}]$	quaternion (Chapter 11)
$[g_i\ ;\ g_j]$	projective factor, or multiplier (Chapter 12); often abbreviated to $[i\ ;\ j]$
$[n_1\ n_2\ n_3]$	components of the unit vector $\mathbf{n}$, usually given without the normalization factor; for example, [1 1 1] are the components of the unit vector that makes equal angles with OX, OY, OZ, the normalization factor $3^{-½}$ being understood. Normalization factors will, however, be given explicitly when they enter into a calculation, as, for example, in calculations using quaternions

Angular momenta

$\mathbf{L}$, $\mathbf{S}$, $\mathbf{J}$	orbital, spin, and total angular momenta
$\hat{\mathbf{L}}$, $\hat{\mathbf{S}}$, $\hat{\mathbf{J}}$	quantum mechanical operators corresponding to $\mathbf{L}$, $\mathbf{S}$, and $\mathbf{J}$
L, S, J	quantum numbers that quantize $\mathbf{L}^2$, $\mathbf{S}^2$, and $\mathbf{J}^2$
$\hat{\mathbf{j}}$	operator that obeys the angular momentum commutation relations
$\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2$	total ($\mathbf{j}$) and individual ($\mathbf{j}_1$, $\mathbf{j}_2$, ...) angular momenta, when angular momenta are coupled

Symmetry operators and their matrix representatives

A	antiunitary operator (Section 13.1); A, B may also denote linear, Hermitian operators according to context
E	identity operator
$\overline{E}$	operator $R(2\pi\ \mathbf{n})$ introduced in the formation of the double group $\overline{G} = \{R\ \overline{R}\}$ from G $= \{R\}$, where $\overline{R} = \overline{E}R$ (Section 8.1)
I	inversion operator
$I_1\ I_2\ I_3$	operators that generate infinitesimal rotations about $\mathbf{x}\ \mathbf{y}\ \mathbf{z}$, respectively (Chapter 11)
$\hat{I}_1\ \hat{I}_2\ \hat{I}_3$	function operators that correspond to $I_1\ \ I_2\ \ I_3$
$\mathtt{I}_3$	matrix representative of I_3, and similarly (note that the usual symbol $\Gamma(R)$ for the matrix representative of symmetry operator R is not used in this context, for brevity)
$\mathbf{I}$	generator of infinitesimal rotations about $\mathbf{n}$, with components I_1, I_2, I_3
$\mathtt{I}_{\mathbf{n}}$	matrix representative of $I_n = \mathbf{n} \cdot \mathbf{I}$
$\mathtt{J}_x\ \mathtt{J}_y\ \mathtt{J}_z$	matrix representatives of the angular momentum operators $\hat{J}_x,\ \hat{J}_y,\ \hat{J}_z$ for the basis $\langle m| = \langle {}^1\!/_2\,,\ \ {}^{-1}\!/_2|$. Without the numerical factors of ½, these are the Pauli matrices $\boldsymbol{\sigma}_1\ \boldsymbol{\sigma}_2\ \boldsymbol{\sigma}_3$

$R(\phi\ \ \mathbf{n})$	rotation through an angle ϕ about an axis which is the unit vector $\mathbf{n}$; here $\phi\ \ \mathbf{n}$ is not a product but a single symbol $\phi\mathbf{n}$ that fixes the three independent parameters necessary to describe a rotation (the three components of $\mathbf{n}$, $[n_1\ n_2\ n_3]$, being connected by the normalization condition); however, a space is inserted between ϕ and $\mathbf{n}$ in rotation operators for greater clarity, as in $R(2\pi/3\ \ \mathbf{n})$. The range of ϕ is $-\pi < \phi \leq \pi$. R acts on configuration space and on all vectors therein (including $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$) (but not on $\{\mathbf{x}\ \mathbf{y}\ \mathbf{z}\}$, which define the space-fixed axes in the active representation)
$\hat{R}(\phi\ \ \mathbf{n})$	function operator that corresponds to the symmetry operator $R(\phi\ \ \mathbf{n})$, defined so that $\hat{R}f(\mathbf{r}) = f(R^{-1}\mathbf{r})$ (Section 3.5)
R, S, T	general symbols for point symmetry operators (point symmetry operators leave at least one point invariant)
$\hat{s}_x\ \hat{s}_y\ \hat{s}_z$	spin operators whose matrix representatives are the Pauli matrices and therefore equal to $\hat{J}_x,\ \hat{J}_y,\ \hat{J}_z$ without the common factor of $1/2$
T	translation operator (the distinction between T a translation operator and T when used as a point symmetry operator will always be clear from the context)
U	a unitary operator
$\mathscr{U}$	time-evolution operator (Section 13.1)
$\Gamma(R)$	matrix representative of the symmetry operator R; sometimes just $\mathbb{R}$, for brevity
$\Gamma(R)_{pq}$	pqth element of the matrix representative of the symmetry operator R
Γ	matrix representation
$\Gamma_1 \approx \Gamma_2$	the matrix representations Γ_1 and Γ_2 are equivalent, that is related by a similarity transformation (Section 4.2)
$\Gamma = \sum_i c^i \Gamma_i$	the representation Γ is a direct sum of irreducible representations Γ_i, and each Γ_i occurs c^i times in the direct sum Γ; when specific representations (for example T_{1u}) are involved, this would be written $c(\mathrm{T}_{1u})$
$\Gamma \supset \Gamma_i$	the reducible representation Γ includes Γ_i
$\Gamma_i = \sum_j c_{i,j}\ \Gamma_j$	the representation Γ_i is a direct sum of irreducible representations Γ_j and each Γ_j occurs $c_{i,j}$ times in the direct sum Γ_i
$\Gamma_{ij} = \sum_k c_{ij,k}\ \Gamma_k$	Clebsch–Gordan decomposition of the direct product $\Gamma_{ij} = \Gamma_i \boxtimes \Gamma_j$; $c_{ij,\ k}$ are the Clebsch–Gordan coefficients
$\sigma_{\mathbf{n}}$	reflection in the plane normal to $\mathbf{n}$
$\sigma_1\ \sigma_2\ \sigma_3$	the Pauli matrices (Section 11.6)
Θ	time-reversal operator

Bases

$\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3 \vert$	basis consisting of the three unit vectors $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ initially coincident with $\{\mathbf{x}\ \mathbf{y}\ \mathbf{z}\}$ but embedded in a unit sphere in configuration space so that $R\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3 \vert = \langle \mathbf{e}_1{}'\ \mathbf{e}_2{}'\ \mathbf{e}_3{}' \vert = \langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3 \vert\ \Gamma(R)$. The 3×3 matrix $\Gamma(R)$ is the matrix representative of the symmetry operator R. Note that $\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3 \vert$ is often abbreviated to $\langle \mathbf{e} \vert$. If $\mathbf{r} \in \Re^3$, $R\ \mathbf{r} = R\langle \mathbf{e} \vert r\rangle = \langle \mathbf{e}' \vert r\rangle = \langle \mathbf{e} \vert \Gamma(R) \vert r\rangle = \langle \mathbf{e} \vert r'\rangle$, which shows that $\langle \mathbf{e} \vert$ and $\vert r\rangle$ are *dual bases*, that is they are transformed by the same matrix $\Gamma(R)$
$\langle R_x\ R_y\ R_z \vert$	basis comprising the three *infinitesimal* rotations R_x, R_y, R_z about OX, OY, OZ respectively (Section 4.6)
$\langle u^j_{-j} \ldots u^j_j \vert$	basis consisting of the $2j + 1$ functions, u^j_m, $-j \leq m \leq j$, which are eigenfunctions of the z component of the angular momentum operator $\hat{J}_z$, and of $\hat{J}^2$, with the Condon and Shortley choice of phase. The angular momentum quantum numbers j and m may be either an integer or a half-integer. For integral j the u^j_m are the spherical harmonics $Y^m_l(\theta\ \varphi)$; $y^m_l(\theta\ \varphi)$ are the spherical harmonics written without normalization factors, for brevity
$\langle u^j_m \vert$	an abbreviation for $\langle u^j_{-j} \ldots u^j_j \vert$, also abbreviated to $\langle m \vert$
$\langle u\ v \vert$	spinor basis, an abbreviation for $\langle u^{1/2}_{1/2} \vert = \langle \vert 1/2\ 1/2\rangle\ \ \vert 1/2\ -1/2\rangle \vert$, or $\langle 1/2\ \ -1/2 \vert$ in the $\langle m \vert$ notation
$\langle u'\ v' \vert$	transform of $\langle u\ v \vert$ in C^2, equal to $\langle u\ v \vert \mathbb{A}$
$\vert\ u\ v\rangle$	dual of $\langle u\ v \vert$, such that $\vert u'\ v'\rangle = \mathbb{A} \vert\ u\ v\rangle$
$\vert\ U_{-1}\ U_0\ U_1\rangle$	matrix representation of the spherical vector $\mathbf{U} \in C^3$ which is the dual of the basis $\langle y^{-1}_1\ y^0_1\ y^1_1 \vert$
N	normalization factor

Crystals

$\mathbf{a}_n = \langle \mathbf{a} \vert\ n\rangle$	lattice translation vector; $\mathbf{a}_n = \langle \mathbf{a}_1\ \mathbf{a}_2\ \mathbf{a}_3 \vert\ n_1\ n_2\ n_3\rangle$ (Section 16.1) (n is often used as an abbreviation for the $\mathbf{a}_n$)
$\mathbf{b}_m = \langle \mathbf{b} \vert\ m\rangle$	reciprocal lattice vector; $\mathbf{b}_m = \langle \mathbf{b}_1\ \mathbf{b}_2\ \mathbf{b}_3 \vert\ m_1\ m_2\ m_3\rangle = \langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3 \vert\ m_x\ m_y\ m_z\rangle$ (Section 16.3); m is often used as an abbreviation for the components of $\mathbf{b}_m$

Abbreviations

1-D	one-dimensional (etc.)
AO	atomic orbital
BB	bilateral binary
bcc	body-centered cubic
CC	complex conjugate
CF	crystal field

CG	Clebsch–Gordan
CR	commutation relation
CS	Condon and Shortley
CT	charge transfer
DP	direct product
fcc	face-centered cubic
FE	free electron
FT	fundamental theorem
hcp	hexagonal close-packed
HSP	Hermitian scalar product
IR	irreducible representation
ITC	*International Tables for Crystallography* (Hahn (1983))
L, R	left and right, respectively, as in L and R cosets
LA	longitudinal acoustic
LCAO	linear combination of atomic orbitals
LI	linearly independent
LO	longitudinal optic
LS	left- side (of an equation)
LVS	linear vector space
MO	molecular orbital
MR	matrix representative
N	north, as in N pole
ORR	Onsager reciprocal relation
OT	orthogonality theorem
PBC	periodic boundary conditions
PF	projective factor
PR	projective representation
RS	right side (of an equation)
RS	Russell–Saunders, as in *RS* coupling or *RS* states
sc	simple cubic
SP	scalar product
TA	transverse acoustic
TO	transverse optic
ZOA	zero overlap approximation

Cross-references

The author (date) system is used to identify a book or article in the list of references, which precedes the index.

Equations in a different section to that in which they appear are referred to by eq. $(n_1 \cdot n_2 \cdot n_3)$, where n_1 is the chapter number, n_2 is the section number, and n_3 is the equation number within that section. Equations occurring within the same section are referred to simply by (n_3). Equations are numbered on the right, as usual, and, when appropriate, a number (or numbers) on the left, in parentheses, indicates that these equations are used in the derivation of that equation so numbered. This convention means that such phrases as “it follows from” or “substituting eq. (n_4) in eq. (n_5)” can largely be dispensed with.

Examples and Exercises are referenced, for example, as Exercise $n_1 \cdot n_2$-n_3, even within the same section. Figures and Tables are numbered $n_1 \cdot n_3$ throughout each chapter. When a Table or Figure is referenced on the left side of an equation, their titles are abbreviated to T or F respectively, as in F16.1, for example.

Problems appear at the end of each chapter, and a particular problem may be referred to as Problem $n_1 \cdot n_3$, where n_1 is the number of the chapter in which Problem n_3 is to be found.

1 The elementary properties of groups

1.1 Definitions

All crystals and most molecules possess symmetry, which can be exploited to simplify the discussion of their physical properties. Changes from one configuration to an indistinguishable configuration are brought about by sets of symmetry operators, which form particular mathematical structures called *groups*. We thus commence our study of group theory with some definitions and properties of groups of abstract elements. All such definitions and properties then automatically apply to all sets that possess the properties of a group, including symmetry groups.

Binary composition in a set of abstract elements $\{g_i\}$, whatever its nature, is always written as a multiplication and is usually referred to as "multiplication" whatever it actually may be. For example, if g_i and g_j are operators then the product $g_i\ g_j$ means "carry out the operation implied by g_j and then that implied by g_i." If g_i and g_j are both n-dimensional square matrices then $g_i\ g_j$ is the matrix product of the two matrices g_i and g_j evaluated using the usual row × column law of matrix multiplication. (The properties of matrices that are made use of in this book are reviewed in Appendix A1.) Binary composition is *unique* but is not necessarily commutative: $g_i\ g_j$ may or may not be equal to $g_j\ g_i$. In order for a set of abstract elements $\{g_i\}$ to be a G, the law of binary composition must be defined and the set must possess the following four properties.

(i) *Closure*. For all g_i, with $g_j \in \{g_j\}$,

$$g_i\ g_j = g_k \in \{g_i\}, \quad g_k \text{ a unique element of } \{g_i\}. \tag{1}$$

Because g_k is a unique element of $\{g_i\}$, if each element of $\{g_i\}$ is multiplied from the left, or from the right, by a particular element g_j of $\{g_i\}$ then the set $\{g_i\}$ is regenerated with the elements (in general) re-ordered. This result is called the *rearrangement theorem*

$$g_j\ \{g_i\} = \{g_i\} = \{g_i\}\ g_j. \tag{2}$$

Note that $\{g_i\}$ means a set of elements of which g_i is a typical member, but in no particular order. The easiest way of keeping a record of the binary products of the elements of a group is to set up a *multiplication table* in which the entry at the intersection of the g_ith row and g_jth column is the binary product $g_i\ g_i = g_k$, as in Table 1.1. It follows from the rearrangement theorem that each row and each column of the multiplication table contains each element of G once and once only.

Table 1.1. *Multiplication table for the group* $\mathrm{G} = \{g_i\}$ *in which the product* $g_i \; g_j$ *happens to be* g_k.

G	g_i	g_j	g_k	...
g_i	g_i^2	g_k	$g_i \; g_k$	
g_j	$g_j \; g_i$	g_j^2	$g_j \; g_k$	
g_k	$g_k \; g_i$	$g_k \; g_j$	g_k^2	
⋮				

(ii) Multiplication is *associative*. For all $g_i, \; g_j, \; g_k \in \{g_i\}$,

$$g_i(g_j \; g_k) = (g_i \; g_j)g_k. \tag{3}$$

(iii) The set $\{g_i\}$ contains the *identity* element E, with the property

$$E \; g_j = g_j \; E = g_j, \; \forall \; g_j \in \{g_i\}. \tag{4}$$

(iv) Each element g_i of $\{g_i\}$ has an *inverse* $g_i^{-1} \in \{g\}_i$ such that

$$g_i^{-1} \; g_i = g_i \; g_i^{-1} = E, \; g_i^{-1} \in \{g_i\}, \; \forall \; g_i \in \{g_i\}. \tag{5}$$

The number of elements g in G is called the *order* of the group. Thus

$$\mathrm{G} = \{g_i\}, \quad i = 1, 2, \ldots, g. \tag{6}$$

When this is necessary, the order of G will be displayed in parentheses G(g), as in G(4) to indicate a group of order 4.

Exercise 1.1-1 With binary composition defined to be addition: (a) Does the set of positive integers $\{p\}$ form a group? (b) Do the positive integers p, including zero (0) form a group? (c) Do the positive (p) and negative ($-p$) integers, including zero, form a group? [*Hint*: Consider the properties (i)–(iv) above that must be satisfied for $\{g_i\}$ to form a group.]

The multiplication of group elements is not necessarily commutative, but if

$$g_i \; g_j = g_j \; g_i, \; \forall \; g_i, g_j \in \mathrm{G} \tag{7}$$

then the group G is said to be *Abelian*. Two groups that have the same multiplication table are said to be *isomorphous*. As we shall see, a number of other important properties of a group follow from its multiplication table. Consequently these properties are the same for isomorphous groups; generally it will be necessary to identify corresponding elements in the two groups that are isomorphous, in order to make use of the isomorphous property. A group G is finite if the number g of its elements is a finite number. Otherwise the group G is infinite, if the number of elements is denumerable, or it is continuous. The group of Exercise 1.1-1(c) is infinite. For finite groups, property (iv) is automatically fulfilled as a consequence of the other three.

If the sequence $g_i,\ g_i^2,\ g_i^3,\ \ldots$ starts to repeat itself at $g_i^{c+1} = g_i$, because $g_i^c = E$, then the set $\{g_i\ \ g_i^2\ \ g_i^3\ \ \ldots\ \ g_i^c = E\}$, which is the period of g_i, is a group called a *cyclic group*, C. The order of the cyclic group C is c.

Exercise 1.1-2 (a) Show that cyclic groups are Abelian. (b) Show that for a finite cyclic group the existence of the inverse of each element is guaranteed. (c) Show that $\omega = \exp(-2\pi\mathrm{i}/n)$ generates a cyclic group of order n, when binary composition is defined to be the multiplication of complex numbers.

If every element of G can be expressed as a finite product of powers of the elements in a particular subset of G, then the elements of this subset are called the *group generators*. The choice of generators is not unique: generally, a minimal set is employed and the defining relations like $g_i = (g_j)^p\ (g_k)^q$, etc., where $\{g_j\ g_k\}$ are group generators, are stated. For example, cyclic groups are generated from just one element g_i.

Example 1.1-1 A permutation group is a group in which the elements are permutation operators. A permutation operator P rearranges a set of indistinguishable objects. For example, if

$$P\{a\ \ b\ \ c\ \ \ldots\} = \{b\ \ a\ \ c\ \ \ldots\} \tag{8}$$

then P is a particular permutation operator which interchanges the objects a and b. Since $\{a\ b\ \ldots\}$ is a set of indistinguishable objects (for example, electrons), the final configuration $\{b\ a\ c\ \ldots\}$ is indistinguishable from the initial configuration $\{a\ b\ c\ \ldots\}$ and P is a particular kind of symmetry operator. The best way to evaluate products of permutation operators is to write down the original configuration, thinking of the n indistinguishable objects as allocated to n boxes, each of which contains a single object only. Then write down in successive rows the results of the successive permutations, bearing in mind that a permutation other than the identity involves the replacement of the contents of two or more boxes. Thus, if P applied to the initial configuration means "interchange the contents of boxes i and j" (which initially contain the objects i and j, respectively) then P applied to some subsequent configuration means "interchange the contents of boxes i and j, whatever they currently happen to be." A number of examples are given in Table 1.2, and these should suffice to show how the multiplication table in Table 1.3 is derived. The reader should check some of the entries in the multiplication table (see Exercise 1.1-3).

The elements of the set $\{P_0\ P_1\ \ldots P_5\}$ are the permutation operators, and binary composition of two members of the set, say $P_3\ P_5$, means "carry out the permutation specified by P_5 and then that specified by P_3." For example, P_1 states "replace the contents of box 1 by that of box 3, the contents of box 2 by that of box 1, and the contents of box 3 by that of box 2." So when applying P_1 to the configuration $\{3\ 1\ 2\}$, which resulted from P_1 (in order to find the result of applying $P_1^2 = P_1\ P_1$ to the initial configuration) the contents of box 1 (currently 3) are replaced by those of box 3 (which happens currently to be 2 – see the line labeled P_1); the contents of box 2 are replaced by those of box 1 (that is, 3); and finally the contents of box 3 (currently 2) are replaced by those of box 2 (that is, 1). The resulting configuration $\{2\ 3\ 1\}$ is the same as that derived from the original configuration $\{1\ 2\ 3\}$ by P_2, and so

Table 1.2. *Definition of the six permutation operators of the permutation group* S(3) *and some examples of the evaluation of products of permutation operators.*

In each example, the initial configuration appears on the first line and the permutation operator and the result of the operation are on successive lines. In the last example, the equivalent single operator is given on the right.

The identity $P_0 = E$

	1	2	3	original configuration (which therefore labels the "boxes")
P_0	1	2	3	final configuration (in this case identical with the initial configuration)

The two cyclic permutations

	1	2	3		1	2	3
P_1	3	1	2	P_2	2	3	1

The three binary interchanges

	1	2	3		1	2	3		1	2	3
P_3	1	3	2	P_4	3	2	1	P_5	2	1	3

Binary products with P_1

	1	2	3	
P_1	3	1	2	P_1
$P_1\ P_1$	2	3	1	P_2
$P_2\ P_1$	1	2	3	P_0
$P_3\ P_1$	3	2	1	P_4
$P_4\ P_1$	2	1	3	P_5
$P_5\ P_1$	1	3	2	P_3

Table 1.3. *Multiplication table for the permutation group* S(3).

The box indicates the subgroup C(3).

S(3)	P_0	P_1	P_2	P_3	P_4	P_5
P_0	P_0	P_1	P_2	P_3	P_4	P_5
P_1	P_1	P_2	P_0	P_5	P_3	P_4
P_2	P_2	P_0	P_1	P_4	P_5	P_3
P_3	P_3	P_4	P_5	P_0	P_1	P_2
P_4	P_4	P_5	P_3	P_2	P_0	P_1
P_5	P_5	P_3	P_4	P_1	P_2	P_0

$$P_1\ P_1\{1\ 2\ 3\} = \{2\ 3\ 1\} = P_2\{1\ 2\ 3\} \tag{9}$$

so that $P_1\ P_1 = P_2$. Similarly, $P_2\ P_1 = P_0$, $P_3\ P_1 = P_4$, and so on. The equivalent single operators (products) are shown in the right-hand column in the example in the last part of Table 1.2. In this way, we build up the multiplication table of the group S(3), which is shown in Table 1.3. Notice that the rearrangement theorem (closure) is satisfied and that each element has an inverse. The set contains the identity P_0, and examples to demonstrate associativity are readily constructed (e.g. Exercise 1.1-4). Therefore this set of permutations is a group. The group of all permutations of N objects is called the symmetric group

S(N). Since the number of permutations of N objects is N!, the order of the symmetric group is N!, and so that of S(3) is 3! = 6.

Exercise 1.1-3 Evaluate the products in the column headed P_3 in Table 1.3.

Exercise 1.1-4 (a) Using the multiplication table for S(3) in Table 1.3 show that $(P_3\ \ P_1)P_2 = P_3(P_1\ \ P_2)$. This is an example of the group property of associativity. (b) Find the inverse of P_2 and also the inverse of P_5.

Answers to Exercises 1.1

Exercise 1.1-1 (a) The set $\{p\}$ does not form a group because it does not contain the identity E. (b) The set $\{p \quad 0\}$ contains the identity 0, $p + 0 = p$, but the inverses $\{-p\}$ of the elements $\{p\}, p + (-p) = 0$, are not members of the set $\{p \quad 0\}$. (c) The set of positive and negative integers, including zero, $\{p\ \overline{p}\ 0\}$, does form a group since it has the four group properties: it satisfies closure, and associativity, it contains the identity (0), and each element p has an inverse $\overline{p}$ or $-p$.

Exercise 1.1-2 (a) $g_i^p\, g_i^q = g_i^{p+q} = g_i^{q+p} = g_i^q\, g_i^p$. (b) *If* $p < c$, $g_i^p\, g_i^{c-p} = g_i^c = E$. Therefore, the inverse of g_i^p is g_i^{c-p}. (c) $\omega^n = \exp(-2\pi \mathrm{i}) = 1 = E$; therefore $\{\omega\ \omega^2\ \ldots\ \omega^n = E\}$ is a cyclic group of order n.

Exercise 1.1-3

P_0	1	2	3	
P_3	1	3	2	P_3
$P_1\ P_3$	2	1	3	P_5
$P_2\ P_3$	3	2	1	P_4
$P_3\ P_3$	1	2	3	P_0
$P_4\ P_3$	2	3	1	P_2
$P_5\ P_3$	3	1	2	P_1

Exercise 1.1-4 (a) From the multiplication table, $(P_3\ \ P_1)\ P_2 = P_4\ \ P_2 = P_3$ and $P_3\ (P_1\ \ P_2) = P_3\ P_0 = P_3$. (b) Again from the multiplication table, $P_2\ P_1 = P_0 = E$ and so $P_2^{-1} = P_1$; $P_5\ \ P_5 = P_0$, $P_5^{-1} = P_5$.

1.2 Conjugate elements and classes

If g_i, g_j, $g_k \in$ G and

$$g_i\ g_j\ g_i^{-1} = g_k \tag{1}$$

then g_k is the *transform* of g_j, and g_j and g_k are *conjugate* elements. A complete set of the elements conjugate to g_i form a *class*, $\mathscr{C}_i$. The number of elements in a class is called the *order* of the class; the order of $\mathscr{C}_i$ will be denoted by c_i.

Exercise 1.2-1 Show that E is always in a class by itself.

Example 1.2-1 Determine the classes of S(3). Note that $P_0 = E$ is in a class by itself; the class of E is always named $\mathscr{C}_1$. Using the multiplication table for S(3), we find

$$\begin{aligned} P_0\,P_1\,P_0^{-1} &= P_1\,P_0 = P_1, \\ P_1\,P_1\,P_1^{-1} &= P_2\,P_2 = P_1, \\ P_2\,P_1\,P_2^{-1} &= P_0\,P_1 = P_1, \\ P_3\,P_1\,P_3^{-1} &= P_4\,P_3 = P_2, \\ P_4\,P_1\,P_4^{-1} &= P_5\,P_4 = P_2, \\ P_5\,P_1\,P_5^{-1} &= P_3\,P_5 = P_2. \end{aligned}$$

Hence $\{P_1\ P_2\}$ form a class $\mathscr{C}_2$. The determination of $\mathscr{C}_3$ is left as an exercise.

Exercise 1.2-2 Show that there is a third class of S(3), $\mathscr{C}_3 = \{P_3\ P_4\ P_5\}$.

Answers to Exercises 1.2

Exercise 1.2-1 For any group G with $g_i \in$ G,

$$g_i\,E\,g_i^{-1} = g_i\,g_i^{-1} = E.$$

Since E is transformed into itself by every element of G, E is in a class by itself.

Exercise 1.2-2 The transforms of P_3 are

$$\begin{aligned} P_0P_3P_0^{-1} &= P_3P_0 = P_3, \\ P_1P_3P_1^{-1} &= P_5P_2 = P_4, \\ P_2P_3P_2^{-1} &= P_4P_1 = P_5, \\ P_3P_3P_3^{-1} &= P_0P_3 = P_3, \\ P_4P_3P_4^{-1} &= P_2P_4 = P_5, \\ P_5P_3P_5^{-1} &= P_1P_5 = P_4. \end{aligned}$$

Therefore $\{P_3\ P_4\ P_5\}$ form a class, $\mathscr{C}_3$, of S(3).

1.3 Subgroups and cosets

A subset H of G, H $\subset$ G, that is itself a group with the same law of binary composition, is a *subgroup* of G. Any subset of G that satisfies closure will be a subgroup of G, since the other group properties are then automatically fulfilled. The region of the multiplication table of S(3) in Table 1.3 in a box shows that the subset $\{P_0\ P_1\ P_2\}$ is closed, so that this set is a subgroup of S(3). Moreover, since $P_1^2 = P_2,\ P_1^3 = P_1\ P_2 = P_0 = E$, it is a cyclic subgroup of order 3, C(3).

Given a group G with subgroup H ⊂ G, then g_r H, where $g_r \in$ G but $g_r \notin$ H unless g_r is $g_1 = E$, is called a *left coset* of H. Similarly, H g_r is a *right coset* of H. The $\{g_r\}$, $g_r \in$ G but $g_r \notin$ H, except for $g_1 = E$, are called *coset representatives*. It follows from the uniqueness of the product of two group elements (eq. (1.1.2)) that the elements of g_r H are distinct from those of g_s H when $s \neq r$, and therefore that

$$\mathrm{G} = \sum_{r=1}^{t} g_r\ \mathrm{H}, \quad g_r \in \mathrm{G},\ g_r \notin \mathrm{H}\ (\text{except for } g_1 = E),\ t = g/h, \tag{1}$$

where t is the *index* of H in G. Similarly, G may be written as the sum of t distinct right cosets,

$$\mathrm{G} = \sum_{r=1}^{t} \mathrm{H}\ g_r, \quad g_r \in \mathrm{G},\ g_r \notin \mathrm{H}\ (\text{except for } g_1 = E),\ t = g/h. \tag{2}$$

If H $g_r = g_r$ H, so that right and left cosets are equal for all r, then

$$g_r\ \mathrm{H}\ g_r^{-1} = \mathrm{H}\ g_r\ g_r^{-1} = \mathrm{H} \tag{3}$$

and H is transformed into itself by any element $g_r \in$ G that is not in H. But for any $h_j \in$ H

$$h_j\ \mathrm{H}\ h_j^{-1} = h_j\ \mathrm{H} = \mathrm{H} \qquad (\text{closure}). \tag{4}$$

Therefore, H is transformed into itself by all the elements of G; H is then said to be an *invariant* (*or normal*) *subgroup* of G.

Exercise 1.3-1 Prove that any subgroup of index 2 is an invariant subgroup.

Example 1.3-1 Find all the subgroups of S(3); what are their indices? Show explicitly which, if any, of the subgroups of S(3) are invariant.

The subgroups of S(3) are

$$\{P_0\ P_1\ P_2\} = \mathrm{C}(3),\ \{P_0\ P_3\} = \mathrm{H}_1,\ \{P_0\ P_4\} = \mathrm{H}_2,\ \{P_0\ P_5\} = \mathrm{H}_3.$$

Inspection of the multiplication table (Table 1.3) shows that all these subsets of S(3) are closed. Since $g = 6$, their indices t are 2, 3, 3, and 3, respectively. C(3) is a subgroup of S(3) of index 2, and so we know it to be invariant. Explicitly, a right coset expansion for S(3) is

$$\{P_0\ P_1\ P_2\} + \{P_0\ P_1\ P_2\}P_4 = \{P_0\ P_1\ P_2\ P_3\ P_4\ P_5\} = \mathrm{S}(3). \tag{5}$$

The corresponding left coset expansion with the same coset representative is

$$\{P_0\ P_1\ P_2\} + P_4\{P_0\ P_1\ P_2\} = \{P_0\ P_1\ P_2\ P_4\ P_5\ P_3\} = \mathrm{S}(3). \tag{6}$$

Note that the elements of G do not have to appear in exactly the same order in the left and right coset expansions. This will only be so if the coset representatives commute with every element of H. All that is necessary is that the two lists of elements evaluated from the coset expansions both contain each element of G once only. It should be clear from eqs. (5) and (6) that H $g_r = g_r$ H, where H = $\{P_0\ P_1\ P_2\}$ and g_r is P_4. An alternative way of testing for invariance is to evaluate the transforms of H. For example,

$$P_4\{C(3)\}P_4^{-1} = P_4\{P_0\ P_1\ P_2\}P_4^{-1} = \{P_4\ P_5\ P_3\}P_4 = \{P_0\ P_2\ P_1\} = C(3). \quad (7)$$

Similarly for P_3 and P_5, showing therefore that C(3) *is* an invariant subgroup of S(3).

Exercise 1.3-2 Show that C(3) is transformed into itself by P_3 and by P_5.

$H_1 = \{P_0\ P_3\}$ is not an invariant subgroup of S(3). Although

$$\{P_0\ P_3\} + \{P_0\ P_3\}P_1 + \{P_0\ P_3\}P_2 = \{P_0\ P_3\ P_1\ P_4\ P_2\ P_5\} = S(3), \quad (8)$$

showing that H_1 is a subgroup of S(3) of index 3,

$$\{P_0\ P_3\}P_1 = \{P_1\ P_4\},\ \text{but}\ P_1\{P_0\ P_3\} = \{P_1\ P_5\}, \quad (9)$$

so that right and left cosets of the representative P_1 are not equal. Similarly,

$$\{P_0\ P_3\}P_2 = \{P_2\ P_5\},\ \text{but}\ P_2\{P_0\ P_3\} = \{P_2\ P_4\}. \quad (10)$$

Consequently, H_1 is not an invariant subgroup. For H to be an invariant subgroup of G, right and left cosets must be equal for each coset representative in the expansion of G.

Exercise 1.3-3 Show that H_2 is not an invariant subgroup of S(3).

Answers to Exercises 1.3

Exercise 1.3-1 If $t = 2$, $G = H + g_2\,H = H + H\,g_2$. Therefore, $H\,g_2 = g_2\,H$ and the right and left cosets are equal. Consequently, H is an invariant subgroup.

Exercise 1.3-2 $P_3\{P_0\,P_1\,P_2\}P_3^{-1} = \{P_3\,P_4\,P_5\}P_3 = \{P_0\,P_2\,P_1\}$ and $P_5\{P_0\,P_1\,P_2\}P_5^{-1} = \{P_5\,P_3\,P_4\}P_5 = \{P_0\,P_2\,P_1\}$, confirming that C(3) *is* an invariant subgroup of S(3).

Exercise 1.3-3 A coset expansion for H_2 is

$$\{P_0\ P_4\} + \{P_0\ P_4\}P_1 + \{P_0\ P_4\}P_2 = \{P_0\ P_4\ P_1\ P_5\ P_2\ P_3\} = S(3).$$

The right coset for P_1 is $\{P_0\,P_4\}P_1 = \{P_1\,P_5\}$, while the left coset for P_1 is $P_1\ \{P_0\,P_4\} = \{P_1\,P_3\}$, which is not equal to the right coset for the same coset representative, P_1. So H_2 is not an invariant subgroup of S(3).

1.4 The factor group

Suppose that H is an invariant subgroup of G of index t. Then the t cosets g_r H of H (including g_1 H = H) each *considered as one element*, form a group of order t called the *factor group*,

$$F = G/H = \sum_{r=1}^{t}(g_r\ H),\ g_r \in G,\ g_r \notin H\ (\text{except for } g_1 = E),\ t = g/h. \tag{1}$$

Each term in parentheses, g_r H, is *one* element of F. Because each element of F is a *set* of elements of G, binary composition of these sets needs to be defined. Binary composition of the elements of F is defined by

$$(g_p\ H)(g_q\ H) = (g_p\ g_q)\ H, \quad g_p, g_q \in \{g_r\}, \tag{2}$$

where the complete set $\{g_r\}$ contains $g_1 =$ E as well as the $t-1$ coset representatives that $\notin$ H. It follows from closure in G that $g_p\ g_q \in$ G. Because H is an invariant subgroup

$$g_r\ H = H\ g_r. \tag{3}$$

(2), (3) $$g_p\ H\ g_q\ H = g_p\ g_p\ H\ H = g_p\ g_q\ H. \tag{4}$$

This means that in F

(4) $$H\ H = H, \tag{5}$$

which is the necessary and sufficient condition for H to be the identity in F.

Exercise 1.4-1 Show that $g_1\ g_1 = g_1$ is both a necessary and sufficient condition for g_1 to be E, the identity element in G. [*Hint*: Recall that the identity element E is defined by

$$E\ g_i = g_i\ E = g_i,\ \forall\ g_i \in G.] \tag{1.1.5}$$

Thus, F contains the identity: that {F} is indeed a group requires the demon-stration of the validity of the other group properties. These follow from the definition of binary composition in F, eq. (2), and the invariance of H in G.

Closure: To demonstrate closure we need to show that $g_p\ g_q$ H $\in$ F for g_p, g_q, $g_r \in \{g_r\}$. Now $g_p\ g_q \in$ G and so

(1) $$g_p\ g_q \in \{g_r\ H\},\ r = 1, 2, \ldots, t, \tag{6}$$

(6) $$g_p\ g_q = g_r\ h_l,\ h_l \in H, \tag{7}$$

(2), (7) $$g_p\ H\ g_q\ H = g_p\ g_q\ H = g_r\ h_l\ H = g_r\ H \in F. \tag{8}$$

Associativity:

(2), (3), (4) $$(g_p\ H\ g_q\ H)g_r\ H = g_p\ g_q\ H\ g_r\ H = g_p\ g_q\ g_r\ H, \tag{9}$$

(2), (3), (4) $$g_p\ H(g_q\ H\ g_r\ H) = g_p\ H\ g_q\ g_r\ H = g_p\ g_q\ g_r\ H, \tag{10}$$

(9), (10) $$(g_p\ H\ g_q\ H)g_r\ H = g_p\ H(g_q\ H\ g_r\ H), \tag{11}$$

and so multiplication of the elements of {F} is associative.

Table 1.4. *Multiplication table of the factor group* $F = \{E' \; P'\}$.

F	E'	P'
E'	E'	P'
P'	P'	E'

Inverse:

$$(2) \qquad (g_r^{-1} \text{ H})(g_r \text{ H}) = g_r^{-1} \, g_r \text{ H} = \text{H}, \qquad (12)$$

so that the inverse of g_r H in F is g_r^{-1} H.

Example 1.4-1 The permutation group S(3) has the invariant subgroup $\text{H} = \{P_0 \; P_1 \; P_2\}$. Here $g = 6$, $h = 3$, $t = 2$, and

$$\text{G} = \text{H} + P_3 \text{ H}, \;\; \text{F} = \{\text{H} \; P_3 \text{ H}\} = \{E' \; P'\}, \qquad (13)$$

where the elements of F have primes to distinguish $\text{E}' = \text{H} \in \text{F}$ from $E \in \text{G}$.

$$(13), (2) \qquad P'P' = (P_3 \text{ H})(P_3 \text{ H}) = P_3 \, P_3 \text{ H} = P_0 \text{ H} = \text{H}. \qquad (14)$$

E' is the identity element in F, and so the multiplication table for the factor group of S(3), $\text{F} = \{E' \; P'\}$, is as given in Table 1.4.

Exercise 1.4-2 Using the definitions of E' and P' in eq. (13), verify explicitly that $E' \, P' = P'$, $P' \, E' = P'$. [*Hint*: Use eq. (2).]

Exercise 1.4-3 Show that, with binary composition as multiplication, the set $\{1 \;\; -1 \;\; \text{i} \;\; -\text{i}\}$, where $\text{i}^2 = -1$, form a group G. Find the factor group $\text{F} = \text{G}/\text{H}$ and write down its multiplication table. Is F isomorphous with a permutation group?

Answers to Exercises 1.4

Exercise 1.4-1

$$(1.1.5) \qquad E \, E \, g_i = E \, g_i \, E = E \, g_i, \;\; \forall \; g_i \in \text{G}, \qquad (15)$$

$$(15) \qquad E \, E = E, \qquad (16)$$

and so $E \, E = E$ is a *necessary* consequence of the definition of E in eq. (1.1.5). If $g_1 \, g_1 = g_1$, then multiplying each side from the left or from the right by g_1^{-1} gives $g_1 = E$, which demonstrates that $g_1 \; g_1 = g_1$ is a *sufficient* condition for g_1 to be E, the identity element in G.

Table 1.5. *Multiplication table of the group* G *of Exercise 1.4-3.*

G	1	–1	i	–i
1	1	–i	i	–i
–1	–1	1	–i	i
i	i	–i	–1	1
–i	–i	i	1	–1

Exercise 1.4-2

$$(13), (2) \qquad E'P' = (\mathrm{H})(P_3\ \mathrm{H}) = (E\ \ \mathrm{H})(P_3\ \mathrm{H}) = P_3\ \mathrm{H} = P',$$

$$(13), (2) \qquad P'E' = (P_3\ \mathrm{H})(\mathrm{H}) = (P_3\ \mathrm{H})(E\ \mathrm{H}) = P_3\ \mathrm{H} = P'.$$

Exercise 1.4-3 With binary composition as multiplication the set $\{1\ \ -1\ \ \mathrm{i}\ \ -\mathrm{i}\}$ is a group G because of the following.

(a) It contains the *identity* $E = 1$; $1\ g_i = g_i\ 1 = g_i$, $\forall\ g_i \in$ G.
(b) The set is *closed* (see Table 1.5).
(c) Since each row and each column of the multiplication table contains E once only, each $g_i \in$ G has an *inverse*.
(d) *Associativity* holds; for example,

$$(-1)[(\mathrm{i})(-\mathrm{i})] = (-1)[1] = -1, \quad [(-1)(\mathrm{i})](-\mathrm{i}) = [(-\mathrm{i})](-\mathrm{i}) = -1.$$

From the multiplication table, the set $\mathrm{H} = \{1\ \ -1\}$ is closed and therefore it is a subgroup of G. The transforms of H for $g_i \notin$ H are

$$\mathrm{i}\{1\ \ -1\}\mathrm{i}^{-1} = \{\mathrm{i}\ \ -\mathrm{i}\}(-\mathrm{i}) = \{1\ \ -1\} = \mathrm{H};$$
$$(-\mathrm{i})\{1\ \ -1\}(-\mathrm{i})^{-1} = \{-\mathrm{i}\ \mathrm{i}\}\mathrm{i} = \{1\ \ -1\} = \mathrm{H}.$$

Therefore H is an invariant subgroup of G. A coset expansion of G on H is G = H + iH, and so F = {H iH}. From binary composition in F (eq. (2)) (H) (iH) = iH, (iH) (H) = iH, (iH) (iH) = i i H = (–1) (H) = $\{-1\ \ 1\}$ = H. (Recall that H is the set of elements $\{1\ \ -1\}$, in no particular order.) The multiplication table of F is

F	H	iH
H	H	iH
iH	iH	H

The permutation group S(2) has just two elements $\{E\ P\}$

	1	2	
E	1	2	
	1	2	
P	2	1	
PP	1	2	E

The multiplication table of S(2)

S(2)	E	P
E	E	P
P	P	E

is the same as that of F, since both are of the form

G	E	g_2
E	E	g_2
g_2	g_2	E

F is therefore isomorphous with the permutation group S(2).

Remark Sections 1.6–1.8 are necessarily at a slightly higher level than that of the first five sections. They could be omitted at a first reading.

1.5 Minimal content of Sections 1.6, 1.7, and 1.8

1.5.1 *The direct product*

Suppose that $\mathrm{A} = \{a_i\}$, $\mathrm{B} = \{b_j\}$ are two groups of order a and b, respectively, with the same law of binary composition. If $\mathrm{A} \cap \mathrm{B} = \{E\}$ and $a_i\, b_j = b_j\, a_i, \forall\, a_i \in \mathrm{A}, \forall\, b_j \in \mathrm{B}$, then the outer *direct product* of A and B is a group G of order $g = a\, b$, written

$$\mathrm{G} = \mathrm{A} \otimes \mathrm{B}, \tag{1}$$

with elements $a_i b_j = b_j a_i$, $i = 1, \ldots, a$, $j = 1, \ldots, b$. A and B are subgroups of G, and therefore

(1.3.1)
$$\mathrm{G} = \sum_{j=1}^{b} \{\mathrm{A}\}\, b_j = \sum_{j=1}^{b} b_j\, \{\mathrm{A}\},\ b_1 = E. \tag{2}$$

Because a_i, b_j commute for all $i = 1, \ldots, a$, $j = 1, \ldots, b$, the right and left cosets are equal, and therefore A is an invariant subgroup of G. Similarly, B is an invariant subgroup

$$\begin{array}{llllll} \mathrm{A} & |\,a_1\ a_2\ a_3 & |\,b_1\ b_2 & |\,c_1\ c_2 \cdots & |\cdots \\ \mathrm{A}' & \quad a' & \quad b' & \quad c' & \cdots \end{array}$$

Figure 1.1. Diagrammatic representation of the mapping f : A = A′. Vertical bars have no significance other than to mark the fibers of a', b', c', . . . , in A.

of G. It is still possible to form a direct product of A, B even when A and B are not both invariant subgroups of G.

(i) If A is an invariant subgroup of G but B is not an invariant subgroup of G, then the direct product of A and B is called the *semidirect product*, written

$$\mathrm{G} = \mathrm{A} \wedge \mathrm{B}. \tag{3}$$

Note that in semidirect products the *invariant subgroup* is always the *first* group in the product. For example,

$$\mathrm{S}(3) = \mathrm{C}(3) \wedge \mathrm{H}_1 = \{P_0\ P_1\ P_2\}\{P_0\ P_3\} = \{P_0\ P_1\ P_2\ P_3\ P_4\ P_5\}. \tag{4}$$

(ii) If neither A nor B are invariant subgroups of G, then the direct product of A with B is called the weak direct product. However, the weak direct product is not used in this book, and the term "direct product" without further qualification is taken to mean the outer direct product. (The inner direct product is explained in Section 1.6.)

1.5.2 Mappings and homomorphisms

A *mapping f* of the set A to the set A′, that is

$$f : \mathrm{A} \rightarrow \mathrm{A}' \tag{5}$$

involves the statement of a rule by which $a_i \in a = \{a_1\ a_2\ a_3\ \ldots\}$ in A becomes a' in A′; a' is the *image* of each $a_i \in a = \{a_i\}$ for the mapping f, and this is denoted by $a' = f(a_i)$. An example of the mapping f : A → A′ is shown in Figure 1.1. In a mapping f, every element $a_i \in$ A must have a unique image $f(a_i) = a' \in$ A′. The images of several different a_i may coincide (Figure 1.1). However, not every element in A′ is necessarily an image of some set of elements in A, and in such cases A is said to be mapped *into* A′. The set of all the elements in A′ that actually are images of some sets of elements in A is called the *range* of the mapping. The set of elements $\{a'\} = \{f(a_i)\}$, $\forall\, a_i \in$ A, is the image of the set A, and this is denoted by

$$f(\mathrm{A}) \subset \mathrm{A}',\ \ \forall\ a \in \mathrm{A}. \tag{6}$$

If f(A) = A′, the set A is said to be mapped *on to* A′. The set $a = \{a_i\}$ may consist of a single element, a one-to-one mapping, or $\{a_i\}$ may contain several elements, in which case the relationship of A to A′ is many-to-one. The set of elements in A that are mapped to a' is called the *fiber* of a', and the number of elements in a fiber is termed the *order of the fiber*. Thus in the example of Figure 1.1 the order of the fiber $\{a_1\ a_2\ a_3\}$ of a' is 3, while that of the fiber of $b' = \{b_1\ b_2\}$ is 2. If A, A′ are groups G, G′, and if a mapping f preserves multiplication so that

$$f(a_i\ b_j) = a'\ b' = f(a_i)\, f(b_j),\ \ \forall\, f(a_i) = a',\ \ \forall\, f(b_j) = b', \tag{7}$$

then G, G′ are *homomorphous*. For example, a group G and its factor group F are homomorphous. In particular, if the fibers of a', b', ... each contain only *one* element, then G, G′ are *isomorphous*. In this case G and G′ are two different realizations of the same abstract group in which $\{g_i\}$ represents different objects, such as two different sets of symmetry operators, for example

Corollary

If multiplication is preserved in the mapping of G on to G′, eq. (7), then any properties of G, G′ that depend only on the multiplication of group elements will be the same in G, G′. Thus isomorphous groups have the same multiplication table and class structure.

Exercise 1.5-1 Show that in a group homomorphism the image of g_j^{-1} is the inverse of the image of g_j..

1.5.3 *More about subgroups and classes*

The *centralizer* Z(g_j|G) of an element $g_j \in$ G is the subset $\{z_i\}$ of all the elements of G that commute with a particular element g_i of G, so that $z_i\, g_j = g_j\, z_i$, $g_j \in$ G, $\forall\, z_i \in$ Z(g_j|G). Now Z = Z(g_j|G) is a subgroup of G (of order z), and so we may write a coset expansion of G on Z as

(1.4.1)
$$\mathrm{G} = \sum_{r=1}^{t} g_r\, \mathrm{Z},\ \ t = g/z,\ \ g_1 = E. \tag{8}$$

It is proved in Section 1.8 that the sum of the elements g_k ($\mathscr{C}_i$) that form the class $\mathscr{C}_i$ in G is given by

$$\Omega(\mathscr{C}_i) = \sum_k g_k\ (\mathscr{C}_i) = \sum_r g_r\ g_i\ g_r^{-1} \tag{9}$$

where $\Omega(\mathscr{C}_i)$ is called the *Dirac character* of the class $\mathscr{C}_i$. The distinct advantage of determining the members of $\mathscr{C}_i$ from eq. (9) instead of from the more usual procedure

$$\mathscr{C}_i = \{g_p\ g_i\ g_p^{-1}\}\quad (p = 1,\ 2,\ \ldots,\ g,\ \text{repetitions deleted}), \tag{10}$$

is that the former method requires the evaluation of only t instead of g transforms. An example of the procedure is provided in Exercise 1.8-3.

Exercise 1.5-2 Prove that Z = Z(g_j|G) is a subgroup of G.

Answers to Exercises 1.5

Exercise 1.5-1 Since $E\, g_j = g_j$, $f(E) f(g_j) = f(g_j)$, and therefore $f(E) = E'$ is the identity in G′. Also, $g_j^{-1} g_j = E$, the identity in G. Therefore, $f(g_j^{-1} g_j) = f(g_j^{-1})\, f(g_j) = f(E) = E'$, and so the inverse of $f(g_j)$, the image of g_j, is $f(g_j^{-1})$, the image of g_j^{-1}.

Exercise 1.5-2 Since Z is the subset of the elements of G that commute with g_j, Z contains the identity E. if $z_i, z_k \in$ Z, then $(z_i\ \ z_k)g_j = g_j(z_i\ \ z_k)$, and so $\{z_i\}$ is closed. Closure, together with the inclusion of the identity, guarantee that each element of Z has an inverse which is $\in$ Z. Note that $\{z_i\} \subset$ G, and so the set of elements $\{z_i\}$ satisfy the associative property. Therefore, Z is a subgroup of G.

1.6 Product groups

If A $= \{a_i\}$, B $= \{b_j\}$ are two groups of order a and b, respectively, then the *outer direct product* of A and B, written A $\otimes$ B, is a group G $= \{g_k\}$, with elements

$$g_k = (a_i,\ b_j). \tag{1}$$

The product of two such elements of the new group is to be interpreted as

$$(a_i,\ b_j)(a_l,\ b_m) = (a_i\ a_l,\ b_j\ b_m) = (a_p,\ b_q) \quad \text{(closure in A and B).} \tag{2}$$

The set $\{(a_i, b_j)\}$ therefore closes. The other necessary group properties are readily proved and so G *is* a group. "Direct product" (DP) without further qualification implies the outer direct product. Notice that binary composition is defined for each group (e.g. A and B) individually, but that, in general, a multiplication rule between elements of different groups does not necessarily exist unless it is specifically stated to do so. However, if the elements of A and B obey the same multiplication rule (as would be true, for example, if they were both groups of symmetry operators) then the product $a_i\ \ b_j$ *is* defined. Suppose we try to take $(a_i,\ b_j)$ as $a_i\ \ b_j$. This imposes some additional restrictions on the DP, namely that

$$a_l\ b_j = b_j\ a_l,\ \forall\ l,j \tag{3}$$

and

$$\mathrm{A} \cap \mathrm{B} = E. \tag{4}$$

For *if*

$$(a_i,\ b_j) = a_i,\ b_j \tag{5}$$

then

$$(a_i,\ b_j)\ (a_l,\ b_m) = (a_i\ \ a_l,\ b_j\ \ b_m) = (a_p,\ b_q) \tag{2}$$

and

$$g_k\ g_n = a_i\ b_j\ a_l\ b_m = a_i\ a_l\ b_j\ b_m = a_p\ b_q = g_s \tag{6}$$

which shows that a_l and b_j commute. The second equality in eq. (6) follows from applying eq. (5) to both sides of the first equality in eq. (2). Equation (6) demonstrates the closure of $\{$G$\}$, provided the result $a_p\ b_q$ is unique, which it must be because A and B are groups and the products $a_i\ a_l$ and $b_j\ b_m$ are therefore unique. But, suppose the intersection of A and B contains a_l ($\neq E$) which is therefore also $\in$ B. Then $a_l\ b_j\ b_m \in$ B, b_r, say, and the product $a_p\ b_q$ would also be $a_i\ b_r$, which is impossible because for eq. (6) to be a valid multiplication rule, the result must be unique. Therefore $a_l \notin$ B, $\forall\ l = 1, \ldots, a$, except when $a_l = E$. Similarly, $b_j \notin$ A, $\forall\ j = 1, 2, \ldots, b$, except when $b_j = E$. The intersection of A and B therefore contains the identity E only, which establishes eq. (4). So the multiplication rule $(a_i, b_j) = a_i\ b_j$ is only valid if the conditions in eqs. (3) and (4) also hold.

A and B are subgroups of G, and from eqs. (5) and (3) the right and left coset expansions of G are

(1.3.1)
$$\mathrm{G} = \sum_{j=1}^{b} \{\mathrm{A}\} b_j,\ b_1 = E, \tag{7}$$

$$\mathrm{G} = \sum_{j=1}^{b} b_j \{\mathrm{A}\},\ b_1 = E. \tag{8}$$

When eq. (5) holds, $a_i\ b_j = b_j\ a_i, \forall\ i = 1, 2, \ldots, a, j = 1, 2, \ldots, b$, the right and left cosets are equal

$$\{\mathrm{A}\}\ b_j = b_j\ \{\mathrm{A}\},\ \forall\ b_j \in \mathrm{B}, \tag{9}$$

and therefore A is an invariant subgroup of G.

Exercise 1.6-1 Why may we not find the outer DP of the subgroups C(3) and H_1 of S(3) using the interpretation $(a_i, b_j) = a_i\ b_j$?

Exercise 1.6-2 If A $\otimes$ B = G and all binary products $a_i\ b_j$ with $a_i \in$ A, $b_j \in$ B commute, show that B is an invariant subgroup of G.

Exercise 1.6-3 Show that if the products (a_i, a_j) in the DP set A $\otimes$ A are interpreted as (a_i, a_j), as in eq. (5), then A $\otimes$ A = $a\{$A$\}$.

To avoid redundancies introduced by the outer DP A $\otimes$ A of a group with itself (Exercise 1.6-3), the *inner direct product* A $\boxtimes$ A is defined by

$$\mathrm{A} \boxtimes \mathrm{A} = \{(a_i,\ a_i)\},\ i = 1,\ 2, \ldots, a. \tag{10}$$

The *semidirect product* and the *weak direct product* have been defined in Section 1.5.

Exercise 1.6-4 (a) Show that if we attempt to use the multiplication rule $(a_i, a_i) = a_i\ a_i$ then the inner DP set does not close. (b) Show that if the inner DP is defined under the multiplication rule, eq. (2), then the inner DP set, eq. (10), is closed, and that the group A $\boxtimes$ A $\subset$ A $\otimes$ A is isomorphous with A.

Answers to Exercises 1.6

Exercise 1.6-1 In the outer DP A $\otimes$ B, the product (a_i, b_j) of elements a_i and b_j may be equated to $a_i\ b_j$ only if A $\cap$ B is E and the elements a_i, b_j commute. In C(3) $\otimes$ $\mathrm{H}_1 = \{P_0\, P_1\, P_2\}$

$\{P_0 P_3\}$, $P_1 P_3 = P_4$, but $P_3 P_1 = P_5$; therefore not all pairs of elements a_i, b_j commute, and so we may not form the outer DP of C(3) and H_1 using the interpretation in eq. (5).

Exercise 1.6-2 In $G = A \otimes B$, if all binary products $a_i\, b_j$ commute then left and right cosets $a_i\{B\}$ and $\{B\}\, a_i$ are equal, for $\forall\, i = 1, 2, \ldots, a$, and so B is an invariant subgroup of G.

Exercise 1.6-3 $A \otimes A = \{(a_i, a_j)\}$; if $\{(a_i, a_j)\}$ is equated to $\{(a_i, a_j)\}$, then since $a_i\, a_j \in A$, and $i = 1, 2, \ldots, a$, $j = 1, 2, \ldots, a$, $A = \{a_i\}$ occurs a times in the outer DP, and so $A \otimes A = a\{A\}$.

Exercise 1.6-4 (a) The product of the ith and jth elements in the inner product $A \boxtimes A = \{(a_i, a_i)\}$, $i = 1, 2, \ldots, a$, is $(a_i, a_i)(a_j, a_j) = (a_i\, a_j, a_i\, a_j) = (a_k, a_k)$, and so the inner DP set $\{(a_i, a_i)\}$ is closed. But if we attempt to interpret (a_i, a_i) as $a_i\, a_i$, then $(a_i, a_i)(a_j, a_j) = a_i\, a_i\, a_j\, a_j$, which is not equal to $(a_i\, a_j, a_i\, a_j) = a_i\, a_j\, a_i\, a_j$, unless A is Abelian.

(b) The inner DP $A \boxtimes A = \{(a_i, a_i)\}$ is closed and is $\subset A \otimes A$, for it is a subset of $\{(a_i, a_j)\}$, which arises when $i = j$. Since the product of the ith and jth elements of A is $a_i\, a_j = a_k$, while that of $A \boxtimes A$ is $(a_i, a_i)(a_j, a_j) = (a_k, a_k)$, $A \boxtimes A$ is isomorphous with A.

1.7 Mappings, homomorphisms, and extensions

Remark If you have not yet done so, read the first part of Section 1.5.2, including eqs. (1.5.5)–(1.5.7), as this constitutes the first part of this section.

A subset $K \subset G$ that is the fiber of E' in G' is called the *kernel* of the homomorphism. If there is a homomorphism of G on to $G'(f(G) = G')$ of which K is the kernel, with $g = k\, g'$, so that all fibers of the elements of G (images in the homomorphism) have the same order, then G is called an *extension* of G' by K. An example of an extension is illustrated in Table 1.6 for the particular case of $k = 3$.

Exercise 1.7-1 (a) Show that K is an invariant subgroup of G. (b) What is the kernel of the homomorphism $f(S(3)) = F = S(3)/C(3)$. (c) If $G \to G'$ is a homomorphism, prove that $g = k\, g'$.

Table 1.6. *Example of a homomorphism* $f(G) = G'$.

G is an extension of G' by K, the kernel of the homomorphism (so that E' in G' is the image of each element in K). Similarly, g'_2 is the image of each one of g_{21}, g_{22}, g_{23}, and so on. In this example $k = 3$.

$K = \{g_{11}\, g_{12}\, g_{13}\}$
$G = \{g_{11}\, g_{12}\, g_{13};\ g_{21}\, g_{22}\, g_{23};\ \ldots\ g_{n1}\, g_{n2}\, g_{n3}\}$
$G' = \{g'_1 = E',\ g'_2,\ g'_3,\ \ldots, g'_n\}$

Answer to Exercise 1.7-1

(a) Because K is the kernel of the homomorphism G $\to$ G$'$, $f((k_i \ \ k_j)) = f(k_i)$ $f(k_j) = E' \, E' = E'$. Therefore, $k_i \, k_j \in$ K. The set K is therefore closed and so K is a subgroup of G. Consider the mapping of $g_j \, k_i \, g_j{}^{-1}$, $k_i \in$ K, $g_j \in$ G,

$$f(g_j \, k_i \, g_j^{-1}) = f(g_j) \, f(k_i) \, f(g_j^{-1}) = f(g_i) E' f(g_j^{-1}) = E', \tag{1}$$

where we have used eq. (1.5.7) and Exercise 1.5-1. Therefore,

(1)
$$g_j \, k_i \, g_j^{-1} \in \mathrm{K}, \tag{2}$$

which shows K $= \{k_i\}$ to be an invariant subgroup of G.

(b) The subgroup C(3) is the kernel of S(3) for the homomorphism of S(3) on to its factor group F because f(C(3)) $= E'$.

(c) No two fibers in G can have a common element; otherwise this common element would have two distinct images in G$'$, which is contrary to the requirements for a mapping. Therefore, there are as many disjoint fibers in G as there are elements in G$'$, namely g'. It remains to be shown that all fibers in G have the same order, which is equal to the order k of the kernel K. Firstly, the necessary and sufficient condition for two elements g_2, g_3 that are $\in$ G to belong to the same fiber of G is that they be related by

$$g_2 = g_3 \, k_i, \ \ k_i \in \mathrm{K}. \tag{3}$$

Sufficiency:

$$f(g_2) = f(g_3 \, k_i) = f(g_3) \, f(k_i) = f(g_3) E' = f(g_3). \tag{4}$$

Necessity: Suppose that $g_2 = g_3 \, g_j$; then $f\,(g_2) = f(g_3)$, $f(g_j)$. But if g_2, g_3 belong to the same fiber then $f(g_j)$ must be E' and so g_j can only be $\in$ K. Secondly, if g_n is a particular element of a fiber F_n, then the other elements of F_n can all be written in the form $g_n \, k_i$, where $k_i \in$ K,

$$F_n = \{g_n \, k_i\}, \ \ k_i \in \mathrm{K}. \tag{5}$$

All the distinct elements of F_n are enumerated by eq. (5) as $i = 1, 2, \dots, k$, the order of K. Therefore, the number of elements in each one of the g' fibers in G is k, whence the order of G is

$$g = k \, g', \tag{6}$$

which establishes the required result.

1.8 More about subgroups and classes

If G and H are two groups for which a multiplication rule exists, that is to say the result $g_i \, h_j$ is defined, then the conjugate of H by an element $g_i \in$ G is

$$g_i \, \mathrm{H} \, g_i^{-1} = \sum_j g_i \, h_j \, g_i^{-1}. \tag{1}$$

When the result is H itself, H is invariant under the element g_i,

$$g_i \; \mathrm{H} \; g_i^{-1} = \mathrm{H}. \tag{2}$$

(2) $$g_i \; \mathrm{H} = \mathrm{H} \; g_i, \tag{3}$$

which is an equivalent condition for the invariance of H under g_i. The set of elements $\{g_i\} \in \mathrm{G}$ that leave H invariant form a subgroup of G called the *normalizer* of H in G, written N(H|G). That N(H|G) does indeed form a subgroup of G follows from the fact that if $g_i, g_j \in \mathrm{N(H|G)}$

$$g_j \; \mathrm{H} \; g_j^{-1} = \mathrm{H}, \tag{4}$$

(2), (4) $$g_i \; g_j \; \mathrm{H} \; (g_i \; g_j)^{-1} = g_i \; \mathrm{H} \; g_i^{-1} = \mathrm{H}, \tag{5}$$

(5) $$g_i \; g_j \in \{g_i, g_j, \; \ldots\} = \mathrm{N(H|G)}, \tag{6}$$

implying closure of $\{g_i, g_j, \ldots\}$, a sufficient condition for $\{g_i, g_j, \ldots\}$ to be a subgroup of G. If the normalizer N(H|G) is G itself, so that H is invariant under all $g_i \in \mathrm{G}$, H is said to be *normal* or *invariant* under G. If H is a subgroup of G (not so far assumed) then H is an invariant subgroup of G if eqs. (2) and (3) hold.

If G, H are two groups for which a multiplication rule exists then the set of all the elements of G that commute with a particular element h_j of H form a subgroup of G called the *centralizer* of h_j in G, denoted by

$$\mathrm{Z}(h_j|\mathrm{G}) \subset \mathrm{G}. \tag{7}$$

H may be the same group as G, in which case h_j will be one element of G, say $g_j \in \mathrm{G}$. Similarly, the centralizer of H in G,

$$\mathrm{Z(H|G)} \subset \mathrm{G}, \tag{8}$$

is the set of all the elements of G that each commute with each element of H; H in eq. (8) may be a subgroup of G. If H is G itself then

$$\mathrm{Z(G|G)} \equiv \mathrm{Z(G)} \tag{9}$$

is the *center* of G, namely the set of all the elements of G that commute with *every* element of G. In general, this set is a subgroup of G, but if Z(G) = G, then G is an Abelian group.

Exercise 1.8-1 Prove that the centralizer $\mathrm{Z}(h_j|\mathrm{G})$ is a subgroup of G.

Exercise 1.8-2 (a) Find the center Z(C(3)) of C(3). (b) What is the centralizer Z(C(3)|S(3)) of C(3) in S(3)? (c) What is the centralizer $\mathrm{Z}(P_1|\mathrm{S}(3))$ of P_1 in S(3)?

A class was defined in Section 1.2 as a complete set of conjugate elements. The sum of the members $g_j(\mathscr{C}_i), j = 1, 2, \ldots, c_i$ of the class $\mathscr{C}_i$ that contains the group element g_i is

$$\Omega(\mathscr{C}_i) = \sum_j g_j(\mathscr{C}_i), \tag{10}$$

$$\mathscr{C}_i = \{g_k\, g_i\, g_k^{-1}\},\ \forall\ g_k \in \mathrm{G}, \tag{11}$$

with repetitions deleted. The sum of all the elements in a class, $\Omega(\mathscr{C}_i)$, is the *Dirac character* of the class $\mathscr{C}_i$, and

(10), (11) $$\Omega(\mathscr{C}_i) = \sum_k g_k\, g_i\, g_k^{-1}, \tag{12}$$

with repetitions deleted. It is rather a waste of effort to evaluate the transforms on the right side (RS) of eq. (12) for all $g_k \in \mathrm{G}$, since many redundancies will be found that will have to be eliminated under the "no repetitions" rule. For instance, see Example 1.2-1, where six transforms of P_1 yield a class that contains just two members, P_1 and P_2, each of which occurred three times. However, it is possible to generate the class $\mathscr{C}_i$ that contains g_i without redundancies, from the coset expansion of G that uses the centralizer of g_i as the subgroup in the expansion. Abbreviating $\mathrm{Z}(g_i|\mathrm{G})$ to Z_i, the coset expansion of G on Z_i is

$$\mathrm{G} = \sum_{r=1}^{t} g_r\ \mathrm{Z}_i,\ \ g_1 = E,\ \ t = g/z, \tag{13}$$

where z is the order of Z_i. From the definition of the coset expansion in eq. (13), the elements of $\{g_r\}$ with $r = 2, \ldots, t$, and Z are disjoint. (E is of course $\in \mathrm{Z}_i$.) We shall now prove that

$$\Omega(\mathscr{C}_i) = \sum_r g_r\, g_i\, g_r^{-1}, \tag{14}$$

where $\{g_r\}$ is the set defined by eq. (13), namely the t coset representatives.

Proof The coset expansion eq. (13) shows that $\mathrm{G} = \{g_k\}$ is the DP set of $\{z_p\}$ and $\{g_r\}$, which means that G may be generated by multiplying each of the z members of $\{z_p\}$ in turn by each of the t members of $\{g_r\}$. Therefore, g_k in eq. (12) may be written as

$$g_k = z_p\, g_r,\ \ g_k \in \mathrm{G},\ \ z_p \in \mathrm{Z}_i, \tag{15}$$

with $\{g_r\}$ defined by eq. (13). In eq. (15), p, which enumerates the z elements of Z_i, runs from 1 to z; r, which enumerates the coset representatives (including $g_1 = E$), runs from 1 to t; and k enumerates all the g elements of the group G as k runs from 1 to g.

(12), (15) $$\sum_{r,\,p} g_r\, z_p\, g_i\, (g_r\, z_p)^{-1} = \sum_{r,\,p} g_r\, z_p\, g_i\, z_p^{-1}\, g_r^{-1} = \sum_{r,\,p} g_r\, g_i\, g_r^{-1} = z \sum_r g_r\, g_i\, g_r^{-1}. \tag{16}$$

The second equality in eq. (16) follows because $z_p \in \mathrm{Z}_i = \mathrm{Z}(g_i|\mathrm{G})$, which, from the definition of the centralizer, all commute with g_i. The third equality follows because the double sum consists of the same t terms repeated z times as p runs from 1 to z. It follows from the uniqueness of the binary composition of group elements that the sum over r in eq. (16) contains no repetitions. Therefore the sum over r on the RS of (16) is $\Omega(\mathscr{C}_i)$, which establishes eq. (14). Since eq. (14) gives the elements of $\mathscr{C}_i$ without repetitions, the order c_i of this class is

$$c_i \equiv t = g/z. \tag{17}$$

Equation (17) shows that the order of a class $\mathscr{C}_i$ is a divisor of the order of the group (Lagrange's theorem). It also yields the value of c_i once we determine z from $\text{Z}_i \equiv \text{Z}(g_i|\text{G})$. The t elements g_r needed to find the Dirac character $\Omega(\mathscr{C}_i)$ of the class $\mathscr{C}_i$, and thus the members of $\mathscr{C}_i$, are the coset representatives of the centralizer $\text{Z}_i \equiv \text{Z}(g_i|\text{G})$.

Exercise 1.8-3 Find the class of P_1 in S(3) by using the coset expansion for the centralizer $\text{Z}(P_1|\text{S}(3))$ and eq. (14).

Answers to Exercises 1.8

Exercise 1.8-1 The centralizer $\text{Z}(h_j|\text{G})$ is the set $\{g_i\}$ of all the elements of G that commute with h_j. Let $g_k \in \{g_i\}$; then g_i, g_k each commute with h_j and

$$(g_i\, g_k)h_j = g_i\, h_j\, g_k = h_j(g_i\, g_k) \tag{18}$$

so that if g_i, $g_k \in \{g_i\}$ that commutes with h_j, then so also is $g_i\ g_k$. Equation (18) demonstrates that $\{g_i\} = \text{Z}(h_j|\text{G})$ is closed, and that therefore it is a subgroup of G. The above argument holds for any $h_j \in \text{H}$, so that Z(H|G) is a subgroup of G. It also holds if h_j is $g_j \in \text{G}$, and for any $\{g_j\}$ which is a subgroup of G, and for $\{g_j\} = \text{G}$ itself. Therefore $\text{Z}(g_j|\text{G})$, Z(H|G), where $\text{H} \subset \text{G}$, and Z(G|G) are all subgroups of G, g_j being but a particular case of h_j.

Exercise 1.8-2 (a) Z(C(3)) is the set of elements of C(3) that commute with every element of C(3). From Table 1.3 we see that each element of C(3) commutes with every other element (the mutiplication table of C(3) is symmetrical about its principal diagonal from upper left to lower right) so that Z(C(3)) = C(3), and consequently C(3) is an Abelian group.

(b) The centralizer of C(3) in S(3) is the set of elements of S(3) that commute with each element of C(3). From Table 1.3 we see that none of P_3, P_4, P_5 commute with all of P_0, P_1, P_2; therefore Z(C(3)|S(3)) = C(3). Notice that here H happens to be a subgroup of G, but this is not a necessary feature of the definition of the centralizer. H needs to be a group for which binary composition with the elements of G is defined. In S(3), and therefore C(3), the product $P_i\ P_j$ means carrying out successively the permutations described by P_j first, and then P_i. Thus, Z(C(3)|S(3)) is necessarily a subgroup of S(3), in this case C(3) again (see Example 1.3-1).

(c) Again from Table 1.3, we see that only P_0, P_1, P_2 commute with P_1 so that $\text{Z}(P_1|\text{S}(3)) = \text{C}(3)$.

Exercise 1.8-3 $Z(P_1|S(3))$ is the set of elements of S(3) which commute with P_1. From Table 1.3 or Exercise 1.8-2(c), $Z(P_1|S(3)) = C(3)$. The coset expansion of S(3) on C(3) is

$$S(3) = P_0C(3) + P_3C(3) = \{P_0\ P_1\ P_2\} + \{P_3\ P_5\ P_4\}$$

so $z = 2$ and $\{g_r\} = \{P_0, P_3\}$. The Dirac character of the class of P_1 is therefore

$$\Omega(\mathscr{C}(P_1)) = \sum_r g_r\ P_1\ g_r^{-1} = P_0\ P_1\ P_0^{-1} + P_3\ P_1\ P_3^{-1} \tag{14}$$
$$= P_1 + P_3\ P_4 = P_1 + P_2.$$

Therefore, $\mathscr{C}(P_1) = \{P_1\ P_2\}$, and eq. (14) yields the class of P_1 without repetitions.

Problems

1.1 Show that the inverse of $g_i\ g_j$ is $g_j^{-1}\ g_i^{-1}$.
1.2 Prove that if each element of a group G commutes with every other element of G (so that G is an Abelian group) then each element of G is in a class by itself.
1.3 Find a generator for the group of Exercise 1.4-3.
1.4 Show that $\{P_1\ P_3\}$ is a generator for S(3).
1.5 Show that conjugation is *transitive*, that is if g_k is the transform of g_j and g_j is the transform of g_i, then g_k is the transform of g_i.
1.6 Show that conjugation is *reciprocal*, that is if g_k is the transform of g_j then g_j is the transform of g_k.
1.7 Prove that binary composition is conserved by conjugation.
1.8 There are only two groups of order 4 that are not isomorphous and so have different multiplication tables. Derive the multiplication tables of these two groups, G_4^1 and G_4^2. [*Hints*: First derive the multiplication table of the cyclic group of order 4. Call this group G_4^1. How many elements of G_4^1 are equal to their inverse? Now try to construct further groups in which a different number of elements are equal to their own inverse. Observe the rearrangement theorem.]
1.9 Arrange the elements of the two groups of order 4 into classes.
1.10 Identify the subgroups of the two groups of order 4.
1.11 Write down a coset expansion of S(3) on its subgroup $H_3 = \{P_0\ P_5\}$. Show that H_3 is not an invariant subgroup of S(3).
1.12 The *inverse class* of a class $\mathscr{C}_j = \{g_j\}$ is $\mathscr{C}_{\bar{j}} = \{g_j^{-1}\}$. Find the inverse class of the class $\{P_1\ P_2\}$ in S(3).
1.13 The classes of S(3) are $\mathscr{C}_1 = \{P_0\}$, $\mathscr{C}_2 = \{P_1\ P_2\}$, $\mathscr{C}_3 = \{P_3\ P_4\ P_5\}$. Prove that $\Omega_3\ \Omega_2 = 2\Omega_3$.
1.14 Prove that for S(3), $c_3 g^{-1} \sum_{g_i \in S(3)} g_i\ P_3\ g_i^{-1} = \Omega_3$.

2 Symmetry operators and point groups

2.1 Definitions

Symmetry operations leave a set of objects in *indistinguishable configurations* which are said to be *equivalent*. A set of symmetry operators always contains at least one element, the *identity* operator E. When operating with E the final configuration is not only indistinguishable from the initial one, it is *identical* to it. A *proper rotation*, or simply *rotation*, is effected by the operator $R(\phi\ \mathbf{n})$, which means "carry out a rotation of configuration space with respect to fixed axes through an angle ϕ about an axis along some unit vector $\mathbf{n}$." The *range* of ϕ is $-\pi < \phi \leq \pi$. Configuration space is the three-dimensional (3-D) space $\mathscr{R}^3$ of real vectors in which physical objects such as atoms, molecules, and crystals may be represented. Points in configuration space are described with respect to a system of three space-fixed right-handed orthonormal axes $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$, which are collinear with OX, OY, OZ (Figure 2.1(a)). (A right-handed system of axes means that a right-handed screw advancing from the origin along OX would rotate OY into OZ, or advancing along OY would rotate OZ into OX, or along OZ would rotate OX into OY.) The convention in which the axes $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ remain fixed, while the whole of configuration space is rotated with respect to fixed axes, is called the *active representation*. Thus, the rotation of configuration space effected by $R(\phi\ \mathbf{n})$ carries with it all vectors in configuration space, including a set of unit vectors $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ initially coincident with $\{\mathbf{x}\ \mathbf{y}\ \mathbf{z}\}$. Figures 2.1(b) and (c) show the effect on $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ of $R(\pi/3\ \mathbf{x})$, expressed by

$$R(\pi/3\ \mathbf{x})\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\} = \{\mathbf{e}_1{}'\ \mathbf{e}_2{}'\ \mathbf{e}_3{}'\} \tag{1}$$

In the *passive representation*, symmetry operators act on the *axes*, and so on $\{\mathbf{x}\ \mathbf{y}\ \mathbf{z}\}$, but leave configuration space fixed. Clearly, one should work entirely in one representation or the other: here we shall work solely in the active representation, and we shall not use the passive representation.

An alternative notation is to use the symbol $C_n^{\pm k}$ for a rotation operator. Here n does not mean $|\mathbf{n}|$, which is 1, but is an integer that denotes the *order* of the axis, so that $C_n^{\pm k}$ means "carry out a rotation through an angle $\phi = \pm 2\pi k/n$." Here n is an integer > 1, and $k = 1, 2, \ldots, (n-1)/2$ if n is an odd integer and, if n is even, $k = 1, 2, \ldots, n/2$, with $C_n^{-n/2}$ excluded by the range of ϕ; $k = 1$ is implicit. In this notation the axis of rotation has not been specified explicitly so that it must either be considered to be self-evident (for example, to be understood from what has gone before) or to be stated separately, as in "a C_4 rotation about the $\mathbf{z}$ axis," or included as a second subscript, as in $C_{4\mathbf{z}}$. (The

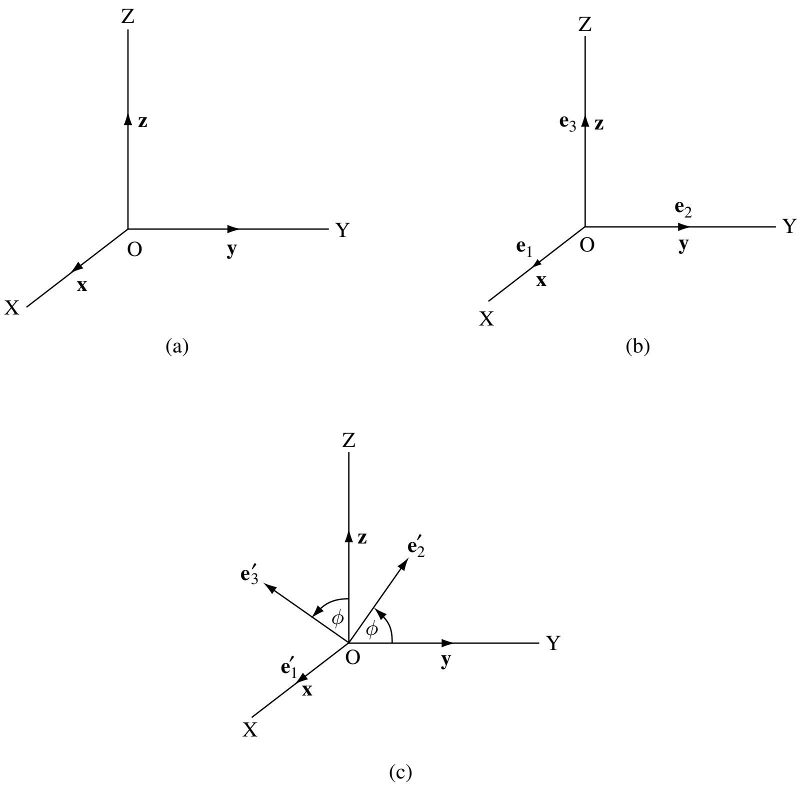


Figure 2.1. (a) Right-handed coordinate axes **x**, **y**, **z** in configuration space. A right-handed screw advancing along OX from O would rotate OY into OZ, and similarly (preserving cyclic order). (b) Initial configuration with $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ coincident with $\{\mathbf{x}\ \mathbf{y}\ \mathbf{z}\}$. (c) The result of a rotation of configuration space by $R(\pi/3\ \ \mathbf{x})$, expressed by eq. (1).

superscript + is often also implicit.) Thus $R(\pi/2\ \ \mathbf{z})$ and $C_{4\mathbf{z}}$ are equivalent notations, and we shall use either one as convenient. When the axis of rotation is not along **x** or **y** or **z**, it will be described by a unit vector **a**, **b**, . . . , where **a**, for example, is defined as a unit vector parallel to the vector with components $[n_1\ \ n_2\ \ n_3]$ along **x**, **y**, and **z**, or by a verbal description, or by means of a diagram. Thus $R(\pi\ \ \mathbf{a})$ or $C_{2\mathbf{a}}$ may be used as alternative notations for the operator which specifies a rotation about a two-fold axis along the unit vector **a** which bisects the angle between **x** and **y**, or which is along the vector with components [1 1 0] (Figure 2.2(a)). A rotation is said to be *positive* $(0 < \phi \leq \pi)$ if, on looking down the axis of rotation towards the origin, the rotation appears to be *anti-clockwise* (Figure 2.2(b)). Equivalently, a positive rotation is the direction of rotation of a right-handed screw as it advances along the axis of rotation away from the origin. Similarly, a rotation that appears to be in a clockwise direction, on looking down the axis of rotation towards O, is a negative rotation with $-\pi < \phi < 0$.

Exercise 2.1-1 (a) Check the sign of the rotation shown in Figure 2.2(c) using both of the criteria given above. (b) Show the effect of $R(-\pi/2\ \ \mathbf{z})$ on $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$.

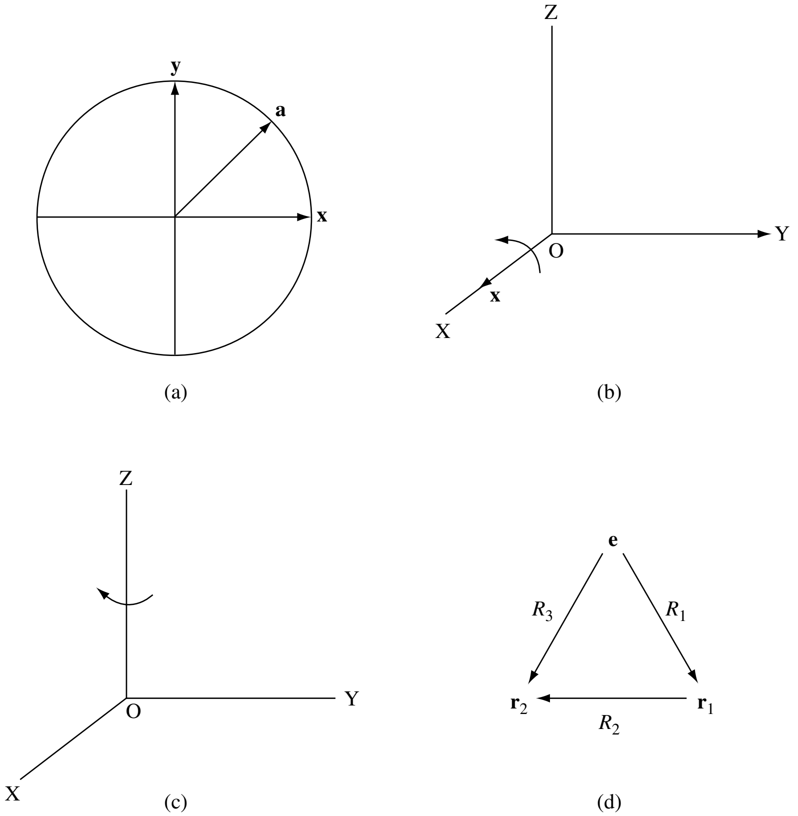


Figure 2.2. (a) The unit vector **a** bisects the angle between **x** and **y** and thus has components $2^{-1/2}$ [1 1 0]. (b) The curved arrow shows the direction of a positive rotation about **x**. (c) The curved arrow shows the direction of a negative rotation about OZ (Exercise 2.1-1(a)). (d) The product of two symmetry operators $R_2\ R_1$ is equivalent to a single operator R_3; **e**, $\mathbf{r}_1$, and $\mathbf{r}_2$ are three indistinguishable configurations of the system.

Products of symmetry operators mean "carry out the operations specified successively, beginning with the one on the right." Thus, R_2R_1 means "apply the operator R_1 *first*, and then R_2." Since the product of two symmetry operators applied to some initial configuration **e** results in an indistinguishable configuration ($\mathbf{r}_2$ in Figure 2.2(d)), it is equivalent to a single symmetry operator $R_3 = R_2\ R_1$. For example,

$$C_4\ C_4 = C_4^2 = C_2 = R(\pi\ \mathbf{n}); \tag{2}$$

$$\begin{aligned}(C_n)^{\pm k} &= C_n^{\pm k} = R(\phi\ \mathbf{n}),\\ \phi &= \pm 2\pi k/n\ (n > 1, k = 1, 2,\ \ldots\ \leq n/2,\ -\pi < \phi \leq \pi).\end{aligned} \tag{3}$$

A negative sign on k in eq. (3) corresponds to a negative rotation with $-\pi < \phi < 0$. Note that $k = 1$ is implicit, as in $C_{3\mathbf{z}}^{-} = R(-2\pi/3\ \mathbf{z})$, for example. A rotation C_2 or $R(\pi\ \mathbf{n})$ is called a *binary rotation*. Symmetry operators do not necessarily commute. Thus, $R_2\ R_1$ may, or may not, be equal to $R_1\ R_2$.

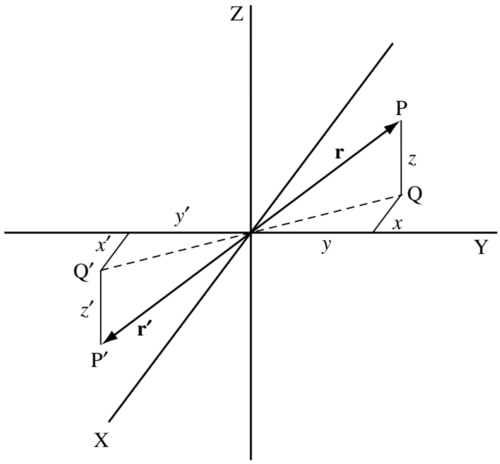


Figure 2.3. Effect of the inversion operator I on the polar vector $\mathbf{r}$. The points Q, Q′ lie in the XY plane.

Exercise 2.1-2 (a) Do successive rotations about the same axis commute? (b) Show that $R(-\phi\ \mathbf{n})$ is the inverse of $R(\phi\ \mathbf{n})$.

A *polar vector* $\mathbf{r}$ is the sum of its projections,

$$\mathbf{r} = \mathbf{e}_1 x + \mathbf{e}_2 y + \mathbf{e}_3 z. \tag{4}$$

Each projection on the RS of eq. (4) is the product of one of the set of basis vectors $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ and the corresponding component of $\mathbf{r}$ along that vector. The *inversion operator* I changes the vector $\mathbf{r}$ into $-\mathbf{r}$,

(4)

$$I\ \mathbf{r} = -\mathbf{r} = -\mathbf{e}_1 x - \mathbf{e}_2 y - \mathbf{e}_3 z \tag{5}$$

(see Figure 2.3). The basis vectors $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ are *pseudovectors*, that is they behave like ordinary polar vectors under rotation but are invariant under inversion. The components of $\mathbf{r}$, $\{x\ y\ z\}$, do change sign under inversion and are therefore *pseudoscalars* (invariant under rotation but change sign on inversion). This is made plain in Figure 2.3, which shows that under inversion $x' = -x,\ y' = -y,\ z' = -z$. A proper rotation $R(\phi\ \mathbf{n})$ followed by inversion is called an *improper rotation*, $IR(\phi\ \mathbf{n})$. Although R and IR are the only *necessary* symmetry operators that leave at least one point invariant, it is often convenient to use the *reflection* operator $\sigma_{\mathbf{m}}$ as well, where $\sigma_{\mathbf{m}}$ means "carry out the operation of reflection in a plane normal to $\mathbf{m}$." For example, the effect on $\mathbf{r}$ of reflection in the plane normal to $\mathbf{x}$ is to change x into $-x$,

$$\sigma_{\mathbf{x}}\{\mathbf{e}_1 x + \mathbf{e}_2 y + \mathbf{e}_3 z\} = \{\mathbf{e}_1 \bar{x} + \mathbf{e}_2 y + \mathbf{e}_3 z\}. \tag{6}$$

Sometimes, the plane itself rather than its normal $\mathbf{m}$ is specified. Thus $\sigma_{\mathbf{yz}}$ is equivalent to $\sigma_{\mathbf{x}}$ and means "reflect in the plane containing $\mathbf{y}$ and $\mathbf{z}$" (called the $\mathbf{yz}$ plane) which is normal to the unit vector $\mathbf{x}$. However, the notation $\sigma_{\mathbf{m}}$ will be seen to introduce simplifications in later work involving the inversion operator and is to be preferred.

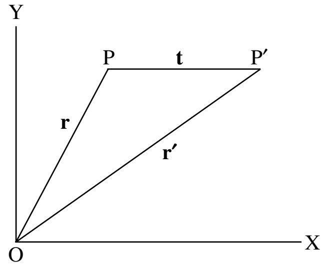


Figure 2.4. Example of a translation **t** in the active representation.

Another symmetry operator in common use is the *rotoreflection* operator

$$S_n^{\pm k} = \sigma_h R(\phi\ \mathbf{n}), \phi = \pm 2\pi k/n\ (n > 1,\ k = 1, 2, \ldots, \leq n/2,\ -\pi < \phi \leq \pi), \tag{7}$$

where σ_h "means reflection in a plane normal to the axis of rotation." All the symmetry operators, E, $R(\phi\ \mathbf{n}) = C_n$, $IR(\phi\ \mathbf{n})$, $\sigma_{\mathbf{m}}$, and S_n, leave at least one point invariant, and so they are called *point symmetry operators*. Contrast this with *translations*, an example of which is shown in Figure 2.4. Any point P in configuration space can be connected to the origin O by a vector **r**. In Figure 2.4, P happens to lie in the **xy** plane. Then under **t**, any point P is transformed into the point P′, which is connected to the origin by the vector **r**′, such that

$$\mathbf{r}' = \mathbf{r} + \mathbf{t}. \tag{8}$$

In Figure 2.4, **t** happens to be parallel to **x**. Translations are not point symmetry operations because *every* point in configuration space is translated with respect to the fixed axes OX, OY, OZ.

A *symmetry element* (which is not to be confused with a group element) is a point, line, or plane with respect to which a point symmetry operation is carried out. The symmetry elements, the notation used for them, the corresponding operation, and the notation used for the symmetry operators are summarized in Table 2.1. It is not necessary to use both $\tilde{n}$ and $\overline{n}$ since all configurations generated by $\tilde{n}$ can be produced by $\overline{n}'$.

Symmetry operations are conveniently represented by means of *projection diagrams*. A projection diagram is a circle which is the projection of a unit sphere in configuration space, usually on the **xy** plane, which we shall take to be the case unless otherwise stipulated. The x, y coordinates of a point on the sphere remain unchanged during the projection. A point on the hemisphere above the plane of the paper (and therefore with a positive z coordinate) will be represented in the projection by a small filled circle, and a point on the hemisphere below the plane of the paper will be represented by a larger open circle. A general point that will be transformed by point symmetry operators is marked by E. This point thus represents the initial configuration. Other points are then marked by the same symbol as the symmetry operator that produced that point from the initial one marked E. Commonly **z** is taken as normal to the plane of the paper, with **x** parallel to the top of the page, and when this is so it will not always be necessary to label the coordinate axes explicitly. An n-fold proper axis is commonly shown by an n-sided filled polygon (Figure 2.5). Improper axes are labeled by open polygons. A digon ($n = 2$) appears as

Table 2.1. *Symmetry elements and point symmetry operations.*

$\phi = 2\pi/n$, $n > 1$; **n** is a unit vector along the axis of rotation.

Symmetry element	Notation for symmetry element: Schönflies	Notation for symmetry element: International	Symmetry operation	Symmetry operator
None	–	–	identity	$E = R(\mathbf{0})$[a]
Center	I	$\bar{1}$	inversion	I
Proper axis	C_n	n	proper rotation	$R(\phi\ \mathbf{n}) = C_n$ or $C_{n\mathbf{n}}$
Improper axis	IC_n	$\bar{n}$	rotation, then inversion	$IR(\phi\ \mathbf{n}) = IC_{n\mathbf{n}}$
Plane	$\sigma_{\mathbf{m}}$	m	reflection in a plane normal to **m**	$\sigma_{\mathbf{m}}$
Rotoreflection axis	S_n	$\tilde{n}$	rotation through $\phi = 2\pi/n$, followed by reflection in a plane normal to the axis of rotation	$S(\phi\ \mathbf{n}) = S_n$ or $S_{n\mathbf{n}}$

[a] For the identity, the rotation parameter (ϕ **n**) is zero, signifying no rotation.

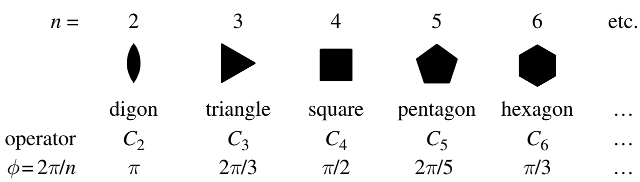


Figure 2.5. Symbols used to show an n-fold proper axis. For improper axes the same geometrical symbols are used but they are not filled in. Also shown are the corresponding rotation operator and the angle of rotation ϕ.

though formed by two intersecting arcs. The point symmetry operations listed in Table 2.1 are illustrated in Figure 2.6.

Exercise 2.1-3 Using projection diagrams (a) prove that $IC_{2\mathbf{z}} = \sigma_{\mathbf{z}}$ and that $IC_{2\mathbf{n}} = \sigma_{\mathrm{h}}$; (b) show that I commutes with an arbitrary rotation $R(\phi\ \mathbf{n})$.

Example 2.1-1 Prove that a rotoreflection axis is an improper axis, though not necessarily of the same order.

In Figure 2.7, **n** is normal to the plane of the paper and $\phi > 0$. The open circle so marked is generated from E by $S(\phi\ \mathbf{n}) = \sigma_{\mathrm{h}} R(\phi\ \mathbf{n})$, while the second filled circle (again so marked) is generated from E by $R(\phi - \pi\ \mathbf{n})$. The diagram thus illustrates the identity

$$S(\pm|\phi|\ \mathbf{n}) = IR((\pm|\phi| \mp \pi)\ \mathbf{n}), \qquad 0 \leq |\phi| \leq \pi. \tag{9}$$

When $\phi > 0$, $R(\phi - \pi\ \mathbf{n})$ means a negative (clockwise) rotation about **n** through an angle of magnitude $\pi - \phi$. When $\phi < 0$, $R(\phi + \pi\ \mathbf{n})$ means a positive rotation through an angle $\pi + \phi$. Usually $\bar{n}$ is used in crystallography and S_n is used in molecular symmetry.

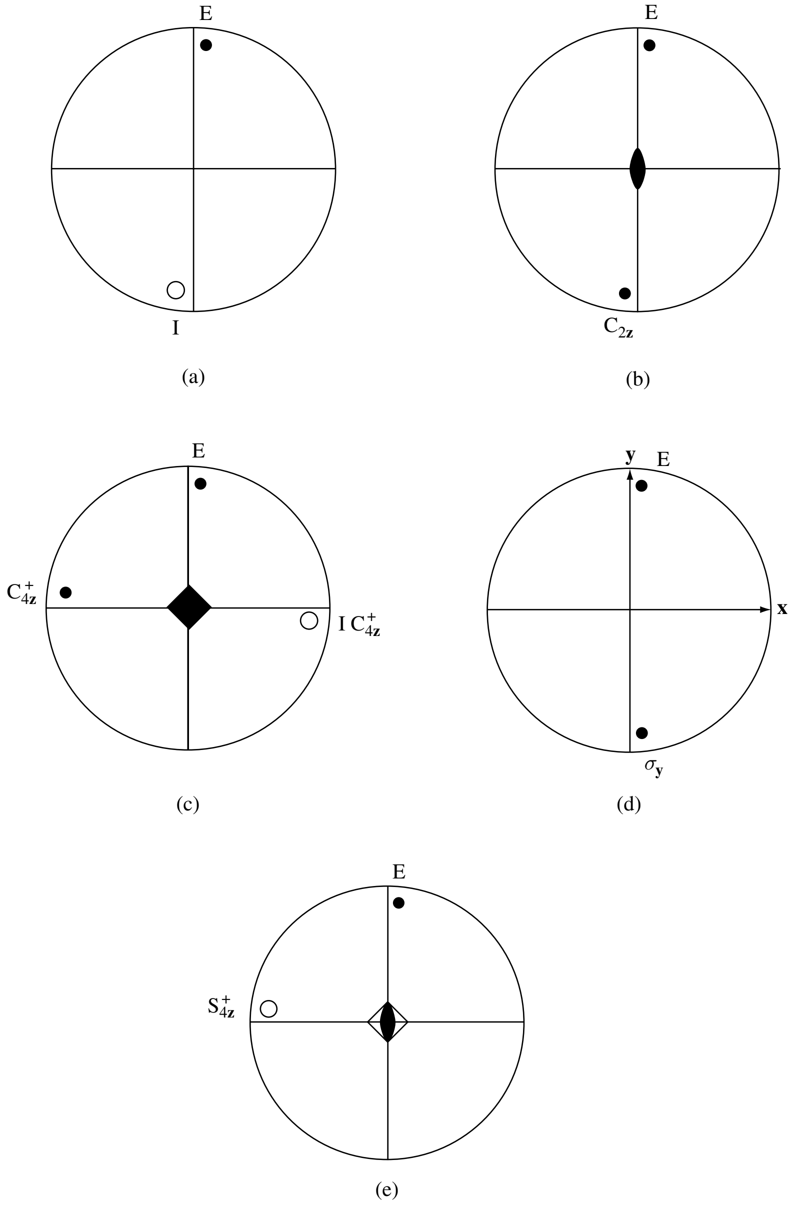


Figure 2.6. Projection diagrams showing examples of the point symmetry operators listed in Table 2.1. (a) I; (b) $C_{2\mathbf{z}}$; (c) $IC_{4\mathbf{z}}^{+}$; (d) $\sigma_{\mathbf{y}}$; (e) $S_{4\mathbf{z}}^{+}$.

It follows from Exercise 2.1-3(a) and Example 2.1-1 that the only necessary point symmetry operations are proper and improper rotations. Nevertheless, it is usually convenient to make use of reflections as well. However, if one can prove some result for R and IR, it will hold for all point symmetry operators.

As shown by Figure 2.8, $S_4^2 = C_2$. Consequently, the set of symmetry elements associated with an S_4 axis is $\{S_4\ C_2\}$, and the corresponding set of symmetry operators is

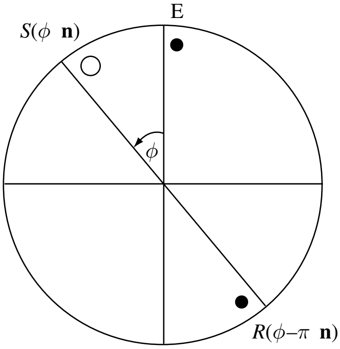


Figure 2.7. Demonstration of the equivalence of $S(\phi\ \ \mathbf{n})$ and $IR(\phi-\pi\ \ \mathbf{n})$ when $\phi > 0$ (see Example 2.1-1).

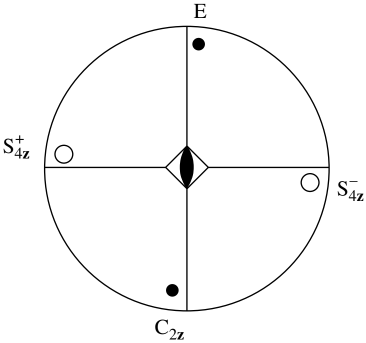


Figure 2.8. Projection diagram showing the operations connected with an S_4 axis.

$\{S_4^+\ \ C_2\ \ S_4^-\ \ E\}$. The identity operator E is always present (whether there is an axis of symmetry or not) and it must always be included once in any list of symmetry operators. The following convention is used in drawing up a list of symmetry operators: where the same configuration may be generated by equivalent symmetry operators we list only the "simplest form," that is the one of lowest n, with $-\pi < \phi \leq \pi$, avoiding redundancies. Thus C_2 and not S_4^2, S_4^- and not S_4^3, E and not S_4^4. The first part of this convention implies that whenever n/k in the operator $C_n^{\pm k}$ (or $S_n^{\pm k}$) is an integer p, then there is a C_p (or S_p), axis coincident with C_n (or S_n), and this should be included in the list of symmetry elements. Thus, for example, a C_6 axis implies coincident C_3 and C_2 axes, and the list of operators associated with C_6 is therefore $\{C_6^+\ \ C_6^-\ \ C_3^+\ \ C_3^-\ \ C_2\ \ E\}$.

The complete set of point symmetry operators that is generated from the operators $\{R_1\ \ R_2 \ldots\}$ that are associated with the symmetry elements (as shown, for example, in Table 2.2) by forming all possible products like $R_2\ R_1$, and including E, satisfies the necessary group properties: the set is complete (satisfies closure), it contains E, associativity is satisfied, and each element (symmetry operator) has an inverse. That this is so may be verified in any particular case: we shall see an example presently. Such groups of point symmetry operators are called *point groups*. For example, if a system has an S_4 axis and no

Table 2.2. *The multiplication table for the point group* S_4.

S_4	E	S_4^+	C_2	S_4^-
E	E	S_4^+	C_2	S_4^-
S_4^+	S_4^+	C_2	S_4^-	E
C_2	C_2	S_4^-	E	S_4^+
S_4^-	S_4^-	E	S_4^+	C_2

other symmetry elements (except the coincident C_2 axis that is necessarily associated with S_4) then the set of symmetry operators $\{E\ S_4^+\ C_2\ S_4^-\}$ satisfies all the necessary group properties and is the cyclic point group S_4.

Exercise 2.1-4 Construct the multiplication table for the set $\{E\ S_4^+\ C_2\ S_4^-\}$. Demonstrate by a sufficient number of examples that this set is a group. [*Hint*: Generally the use of projection diagrams is an excellent method of generating products of operators and of demonstrating closure.] In this instance, the projection diagram for S_4 has already been developed (see Figure 2.8).

Answers to Exercises 2.1

Exercise 2.1-1 (a) Figure 2.2(c) shows that the arrow has the opposite direction to the rotation of a right-handed screw as it moves along OZ from O. Also, on looking down the OZ axis towards O, the rotation appears to be in a clockwise direction. It is therefore a negative rotation with $-\pi < \phi < 0$.
(b) From Figure 2.9(a), $R(-\pi/2\ \mathbf{z})\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\} = \{\mathbf{e}_1'\ \mathbf{e}_2'\ \mathbf{e}_3'\} = \{\bar{\mathbf{e}}_2\ \mathbf{e}_1\ \mathbf{e}_3\}$.

Exercise 2.1-2 Both (a) and (b) are true from geometrical considerations. Formally, for (a) $R(\phi'\ \mathbf{n})\,R(\phi\ \mathbf{n}) = R(\phi'+\phi\ \mathbf{n}) = R(\phi+\phi'\ \mathbf{n}) = R(\phi\ \mathbf{n})\,R(\phi'\ \mathbf{n})$, and therefore rotations about the same axis commute.
(b) Following $R(\phi\ \mathbf{n})$ by $R(-\phi\ \mathbf{n})$ returns the representative point to its original position, a result which holds whether ϕ is positive or negative (see Figure 2.9(b)). Consequently, $R(-\phi\ \mathbf{n})\,R(\phi\ \mathbf{n}) = E$, so that $R(-\phi\ \mathbf{n}) = [R(\phi\ \mathbf{n})]^{-1}$.

Exercise 2.1-3 (a) Figure 2.9(c) shows that $IC_{2\mathbf{z}}$ is equivalent to $\sigma_{\mathbf{z}}$. Since the location of the axes is arbitrary, we may choose $\mathbf{n}$ (instead of $\mathbf{z}$) normal to the plane of the paper in Figure 2.9(c). The small filled circle would then be labeled by $C_{2\mathbf{n}}$ and the larger open circle by $I\,C_{2\mathbf{n}} = \sigma_{\mathbf{n}} = \sigma_{\mathrm{h}}$ (since σ_{h} means reflection in a plane normal to the axis of rotation). (b) Locate axes so that $\mathbf{n}$ is normal to the plane of the paper. Figure 2.9(d) then shows that $IR(\phi\ \mathbf{n}) = R(\phi\ \mathbf{n})I$, so that I commutes with an arbitrary rotation $R(\phi\ \mathbf{n})$.

Exercise 2.1-4 The set contains the identity E. Each column and each row of the multiplication table in Table 2.2 contains each member of the set once and once only

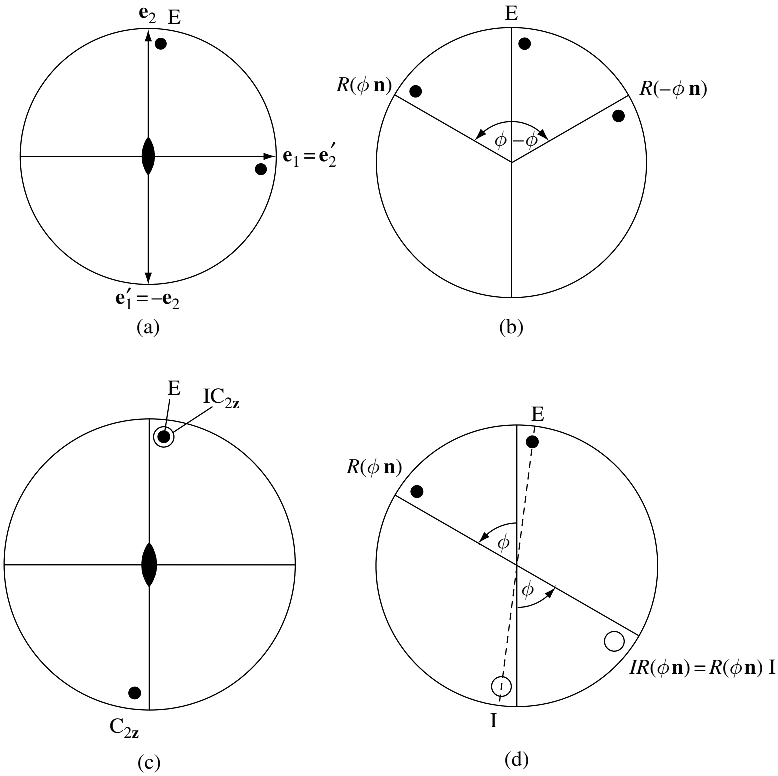


Figure 2.9. (a) The effect of $R(-\pi/2\ \mathbf{z})$ on $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$. (b) When $\phi > 0$ the rotation $R(-\phi\ \ \mathbf{n})$ means a *clockwise* rotation through an angle of magnitude ϕ about $\mathbf{n}$, as illustrated. If $\phi < 0$, then $R(-\phi\ \ \mathbf{n})$ is an anticlockwise rotation about $\mathbf{n}$, and in either case the second rotation cancels the first. (c) This figure shows that $IC_{2\mathbf{z}} = \sigma_{\mathbf{z}}$. (d) The location of the coordinate axes is arbitrary; here the plane of the projection diagram is normal to $\mathbf{n}$.

(rearrangement theorem) so that the set is closed. Since E appears in each row or column, each element has an inverse. As a test of associativity, consider the following:

$$S_4^+(C_2\ \ S_4^-) = S_4^+\ \ S_4^+ = C_2; \quad (S_4^+\ \ C_2)S_4^- = S_4^-\ \ S_4^- = C_2,$$

which demonstrates that associativity is satisfied for this random choice of three elements from the set. Any other three elements chosen at random would also be found to demonstrate that binary combination is associative. Therefore, the group properties are satisfied. This is the cyclic group S_4.

2.2 The multiplication table – an example

Consider the set of point symmetry operators associated with a pyramid based on an equilateral triangle. Choose $\mathbf{z}$ along the C_3 axis. The set of distinct (non-equivalent) symmetry operators is $G = \{E\ \ C_3^+\ \ C_3^-\ \ \sigma_{\mathbf{d}}\ \ \sigma_{\mathbf{e}}\ \ \sigma_{\mathbf{f}}\}$ (Figure 2.10). Symmetry elements

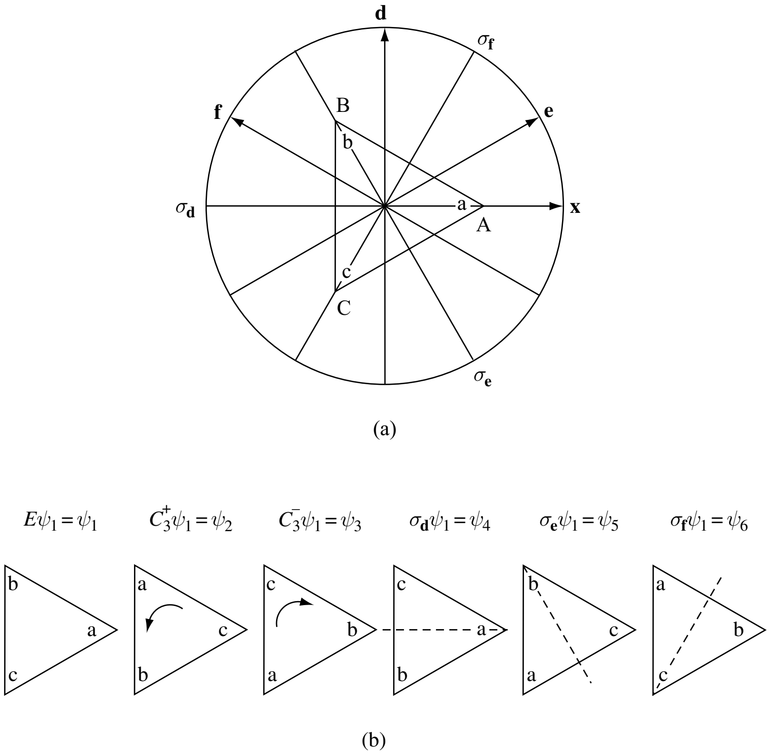


Figure 2.10. Effect of the set of symmetry operators G $= \{E \;\; C_3^+ \;\; C_3^- \;\; \sigma_{\mathbf{d}} \;\; \sigma_{\mathbf{e}} \;\; \sigma_{\mathbf{f}}\}$ on the triangular-based pyramid shown in (a). The C_3 principal axis is along **z**. The symmetry planes $\sigma_{\mathbf{d}}$, $\sigma_{\mathbf{e}}$, and $\sigma_{\mathbf{f}}$ contain **z** and make angles of zero, $-\pi/3$, and $+\pi/3$, respectively, with the **zx** plane. The apices of the triangle are marked a, b, and c for identification purposes only. Curved arrows in (b) show the direction of rotation under C_3^+ and C_3^-. Dashed lines show the reflecting planes.

(which here are $\{C_3 \;\; \sigma_{\mathbf{d}} \;\; \sigma_{\mathbf{e}} \;\; \sigma_{\mathbf{f}}\}$) are defined with respect to the Cartesian axes OX, OY, OZ, and remain *fixed*, while symmetry operators rotate or reflect the whole of configuration space including any material system – the pyramid – that exists in this space. The apices of the equilateral triangle are marked a, b, and c merely for identification purposes to enable us to keep track of the rotation or reflection of the pyramid in (otherwise) indistinguishable configurations. The three symmetry planes are *vertical* planes (σ_v) because they each contain the principal axis which is along **z**. The *reflecting plane* in the operation with $\sigma_{\mathbf{d}}$ contains the OX axis, while the reflecting planes in operations with $\sigma_{\mathbf{e}}$ and $\sigma_{\mathbf{f}}$ make angles of $-\pi/3$ and $+\pi/3$, respectively, with the **zx** plane. To help follow the configurations produced by these symmetry operators, we label the initial one ψ_1 and the other unique, indistinguishable configurations by $\psi_2, \ldots, \psi_6$. Thus, ψ_1 represents the state in which the apex marked a is adjacent to point A on the OX axis, and so on. The effect on ψ_1 of the symmetry operators that are $\in$ G is also shown in Figure 2.10, using small labeled triangles to show the configuration produced. Binary products are readily evaluated. For example,

$$C_3^+ C_3^+ \psi_1 = C_3^+ \psi_2 = \psi_3 = C_3^- \psi_1; \;\text{ therefore } C_3^+ C_3^+ = C_3^-; \tag{1}$$

Table 2.3. *Multiplication table for the set* $G = \{E\ C_3^+\ C_3^-\ \sigma_{\mathbf{d}}\ \sigma_{\mathbf{e}}\ \sigma_{\mathbf{f}}\}$.

G	E	C_3^+	C_3^-	$\sigma_{\mathbf{d}}$	$\sigma_{\mathbf{e}}$	$\sigma_{\mathbf{f}}$
E	E	C_3^+	C_3^-	$\sigma_{\mathbf{d}}$	$\sigma_{\mathbf{e}}$	$\sigma_{\mathbf{f}}$
C_3^+	C_3^+	C_3^-	E	$\sigma_{\mathbf{f}}$	$\sigma_{\mathbf{d}}$	$\sigma_{\mathbf{e}}$
C_3^-	C_3^-	E	C_3^+	$\sigma_{\mathbf{e}}$	$\sigma_{\mathbf{f}}$	$\sigma_{\mathbf{d}}$
$\sigma_{\mathbf{d}}$	$\sigma_{\mathbf{d}}$	$\sigma_{\mathbf{e}}$	$\sigma_{\mathbf{f}}$	E	C_3^+	C_3^-
$\sigma_{\mathbf{e}}$	$\sigma_{\mathbf{e}}$	$\sigma_{\mathbf{f}}$	$\sigma_{\mathbf{d}}$	C_3^-	E	C_3^+
$\sigma_{\mathbf{f}}$	$\sigma_{\mathbf{f}}$	$\sigma_{\mathbf{d}}$	$\sigma_{\mathbf{e}}$	C_3^+	C_3^-	E

$$C_3^+ C_3^- \psi_1 = C_3^+ \psi_3 = \psi_1 = E\psi_1;\ \text{therefore}\ C_3^+ C_3^- = E; \tag{2}$$

$$C_3^+ \sigma_{\mathbf{d}} \psi_1 = C_3^+ \psi_4 = \psi_6 = \sigma_{\mathbf{f}} \psi_1;\ \text{therefore}\ C_3^+ \sigma_{\mathbf{d}} = \sigma_{\mathbf{f}}; \tag{3}$$

$$\sigma_{\mathbf{d}} C_3^+ \psi_1 = \sigma_{\mathbf{d}} \psi_2 = \psi_5 = \sigma_{\mathbf{e}} \psi_1;\ \text{therefore}\ \sigma_{\mathbf{d}} C_3^+ = \sigma_{\mathbf{e}}. \tag{4a}$$

Thus C_3^+ and $\sigma_{\mathbf{d}}$ do not commute. These operator equalities in eqs. (1)–(4a) are true for *any* initial configuration. For example,

$$\sigma_{\mathbf{d}} C_3^+ \psi_4 = \sigma_{\mathbf{d}} \psi_6 = \psi_3 = \sigma_{\mathbf{e}} \psi_4;\ \text{therefore}\ \sigma_{\mathbf{d}} C_3^+ = \sigma_{\mathbf{e}}. \tag{4b}$$

Exercise 2.2-1 Verify eqs. (1)–(4), using labeled triangles as in Figure 2.10.

Exercise 2.2-2 Find the products $C_3^- \sigma_{\mathbf{e}}$ and $\sigma_{\mathbf{e}} C_3^-$. The multiplication table for this set of operators $G = \{E\ C_3^+\ C_3^-\ \sigma_{\mathbf{d}}\ \sigma_{\mathbf{e}}\ \sigma_{\mathbf{f}}\}$ is shown in Table 2.3. The complete multiplication table has the following properties.

(a) Each column and each row contains each element of the set once and once only. This is an example of the rearrangement theorem, itself a consequence of closure and the fact that all products $g_i\ g_j$ are unique.
(b) The set contains the identity E, which occurs once in each row or column.
(c) Each element $g_i \in G$ has an inverse g_i^{-1} such that $g_i^{-1}\ g_i = E$.
(d) Associativity holds: $g_i(g_j\ g_k) = (g_i\ g_j)g_k,\ \forall\ g_i,\ g_j,\ g_k \in G$.

Exercise 2.2-3 Use the multiplication Table 2.3 to verify that $\sigma_{\mathbf{d}}(C_3^+\ \sigma_{\mathbf{f}}) = (\sigma_{\mathbf{d}}\ C_3^+)\sigma_{\mathbf{f}}$.

Any set with the four properties (a)–(d) forms a group: therefore the set G is a group for which the group elements are point symmetry operators. This point group is called C_{3v} or 3*m*, because the pyramid has these symmetry elements: a three-fold principal axis and a vertical mirror plane. (If there is one vertical plane then there must be three, because of the three-fold symmetry axis.)

Exercise 2.2-4 Are the groups C_{3v} and S(3) isomorphous? [*Hint*: Compare Table 2.3 with Table 1.3.]

Answers to Exercises 2.2

Exercise 2.2-1 The orientation of the triangular base of the pyramid is shown for each of the indistinguishable configurations.

$C_3^+C_3^+\ \psi_1$	$=$	$C_3^+\ \psi_2$	$=$	ψ_3	$=$	$C_3^-\ \psi_1$	
b		a		c		b	
a		c		b		a	(1′)
c		b		a		c	

$C_3^+C_3^-\ \psi_1$	$=$	$C_3^+\ \psi_3$	$=$	ψ_1	$=$	$E\ \psi_1$	
b		c		b		b	
a		b		a		a	(2′)
c		a		c		c	

$C_3^+\sigma_{\mathbf{d}}\ \psi_1$	$=$	$C_3^+\ \psi_4$	$=$	ψ_6	$=$	$\sigma_{\mathbf{f}}\ \psi_1$	
b		c		a		b	
a		a		b		a	(3′)
c		b		c		c	

$\sigma_{\mathbf{d}}C_3^+\ \psi_1$	$=$	$\sigma_{\mathbf{d}}\ \psi_2$	$=$	ψ_5	$=$	$\sigma_{\mathbf{e}}\ \psi_1$	
b		a		b		b	
a		c		c		a	(4a′)
c		b		a		c	

$\sigma_{\mathbf{d}}C_3^+\ \psi_4$	$=$	$\sigma_{\mathbf{d}}\ \psi_6$	$=$	ψ_3	$=$	$\sigma_{\mathbf{e}}\ \psi_4$	
c		a		c		c	
a		b		b		a	(4b′)
b		c		a		b	

Exercise 2.2-2

$C_3^-\sigma_{\mathbf{e}}\psi_1$	$=$	$C_3^-\psi_5$	$=$	ψ_6	$=$	$\sigma_{\mathbf{f}}\psi_1$
b		b		a		b
a		c		b		a
c		a		c		c

Exercise 2.2-3 $\sigma_{\mathbf{d}}(C_3^+\ \sigma_{\mathbf{f}}) = \sigma_{\mathbf{d}}\sigma_{\mathbf{e}} = C_3^+$ and $(\sigma_{\mathbf{d}}\ C_3^+)\sigma_{\mathbf{f}} = \sigma_{\mathbf{e}}\sigma_{\mathbf{f}} = C_3^+$.

Exercise 2.2-4 A comparison of the group multiplication tables in Table 2.3 and Table 1.3 shows that the point group C_{3v} (or $3m$) is isomorphous with the permutation group S(3). Corresponding elements in the two groups are

S(3)	P_0	P_1	P_2	P_3	P_4	P_5
C_{3v}	E	C_3^+	C_3^-	$\sigma_{\mathbf{d}}$	$\sigma_{\mathbf{e}}$	$\sigma_{\mathbf{f}}$

2.3 The symmetry point groups

We first describe the *proper point groups*, P, that is the point groups that contain the identity and proper rotations only.

(i) In the *cyclic groups*, denoted by n or C_n, with $n > 1$, there is only one axis of rotation and the group elements (symmetry operators) are E and $C_{n\mathbf{z}}^{\pm k}$, or $R(\phi \;\mathbf{n})$ with $\phi = \pm 2\pi k/n$, $-\pi < \phi \leq \pi$. Note that $C_{n\mathbf{z}}^{\pm k}$, becomes $C_{p\mathbf{z}}^{\pm}$, when $^{n}/_{k}$ is an integer p; $k = 1, 2, \ldots,$ $(n-1)/2$, if n is an odd integer, and if n is even $k = 1, 2, \ldots, {}^{n}/_{2}$, with $C_{n\mathbf{z}}^{-n/2}$, excluded by the range of ϕ. For example, if $n = 4$, $k = 1, 2$, and $\phi = \pm\pi/2, \pi$. The symmetry elements are the C_4 axis, and a coincident C_2 axis, and the group elements (symmetry operators) are $\{E \; C_4^+ \; C_4^- \; C_2\}$; $k = 1$ is implicit in $C_n^{\pm k}$. The projection diagram for C_4 is shown in Figure 2.11(a). C_1 is also a cyclic group (though not an axial group) with period $\{g_1 = E\}$ and order $c = 1$. There are no symmetry elements and the group consists solely of the identity E. The International notation used to describe the point groups is given in Table 2.4. Some International symbols are unnecessarily cumbersome, and these are abbreviated in Table 2.5.

(ii) The *dihedral groups* consist of the proper rotations that transform a regular n-sided prism into itself. The symmetry elements are C_n and $n\,C_2'$, where C_2' denotes a binary axis normal to the n-fold principal axis. (The prime is not essential but is often used to

Table 2.4. *International notation used to name the point groups comprises a minimal set of symmetry elements.*

n	n-fold proper axis ($n = 1$ means there is no axis of symmetry)
$\overline{n}$	n-fold improper axis ($\overline{n} = \overline{1}$ means an inversion center)
nm	n-fold proper axis with a vertical plane of symmetry that contains n
n/m	n-fold proper axis with a horizontal plane of symmetry normal to n
$n2$	n-fold proper axis with n binary axes normal to n

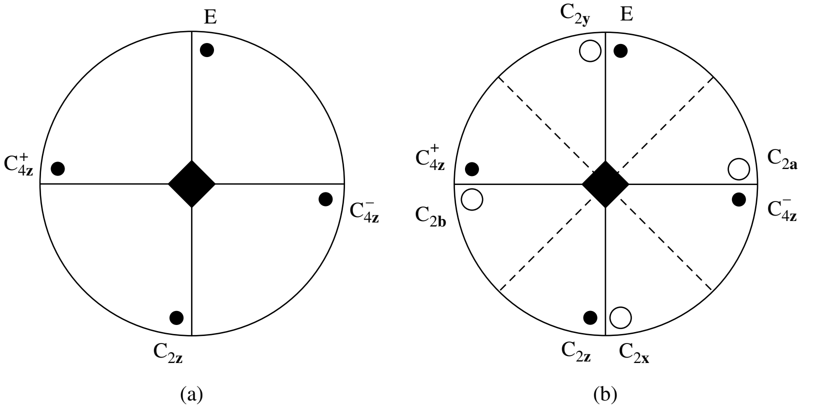


Figure 2.11. Projection diagrams (a) for the proper point group 4, or C_4, and (b) for the dihedral group 422, or D_4. The components of the unit vector **a** are $2^{-1/2}$ [1 1 0] and those of **b** are $2^{-1/2}$ [$\overline{1}$ 1 0].

Table 2.5. *Abbreviated International symbols and Schönflies notation.*

Schönflies symbol	Full International symbol	Abbreviated symbol
D_{2h}	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	*mmm*
D_{4h}	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	4/*mmm*
D_{6h}	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	6/*mmm*
D_{3d}	$\bar{3}\frac{2}{m}$	$\bar{3}m$
T_h	$\frac{2}{m}\bar{3}$	*m*3
O_h	$\frac{4}{m}\bar{3}\frac{2}{m}$	*m*3*m*

stress that a binary axis is normal to the principal axis and hence lies in the **xy** plane. In projective diagrams and descriptive text one refers to specific axes such as $C_{2\mathbf{x}}$ when greater precision is required.) The symmetry operators are $C_{n\mathbf{z}}^{\pm k}$ or $R(\phi\ \mathbf{z})$, with ϕ and k as in (i), and $R(\pi\ \mathbf{n}_i)$, with $\mathbf{n}_i$ normal to **z** and $i = 1, \ldots, n$. In general, we shall use particular symbols for the $\mathbf{n}_i$, such as **x**, **y**, **a**, **b**, . . . , with **a**, **b**, . . . appropriately defined (see, for example, Figure 2.11(b)). The group symbol is D_n in Schönflies notation and in International notation it is $n2$ if n is odd and $n22$ if n is even, because there are then two sets of C_2' axes which are geometrically distinct. The projection diagram for 422 or D_4 is shown in Figure 2.11(b). The four binary axes normal to **z** lie along **x**, **y**, **a**, **b**, where **a** bisects the angle between **x** and **y** and **b** bisects that between $\bar{\mathbf{x}}$ and **y**. These axes can be readily identified in Figure 2.11(b) because each transformed point is labeled by the same symbol as that used for the operator that effected that particular transformation from the representative point E.

(iii) The *tetrahedral* point group, called 23 or T, consists of the proper rotations that transform a tetrahedron into itself. The symmetry elements are $3C_2$ and $4C_3$, and the easiest way of visualizing these is to draw a cube (Figure 2.12) in which alternate (second neighbor) points are the apices of the tetrahedron. These are marked 1, 2, 3, and 4 in Figure 2.12. The symmetry operators are

$$\mathrm{T} = \{E\ R(\pi\ \mathbf{p})\ R(\pm 2\pi/3\ \ \mathbf{j})\}, \tag{1}$$

with $\mathbf{p} = \mathbf{x}, \mathbf{y}, \mathbf{z}$, and **j** a unit vector along O1, O2, O3, O4.

(iv) The *octahedral* or *cubic* group, named 432 or O, consists of the proper rotations that transform a cube or an octahedron into itself. The proper axes of the cube or octahedron are $\{3C_4\ 4C_3\ 9C_2\}$ and the symmetry operators are

$$\mathrm{O} = \{\mathrm{T}\} + \{R(\pi/2\ \ \mathbf{p})\ R(\pi\ \mathbf{n})\}, \tag{2}$$

where **n** is a unit vector along Oa, Ob, Oc, Od, Oe, Of in Figure 2.12 .

(v) The *icosahedral* group, named 532 or Y, consists of the proper rotations that transform an icosahedron or pentagonal dodecahedron into itself (Figure 2.13). The *pentagonal*

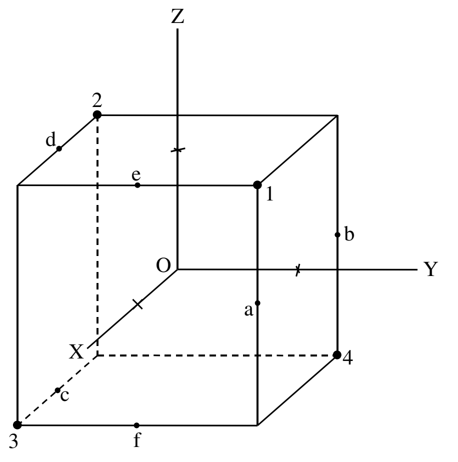
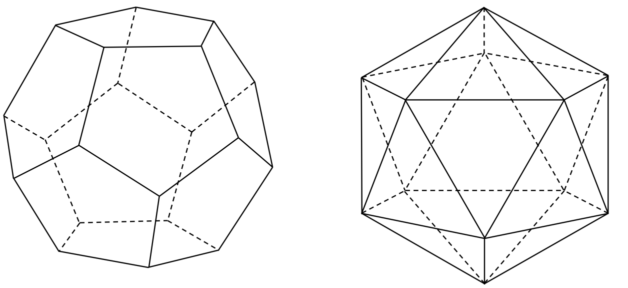


Figure 2.12. Alternate vertices of the cube (marked 1, 2, 3, and 4) are the apices of a regular tetrahedron. O1, O2, O3, and O4 are three-fold axes of symmetry. Small crosses show where the C_4 axes, OX, OY, and OZ, intersect the cube faces. Oa, Ob, Oc, Od, Oe, and Of are six binary axes.



(a) (b)

Figure 2.13. The dodecahedron and the icosahedron are two of the five Platonic solids (regular polyhedra), the others being the tetrahedron, the cube, and the octahedron. (a) The dodecahedron has twelve regular pentagonal faces with three pentagonal faces meeting at a point. (b) The icosahedron has twenty equilateral triangular faces, with five of these meeting at a point.

dodecahedron has six C_5 axes through opposite pairs of pentagonal faces, ten C_3 axes through opposite pairs of vertices, and fifteen C_2 axes that bisect opposite edges. The *icosahedron* has six C_5 axes through opposite vertices, ten C_3 axes through opposite pairs of faces, and fifteen C_2 axes that bisect opposite edges. For both these polyhedra, the symmetry elements that are proper axes are $\{6C_5 \;\; 10C_3 \;\; 15C_2\}$ and the point group of symmetry operators is therefore

$$\mathrm{Y} = \{E \;\; 6C_5^{\pm} \;\; 6C_5^{2\pm} \;\; 10C_3^{\pm} \;\; 15C_2\} \tag{3}$$

for a total $g(\mathrm{Y})$ of 60. It is isomorphous to the group of even permutations on five objects, which number $5!/2$.

This completes the list of proper point groups, P. A summary is given in the first column of Table 2.6. All the remaining axial point groups may be generated from the proper point groups P by one or other of two methods.

2.3.1 First method

This consists of taking the direct product (DP) of P with $\bar{1}$ or $C_i = \{E\ I\}$.

(i) From C_n, if n is odd,

$$C_n \otimes C_i = S_{2n},\ \ n \otimes \bar{1} = \bar{n}. \tag{4}$$

But if n is even,

$$C_n \otimes C_i = C_{nh},\ \ n \otimes \bar{1} = n/m, \tag{5}$$

where h, or $/m$, denotes a mirror plane normal to the principal axis, which arises because $IC_2 = \sigma_h$.

Example 2.3-1 (a) $C_2 \otimes C_i = \{E\ \ C_{2\mathbf{z}}\} \otimes \{E\ \ I\} = \{E\ \ C_{2\mathbf{z}}\ \ I\ \ \sigma_{\mathbf{z}}\} = C_{2h}$. (b) $C_3 \otimes C_i = \{E\ C_{3\mathbf{z}}^+\ C_{3\mathbf{z}}^-\} \otimes \{E\ I\} = \{E\ C_{3\mathbf{z}}^+\ C_{3\mathbf{z}}^-\ I\ S_{6\mathbf{z}}^-\ S_{6\mathbf{z}}^+\} = S_6$. Projection diagrams are illustrated in Figure 2.14.

(ii) From D_n, if n is odd,

$$D_n \otimes C_i = D_{nd},\ \ n2 \otimes \bar{1} = nm. \tag{6}$$

The subscript d denotes the presence of dihedral planes which bisect the angles between C_2' axes that are normal to the principal axis. If n is even,

$$D_n \otimes C_i = D_{nh};\ \ n22 \otimes \bar{1} = n/mmm. \tag{7}$$

If n is 2, the International symbol is abbreviated to mmm (Table 2.4).

Example 2.3-2

$$\begin{aligned} D_3 \otimes C_i &= \{E\ C_{3\mathbf{z}}^+\ C_{3\mathbf{z}}^-\ C_{2\mathbf{a}}\ C_{2\mathbf{b}}\ C_{2\mathbf{c}}\} \otimes \{E\ I\} \\ &= \{D_3\} + \{I\ S_{6\mathbf{z}}^-\ S_{6\mathbf{z}}^+\ \sigma_{\mathbf{a}}\ \sigma_{\mathbf{b}}\ \sigma_{\mathbf{c}}\} = D_{3d}; \end{aligned} \tag{8}$$

$\sigma_{\mathbf{c}}$, for example, denotes reflection in a dihedral plane **zf** that bisects the angle between **a** and **b**, which are the binary axes normal to the C_3 axis (Figure 2.10). The notation in eq. (8) is intentionally detailed, but may be compressed, as in

$$D_3 \otimes C_i = \{E\ 2C_3\ 3C_2'\} \otimes \{E\ I\} = \{E\ 2C_3\ 3C_2'\ I\ 2S_6\ 3\sigma_d\} = D_{3d}. \tag{9}$$

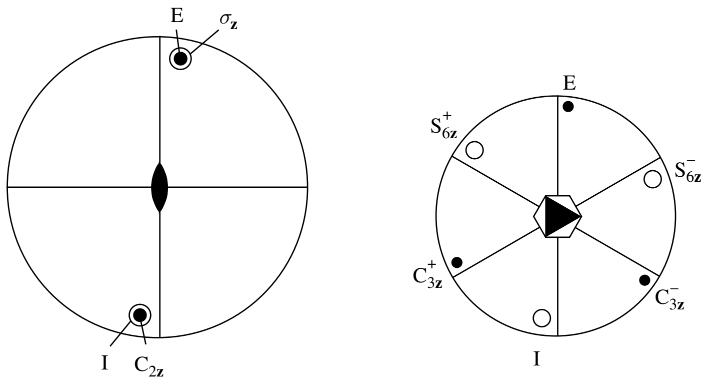
Exercise 2.3-1 Confirm the DP $D_3 \otimes C_i$ in eq. (9) by constructing the (labeled) projection diagram for D_{3d}. Identify the dihedral planes.

(iii)
$$T \otimes C_i = T_h;\quad 23 \otimes \bar{1} = m3. \tag{10}$$

Table 2.6. *Derivation of commonly used finite point groups from proper point groups.*

If P has an invariant subgroup Q of index 2 so that $\mathrm{P} = \{\mathrm{Q}\} + R\{\mathrm{Q}\}$, $R \in \mathrm{P}$, $R \notin \mathrm{Q}$, then $\mathrm{P}' = \{\mathrm{Q}\} + IR\{\mathrm{Q}\}$ is a group isomorphous with P. In each column, the symbol for the point group is given in International notation on the left and in Schönflies notation on the right. When $n = 2$, the International symbol for $\mathrm{D}_{2\mathrm{h}}$ is *mmm*. When n is odd, the International symbol for $\mathrm{C}_{n\mathrm{v}}$ is *nm*, and when n is even it is *nmm*. Note that $n' = n/2$. In addition to these groups, which are either a proper point group P, or formed from P, there are the three cyclic groups: 1 or $\mathrm{C}_1 = \{E\}$, $\bar{1}$ or $\mathrm{C}_i = \{E\ I\}$, and m or $\mathrm{C}_\mathrm{s} = \{E\ \sigma\}$.

P		$\mathrm{P} \otimes \mathrm{C}_i$		$\mathrm{P} = \mathrm{Q} + IR\{\mathrm{Q}\}$		Q	
n $(n = 2, 3, \ldots, 8)$	C_n	$\bar{n}$ $(n = 3, 5)$	$\mathrm{S}_{2\mathrm{n}}$	$\bar{n}$ $(n' = 3, 5)$	$\mathrm{C}_{n'\mathrm{h}}$	n'	$\mathrm{C}_{n'}$
		n/m $(n = 2, 4, 6)$	$\mathrm{C}_{n\mathrm{h}}$	$\bar{n}$ $(n' = 2, 4)$	$\mathrm{S}_{2n'}$		
$n2$ $(n = 3, 5)$	D_n	$\bar{n}m$ $(n = 3, 5)$	$\mathrm{D}_{n\mathrm{d}}$	nm, nmm $(n = 2, 3, \ldots, 6)$	$\mathrm{C}_{n\mathrm{v}}$	n	C_n
$n22$ $(n = 2, 4, 6)$	D_n	n/mmm $(n = 2, 4, 6, 8)$	$\mathrm{D}_{n\mathrm{h}}$	$\bar{n}2m$ $(n' = 3, 5)$	$\mathrm{D}_{n'\mathrm{h}}$	$n'2$	$\mathrm{D}_{n'}$
				$(n' = 2, 4, 6)$	$\mathrm{D}_{n'\mathrm{d}}$	$n'22$	$\mathrm{D}_{n'}$
23	T	$m3$	T_h				
432	O	$m3m$	O_h	$\bar{4}3m$	T_d	23	T
532	Y	$53m$	Y_h				



(a) (b)

Figure 2.14. Projection diagrams for the point groups (a) C_{2h} and (b) S_6.

In abbreviated notation,

$$\begin{aligned} T \otimes C_i &= \{E\ 4C_3^+\ 4C_3^-\ 3C_2\} \otimes \{E\ I\} \\ &= \{T\} + \{I\ 4S_6^-\ 4S_6^+\ 3\sigma_h\} = T_h. \end{aligned} \tag{11}$$

As shown in Figure 2.15(a), $IC_{2\mathbf{y}}$ (for example) is $\sigma_{\mathbf{y}}$. The plane normal to **y**, the **zx** plane, *contains* $C_{2\mathbf{z}}$ and $C_{2\mathbf{x}}$, and so this is a horizontal plane (normal to $C_{2\mathbf{y}}$) and *not* a dihedral plane, because it contains the other C_2 axes ($C_{2\mathbf{z}}$ and $C_{2\mathbf{x}}$) and does not bisect the angle between them. Note that $T = C_2 \wedge C_3$ is 23 in International notation but that $D_3 = C_3 \wedge C_2$ is 32.

(iv) $$O \otimes C_i = O_h, \quad 432 \otimes \bar{1} = m3m. \tag{12}$$

In abbreviated notation,

$$\begin{aligned} O \otimes C_i &= \{E\ 6C_4\ 3C_2\ 6C_2'\ 8C_3\} \otimes \{E\ I\} \\ &= \{O\} + \{I\ 6S_4\ 3\sigma_h\ 6\sigma_d\ 8S_6\}. \end{aligned} \tag{13}$$

The three S_4 axes are coincident with the three C_4 (and coincident C_2) axes along **x**, **y**, **z**. The three horizontal planes $\sigma_{\mathbf{x}}$, $\sigma_{\mathbf{y}}$, and $\sigma_{\mathbf{z}}$ and two of the six dihedral planes $\sigma_{\mathbf{a}}$, $\sigma_{\mathbf{b}}$ are shown in Figures 2.15(b) and (c).

(v) $$Y \otimes C_i = Y_h, \quad 532 \otimes \bar{1} = 53m; \tag{14}$$

$$\begin{aligned} Y \otimes C_i &= \{E\ 24C_5\ 20C_3\ 15C_2\} \otimes \{E\ I\} \\ &= \{Y\} + \{I\ 24S_{10}\ 20S_6\ 15\sigma_h\}. \end{aligned} \tag{15}$$

The six S_{10} axes are coincident with the six C_5 axes of Y, and the ten S_6 axes are coincident with the ten C_3 axes of Y. The fifteen mirror planes each contain two C_2 axes and two C_5 axes. All these DPs are given in the second column of Table 2.6.

Exercise 2.3-2 Draw a projection diagram showing that $C_5 \otimes C_i = S_{10}$.

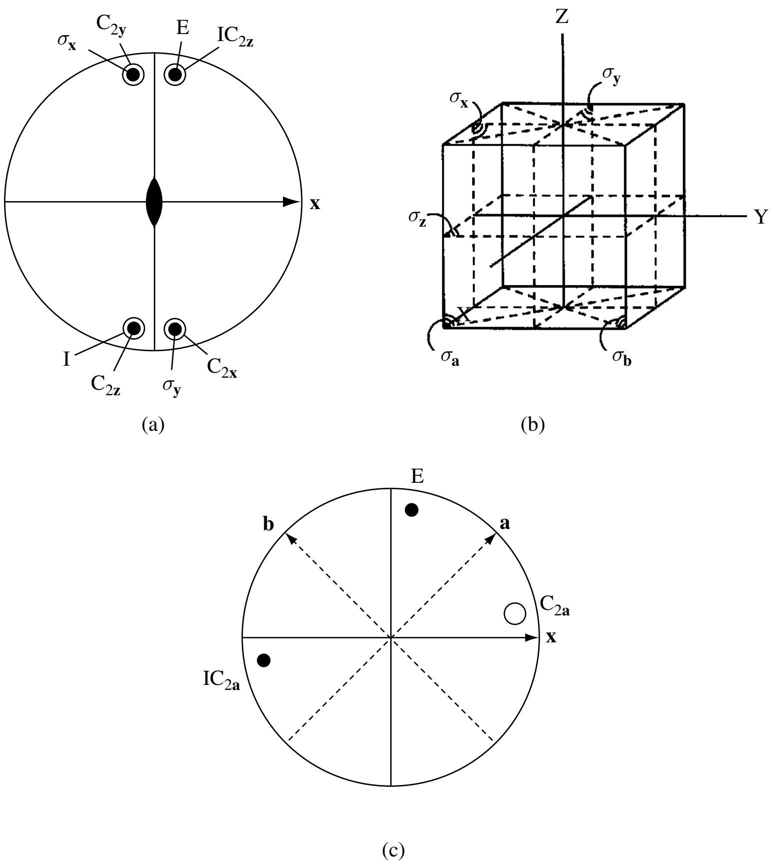


Figure 2.15. (a) In $T \otimes C_i$, $IC_{2\mathbf{y}} = \sigma_{\mathbf{y}}$, and $\sigma_{\mathbf{y}}$ contains the other two C_2 axes, $C_{2\mathbf{z}}$ and $C_{2\mathbf{x}}$. Since $\sigma_{\mathbf{y}}$ is normal to the axis of rotation $\mathbf{y}$, it is a horizontal plane, not a dihedral plane. (b) In $O \otimes C_i$, $IC_2 = \sigma_h$, as, for example, $IC_{2\mathbf{x}} = \sigma_{\mathbf{x}}$, which contains $\mathbf{y}$ and $\mathbf{z}$. In (c), $\mathbf{a}$ is the unit vector along Oa in Figure 2.12, and $IC_{2\mathbf{a}} = \sigma_{\mathbf{a}}$. This dihedral plane is also shown in (b).

2.3.2 *Second method*

The second method is applicable to proper point groups P that have an invariant subgroup Q of index 2, so that

$$P = \{Q\} + R\{Q\}, \ R \in P, \ R \notin Q. \tag{16}$$

Then $\{Q\} + IR\{Q\}$ is a point group P′ which is isomorphous with P and therefore has the same class structure as P. The isomorphism follows from the fact that I commutes with any proper or improper rotation and therefore with any other symmetry operator. Multiplication tables for P and P′ are shown in Table 2.7; we note that these have the same structure and that the two groups have corresponding classes, the only difference being that some products X are replaced by IX in P′. Examples are given below.

Table 2.7. *Multiplication tables for* P *and* P′, *where* $P = \{Q\} + R\{Q\}$ *and* $P' = Q + IR\{Q\}$. $A, B \in Q$ and $C, D \in R\,Q$. Use has been made of the commutation property of I with any other symmetry operator.

P	{Q}	R{Q}
{Q}	{AB}	{AD}
R{Q}	{CB}	{CD}

P′	{Q}	IR{Q}
{Q}	{AB}	I{AD}
IR{Q}	I{CB}	{CD}

Exercise 2.3-3 If $X \in R\{Q\}$ and X, Y are conjugate elements in P, show that IX and IY are conjugate elements in P′.

(i) C_{2n} has the invariant subgroup C_n of index 2, because

$$C_{2n} = \{C_n\} + C_{2n}\{C_n\}. \tag{17}$$

Note that C_n means the point group C_n, but $\{C_n\}$ means the set of operators forming the point group C_n. Then

$$\{C_n\} + IC_{2n}\{C_n\} = S_{2n}\ (n \text{ even}),\ \text{or}\ = C_{nh}\ (n \text{ odd}). \tag{18}$$

In Table 2.6, n' is defined as $n/2$ to avoid any possible confusion when using International notation; $S_{2n'}$ is, of course, S_n.

Example 2.3-3

$$C_2 = E + C_2\{E\} = \{E\ C_2\}, \tag{19}$$

$$E + IC_2\{E\} = \{E\ \sigma_h\} = C_s. \tag{20}$$

The multiplication tables are

C_2	E	C_2
E	E	C_2
C_2	C_2	E

C_s	E	σ_h
E	E	σ_h
σ_h	σ_h	E

This is a rather trivial example: the classes of C_2 are E, C_2 and those of C_s are E, σ_h. Elements $X \in P$ and $IX \in P'$ are called *corresponding elements*, so here C_2 and $IC_2 = \sigma_h$ are corresponding elements.

Exercise 2.3-4 Use the second method to derive the point group P′ corresponding to the proper point group C_4. Show that C_4 and P′ are isomorphous and find the classes of both groups.

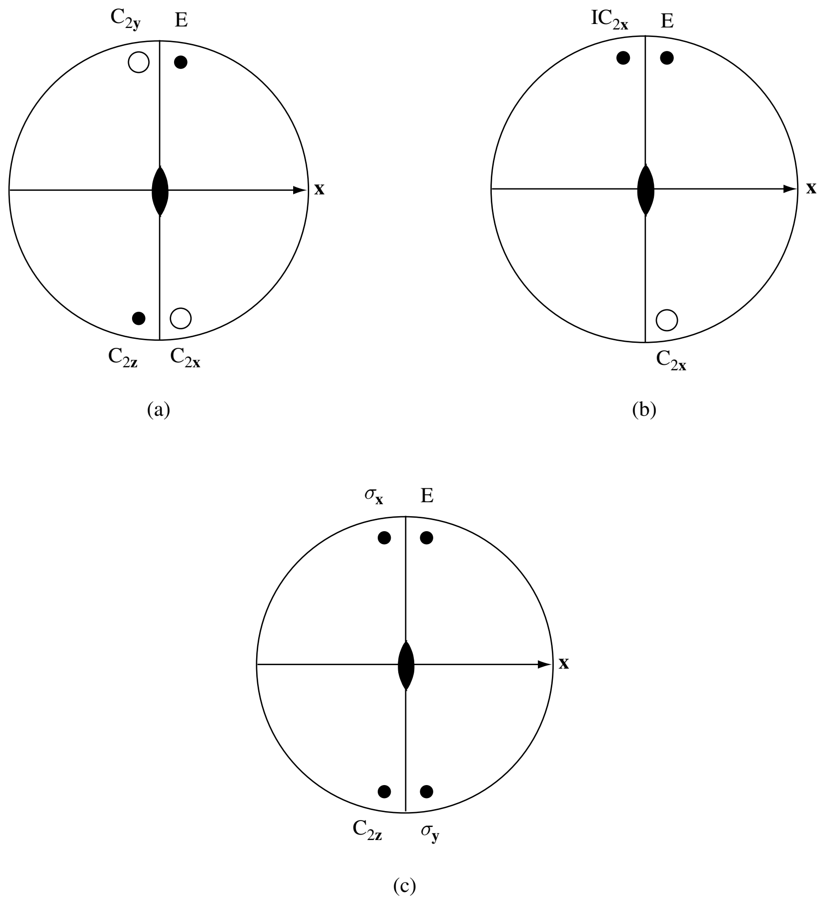


Figure 2.16. Projection diagrams (a) for D_2; (b) showing that $IC_{2x} = \sigma_{\mathbf{x}}$; and (c) for $C_{2v.}$

(ii) D_n has the invariant subgroup C_n. The coset expansion of D_n on C_n is

$$D_n = \{C_n\} + C_2{}'\{C_n\}. \tag{21}$$

(21) $$\{C_n\} + IC_2{}'\{C_n\} = \{C_n\} + \sigma_v\{C_n\} = C_{nv}. \tag{22}$$

For example, for $n = 2$,

$$D_2 = \{E\ C_{2\mathbf{z}}\} + C_{2\mathbf{x}}\{E\ C_{2\mathbf{z}}\} = \{E\ C_{2\mathbf{z}}\ C_{2\mathbf{x}}\ C_{2\mathbf{y}}\}, \tag{23}$$

(23) $$\begin{aligned}\{E\ C_{2\mathbf{z}}\} + IC_{2\mathbf{x}}\{E\ C_{2\mathbf{z}}\} &= \{E\ C_{2\mathbf{z}}\} + \sigma_{\mathbf{x}}\{E\ C_{2\mathbf{z}}\} \\ &= \{E\ C_{2\mathbf{z}}\ \sigma_{\mathbf{x}}\ \sigma_{\mathbf{y}}\} = C_{2v}.\end{aligned} \tag{24}$$

The projection diagrams illustrating D_2 and C_{2v} are in Figure 2.16.

D_{2n} has the invariant subgroup D_n of index 2, with the coset expansion

$$D_{2n} = \{D_n\} + C_{2n}\{D_n\}; \tag{25}$$

Table 2.8. *The relation of the point groups* O *and* T_d *to their invariant subgroup* T.

C_{31}^+ means a positive rotation through $2\pi/3$ about the axis O1 and similarly (see Figure 2.12). $C_{2\mathbf{a}}$ means a rotation through π about the unit vector **a** along [1 1 0], and $\sigma_{\mathbf{a}}$ means a reflection in the mirror plane normal to **a**.

$\{T\} = \{E\ C_{2z}\ C_{2x}\ C_{2y}\ C_{31}^+\ C_{31}^-\ C_{32}^+\ C_{32}^-\ C_{33}^+\ C_{33}^-\ C_{34}^+\ C_{34}^-\}$
$C_{4z}^+\{T\} = \{C_{4z}^+\ C_{4z}^-\ C_{2\mathbf{a}}\ C_{2\mathbf{b}}\ C_{2\mathbf{c}}\ C_{4y}^-\ C_{2\mathbf{f}}\ C_{4y}^+\ C_{4x}^+\ C_{2\mathbf{d}}\ C_{4x}^-\ C_{2\mathbf{e}}\}$
$IC_{4z}^+\{T\} = \{S_{4z}^-\ S_{4z}^+\ \sigma_{\mathbf{a}}\ \sigma_{\mathbf{b}}\ \sigma_{\mathbf{c}}\ S_{4y}^+\ \sigma_{\mathbf{f}}\ S_{4y}^-\ S_{4x}^-\ \sigma_{\mathbf{d}}\ S_{4x}^+\ \sigma_{\mathbf{e}}\}$

(25)

$$\{D_n\} + IC_{2n}\{D_n\} = D_{nd}\ (n \text{ even}),\ \text{or } D_{nh}\ (n \text{ odd}). \tag{26}$$

For example, if $n = 2$,

$$D_4 = \{D_2\} + C_{4z}^+\{D_2\} = \{E\ C_{2z}\ C_{2x}\ C_{2y}\ C_{4z}^+\ C_{4z}^-\ C_{2\mathbf{a}}\ C_{2\mathbf{b}}\}, \tag{27}$$

where **a** is the unit vector bisecting the angle between **x** and **y**, and **b** is that bisecting the angle between $\bar{\mathbf{x}}$ and **y**. The projection diagram for D_4 is shown in Figure 2.11(b). Applying the second method,

$$\begin{aligned}\{D_2\} + IC_{4z}^+\{D_2\} &= \{E\ C_{2z}\ C_{2x}\ C_{2y}\} + S_{4z}^-\{E\ C_{2z}\ C_{2x}\ C_{2y}\} \\ &= \{E\ C_{2z}\ C_{2x}\ C_{2y}\ S_{4z}^-\ S_{4z}^+\ \sigma_{\mathbf{a}}\ \sigma_{\mathbf{b}}\} = D_{2d}.\end{aligned} \tag{28}$$

(iv) O has the invariant subgroup T of index 2:

$$O = \{T\} + C_4^+\{T\} = \{E\ 3C_2\ 8C_3\ 6C_4\ 6C_2{}'\} \tag{29}$$

$$\{T\} + IC_{4z}^+\{T\} = \{E\ 3C_2\ 8C_3\ 6S_4\ 6\sigma_d\} = T_d. \tag{30}$$

The detailed verification of eqs. (29) and (30) is quite lengthy, but is summarized in Table 2.8.

(iii), (v) The point groups T, Y have no invariant subgroups of index 2.

This completes the derivation of the point groups that are important in molecular symmetry, with the exception of the two continuous rotation groups $C_{\infty v}$ and $D_{\infty h}$, which apply to linear molecules.

The rotation of a heteronuclear diatomic molecule like HCl through any angle ϕ about **z** (which is always chosen to lie along the molecular axis) leaves the molecule in an indistinguishable configuration. The point group therefore contains an infinite number of rotation operators $R(\phi\ \mathbf{z})$. Similarly, there are an infinite number of vertical planes of symmetry in the set of symmetry elements and the point group contains $\infty\sigma_v$. The point group is therefore called $C_{\infty v}$. For homonuclear diatomic molecules like O_2, or polyatomic linear molecules with a horizontal plane of symmetry, the point group also contains σ_h and an infinite number of C_2' axes normal to the principal axis (which is along the molecular axis). Such molecules belong to the point group $D_{\infty h}$.

For crystals, the point group must be compatible with translational symmetry, and this requirement limits n to 2, 3, 4, or 6. (This restriction applies to both proper and improper axes.) Thus the *crystallographic point groups* are restricted to ten proper point groups and a total of

Table 2.9. *The thirty-two crystallographic point groups in both International and Schönflies notation.*

In addition to the proper point groups P and the improper point groups that are either isomorpous with P or equal to P $\otimes$ C_i, there is the non-axial group 1 or $C_1 = \{E\}$.

Proper point group P		Improper group P′ isomorphous to P		P $\otimes$ C_i		Proper group isomorphous to P $\otimes$ C_i
2	C_2	$\{m$ / $\bar{1}$	C_s / $C_i\}$	$2/m$	C_{2h}	D_2
3	C_3			$\bar{3}$	S_6	C_6
4	C_4	$\bar{4}$	S_4	$4/m$	C_{4h}	
6	C_6	$\bar{6}$	C_{3h}	$6/m$	C_{6h}	
222	D_2	$2mm$	C_{2v}	mmm	D_{2h}	
32	D_3	$3m$	C_{3v}	$\bar{3}m$	D_{3d}	D_6
422	D_4	$\{4mm$ / $\bar{4}2m$	C_{4v} / $D_{2d}\}$	$4/mmm$	D_{4h}	
622	D_6	$\{6mm$ / $\bar{6}m2$	C_{6v} / $D_{3h}\}$	$6/mmm$	D_{6h}	
23	T			$m3$	T_h	
432	O	$\bar{4}3m$	T_d	$m3m$	O_h	

thirty-two point groups, thirteen of which are isomorphous with at least one other crystallographic point group. The thirty-two crystallographic point groups are listed in Table 2.9.

Answers to Exercises 2.3

Exercise 2.3-1 The projection diagram is given in Figure 2.17. The dihedral planes are $\sigma_{\mathbf{x}}$, $\sigma_{\mathbf{b}}$, and $\sigma_{\mathbf{c}}$, where $\sigma_{\mathbf{x}}$ bisects the angle between $-\mathbf{b}$ and $\mathbf{c}$, $\sigma_{\mathbf{b}}$ bisects the angle between $\mathbf{x}$ and $\mathbf{c}$, and $\sigma_{\mathbf{c}}$ bisects the angle between $\mathbf{x}$ and $\mathbf{b}$.

Exercise 2.3-2 See Figure 2.18.

Exercise 2.3-3 If X, $Y \in$ P are conjugate, then for some $p_j \in$ P, $p_j \; X \; p_j^{-1} = Y$. But if $X \in R\{\mathrm{Q}\}$ in P, then $IX \in IR\{\mathrm{Q}\}$ in P′ and $p_j \; IX \; p_j^{-1} = IY$, so that IX and IY are conjugate in P′.

Exercise 2.3-4 $C_4 = \{C_2\} + C_4^+ \; \{C_2\} = \{E \; C_2\} + C_4^+ \; \{E \; C_2\} = \{E \; C_2 \; C_4^+ \; C_4^-\}$. But $\{C_2\} + IC_4^+ \; \{C_2\} = \{E \; C_2\} + S_4^- \; \{E \; C_2\} = \{E \; C_2 \; S_4^- \; S_4^+\} = S_4$. Use projection diagrams, if necessary, to verify the multiplication tables given in Tables 2.10 and 2.11. Clearly, the two multiplication tables are the same, corresponding elements being C_4^+ and $IC_4^+ = S_4^-$; C_4^- and $IC_4^- = S_4^+$. Both groups are Abelian.

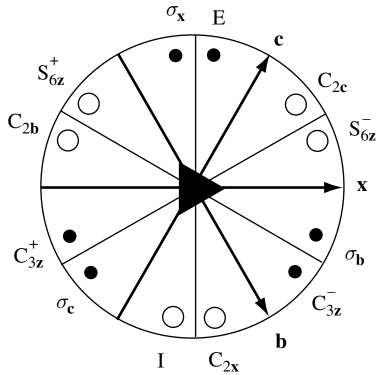


Figure 2.17. Projection diagram for the point group $D_{3d} = D_3 \otimes C_i$ (see eq. (2.3.9)). For example, $IC_{2\mathbf{b}} = \sigma_{\mathbf{b}}$, and this mirror plane normal to **b** bisects the angle between the C_2' axes $C_{2\mathbf{x}}$ and $C_{2\mathbf{c}}$ so that it is a dihedral plane. Similarly, $\sigma_{\mathbf{x}}$ and $\sigma_{\mathbf{c}}$ are dihedral planes.

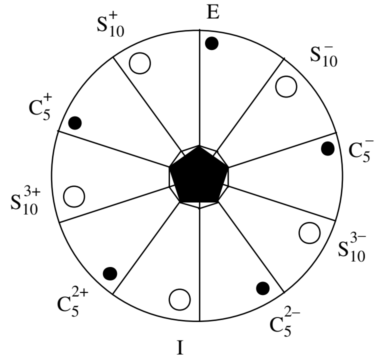


Figure 2.18. Projection diagram for the point group S_{10}.

Table 2.10. *Multiplication table for* C_4.

C_4	E	C_4^+	C_2	C_4^-
E	E	C_4^+	C_2	C_4^-
C_4^+	C_4^+	C_2	C_4^-	E
C_2	C_2	C_4^-	E	C_4^+
C_4^-	C_4^-	E	C_4^+	C_2

Table 2.11. *Multiplication table for* S_4.

S_4	E	S_4^-	C_2	S_4^+
E	E	S_4^-	C_2	S_4^+
S_4^-	S_4^-	C_2	S_4^+	E
C_2	C_2	S_4^+	E	S_4^-
S_4^+	S_4^+	E	S_4^-	C_2

2.4 Identification of molecular point groups

A systematic method for identifying the point group of any molecule is given in Figure 2.19. Some practice in the recognition of symmetry elements and in the assignment of point groups may be obtained through working through the following exercises and problems.

Exercise 2.4-1 Identify the symmetry point groups to which the following molecules belong. [*Hint*: For the two staggered configurations, imagine the view presented on looking down the C—C molecular axis.]

(a) nitrosyl chloride NOCl (non-linear),
(b) carbon dioxide O═C═O (linear),
(c) methane CH_4 (Figure 2.20),
(d) formaldehyde $H_2C{=}O$,
(e) carbonate ion CO_3^{-2} (planar),
(f) BrF_5 (pyramidal),
(g) staggered $H_3C—CCl_3$,
(h) $[PtCl_4]^{-2}$ (planar),
(i) staggered ethane $H_3C—CH_3$,
(j) $B(OH)_3$ (planar, Figure 2.20),
(k) IF_7 (pentagonal bipyramid),
(l) S_4 (non-planar).

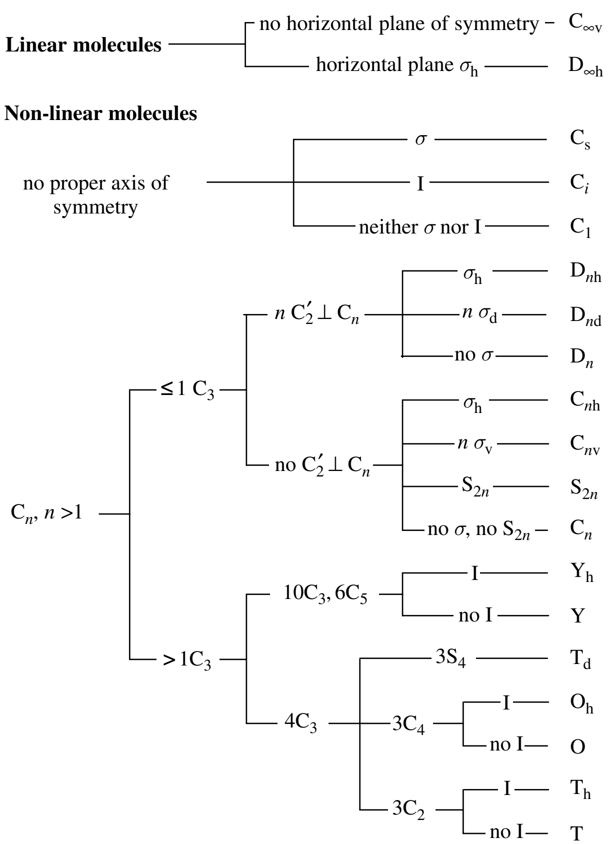


Figure 2.19. Identification of molecular point groups.

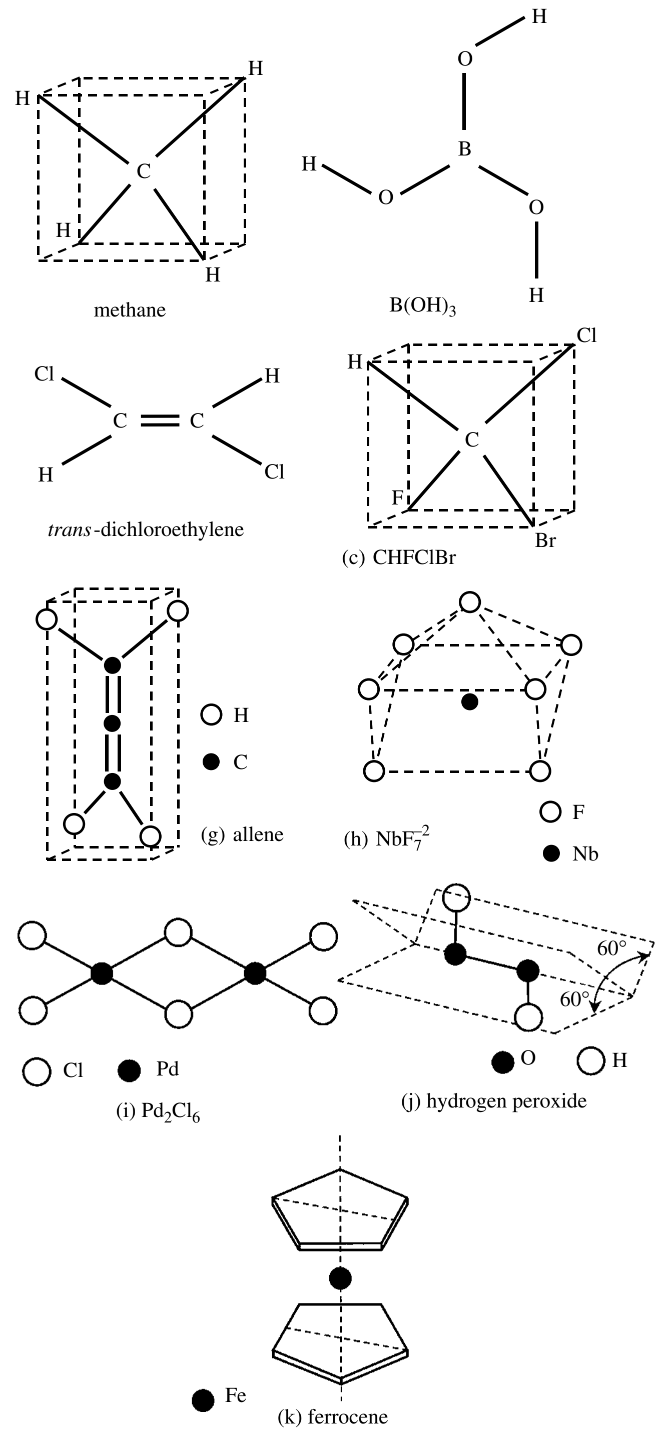


Figure 2.20. Structure of several molecules referred to in Exercise 2.4-1 and in the problems to this chapter. Lower case letters (c) and (g)–(k) refer to Problem 2.3.

Answer to Exercise 2.4-1

C_s; $D_{\infty h}$; T_d; C_{2v}; D_{3h}; C_{4v}; C_{3v}; D_{4h}; D_{3d}; C_{3h}; D_{5h}; T_d.

Problems

2.1 Prove the following results by using projection diagrams.

(a) Show that $R(\pi\ \mathbf{m})$ and $R(\pi\ \mathbf{n})$ commute when $\mathbf{m}$ is normal to $\mathbf{n}$.

(b) Show that $\sigma_{\mathbf{y}}\sigma_{\mathbf{x}} = C_{2\mathbf{z}}$.

(c) Two planes σ_1, σ_2 intersect along $\mathbf{n}$ and make an angle $\phi/2$ with one another. Show that $\sigma_2\sigma_1 = R(\phi\ \mathbf{n})$. Do σ_1 and σ_2 commute?

(d) Show that $R(\pi\ \mathbf{x})\ R(\beta\ \mathbf{z}) = R(-\beta\ \mathbf{z})\ R(\pi\ \mathbf{x})$.

2.2 Identify the set of symmetry operators associated with the molecule *trans*-dichloroethylene (Figure 2.20). Set up the multiplication table for these operators and hence show that they form a group. Name this symmetry group. [*Hint*: Set up a right-handed system of axes with **y** along the C═C bond and **z** normal to the plane of the molecule.]

2.3 Determine the symmetry elements of the following molecules and hence identify the point group to which each one belongs. [*Hints*: Adhere to the convention stated in Section 2.1. Many of these structures are illustrated in Figure 2.20. Sketching the view presented on looking down the molecular axis will be found helpful for (k) and (l).]

(a) NH_3 (non-planar),

(b) $H_3C—CCl_3$ (partly rotated),

(c) CHFClBr,

(d) $C_5H_5^-$ (planar),

(e) C_6H_6 (planar),

(f) $[TiF_6]^{-3}$ (octahedral),

(g) allene,

(h) $[NbF_7]^{-2}$,

(i) Pd_2Cl_6,

(j) hydrogen peroxide,

(k) bis(cyclopentadienyl)iron or ferrocene (staggered configuration),

(l) dibenzenechromium (like ferrocene, a "sandwich compound," but the two benzene rings are in the eclipsed configuration in the crystal).

2.4 List a sufficient number of symmetry elements in the molecules sketched in Figure 2.21 to enable you to identify the point group to which each belongs. Give the point group symbol in both Schönflies and International notation.

2.5 Show that each of the following sets of symmetry operators is a generator for a point group. State the point group symbol in both Schönflies and International notation. [*Hints*: The use of projection diagrams is generally an excellent method for calculating products of symmetry operators. See Figure 2.10(a) for the location of the $C_{2\mathbf{a}}$ axis.]

(a) $\{C_{2\mathbf{y}}\ C_{2\mathbf{z}}\}$,

(b) $\{C_{4\mathbf{z}}\ I\}$,

(c) $\{S_{4\mathbf{z}}\ C_{2\mathbf{x}}\}$,

(d) $\{C_{3\mathbf{z}}\ C_{2\mathbf{a}}\ I\}$,

(e) $\{C_{4\mathbf{z}}\ \sigma_{\mathbf{x}}\}$,

(f) $\{\bar{6}\}$,

(g) $\{S_{3\mathbf{z}}\ C_{2\mathbf{a}}\}$.

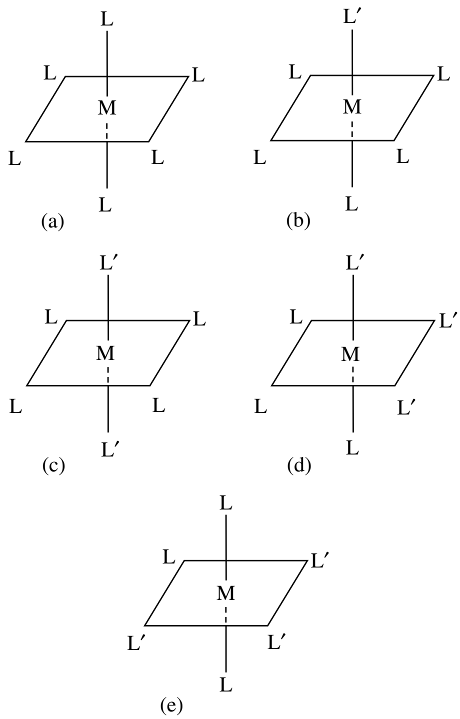


Figure 2.21. Configurations of an ML_6 complex ion and of some $ML_nL'_{6-n}$ complexes.

2.6 List a sufficient number of symmetry elements (and also significant absences) in the following *closo* $B_n H_n^{-2}$ ions that will enable you to determine the point group to which each belongs. The shapes of these molecules are shown in Figure 2.22.

(a) $B_5H_5^{-2}$,
(b) $B_6H_6^{-2}$,
(c) $B_9H_9^{-2}$,
(d) $B_{10}H_{10}^{-2}$,
(e) $B_{12}H_{12}^{-2}$.

2.7 Evaluate the following DPs showing the symmetry operators in each group. [*Hint*: For (a)–(e), evaluate products using projection diagrams. This technique is not useful for products that involve operators associated with the C_3 axes of a cube or tetrahedron, so in these cases study the transformations induced in a cube.] Explain why the DPs in (d)–(f) are semidirect products.

(a) $D_2 \otimes C_i$,
(b) $D_3 \otimes C_i$,
(c) $D_3 \otimes C_s$,
(d) $S_4 \wedge C_2$ ($C_2 = \{E\ C_{2\mathbf{x}}\}$),
(e) $D_2 \wedge C_2$ ($C_2 = \{E\ C_{2\mathbf{a}}\}$),
(f) $D_2 \wedge C_3$ ($C_3 = \{E\ C_{31}^{\pm}\}$).

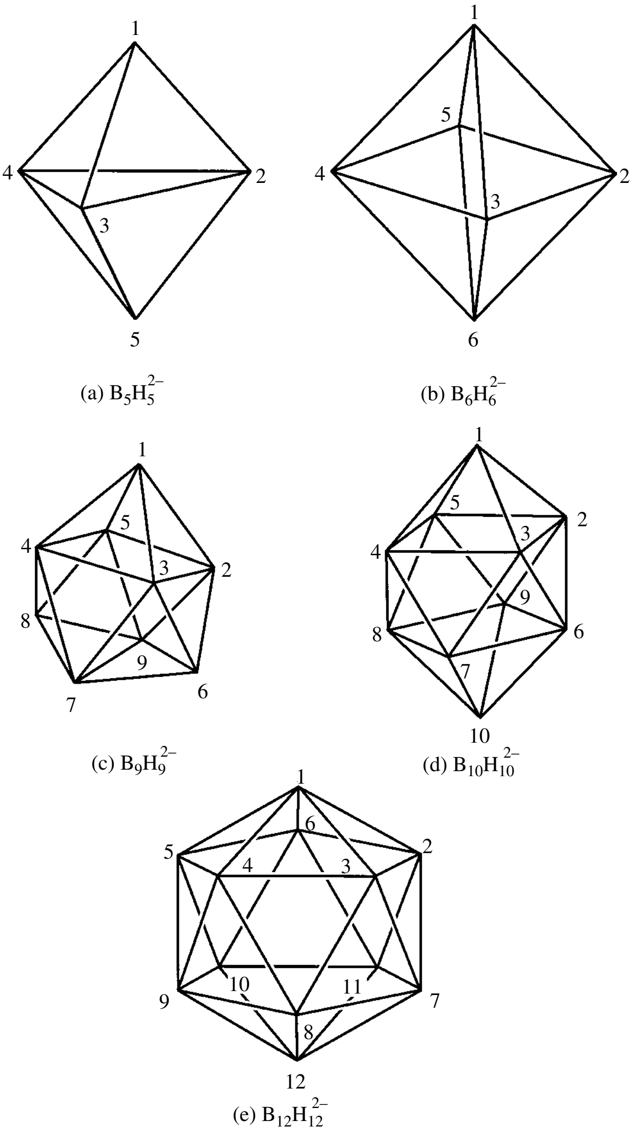


Figure 2.22. Some *closo* $B_nH_n^{-2}$ anions. The numbering scheme shown is conventional and will be an aid in identifying and describing the symmetry elements.

3 Matrix representatives

3.1 Linear vector spaces

In three-dimensional (3-D) configuration space (Figure 3.1) a position vector $\mathbf{r}$ is the *sum of its projections*,

$$\mathbf{r} = \mathbf{e}_1 x + \mathbf{e}_2 y + \mathbf{e}_3 z. \tag{1}$$

The set of three orthonormal basis vectors $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ in eq. (1) is the *basis* of a *linear vector space* (LVS), and the *coordinates* of the point P($x\ y\ z$) are the *components* of the vector $\mathbf{r}$. The *matrix representation* of $\mathbf{r}$ is

$$\mathbf{r} = \langle \mathbf{e}_1\ \ \mathbf{e}_2\ \ \mathbf{e}_3 | x\ y\ z \rangle. \tag{2}$$

$\langle \mathbf{e}_1\ \ \mathbf{e}_2\ \ \mathbf{e}_3|$ is a matrix of one row that contains the elements of the basis set, and $|\,x\ y\ z\rangle$ is a matrix of a single column containing the components of $\mathbf{r}$. The row × column law of matrix multiplication applied to the RS of eq. (2) yields eq. (1). The choice of basis vectors is arbitrary: they do not have to be mutually orthogonal but they must be linearly independent (LI) and three in number in 3-D space. Thus, $\{\mathbf{e}_1\ \ \mathbf{e}_2\ \ \mathbf{e}_3\}$ form a basis in 3-D space if it is impossible to find a set of numbers $\{v_1\ \ v_2\ \ v_3\}$ such that $\mathbf{e}_1 v_1 + \mathbf{e}_2 v_2 + \mathbf{e}_3 v_3 = 0$, except $v_j = 0, j = 1, 2, 3$. But any set of four or more vectors is linearly dependent in 3-D space. That is, the *dimensionality* of a vector space is the *maximum number of LI vectors* in that space. This is illustrated in Figure 3.2 for the example of two-dimensional (2-D) space, which is a subspace of 3-D space.

For a vector $\mathbf{v}$ in an LVS of n dimensions, eq. (1) is generalized to

$$\mathbf{v} = \sum_{i=1}^{n} \mathbf{e}_i\, v_i = \mathbf{e}_1 v_1 + \mathbf{e}_2 v_2 + \cdots + \mathbf{e}_n v_n$$
$$\neq 0,\ \text{unless}\ v_i = 0, \forall\ i = 1, \ldots, n. \tag{3}$$

In eq. (3), the vector $\mathbf{v}$ is the sum of its projections. The matrix representation of eq. (3) is

$$\mathbf{v} = \langle \mathbf{e}_1\ \mathbf{e}_2\ \ldots\ \mathbf{e}_n | v_1 v_2\ \ldots\ v_n \rangle \tag{4}$$

$$= \langle \mathbf{e} | v \rangle, \tag{5}$$

where, in eq. (5), the *row* matrix $\langle \mathbf{e}|$ implies the whole *basis* set, as given explicitly in eq. (4), and similarly v in the *column* matrix $|v\rangle$ implies the whole set of n *components*

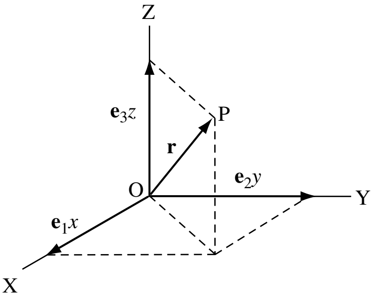


Figure 3.1. Projection of a vector OP along three orthogonal axes OX, OY, OZ.

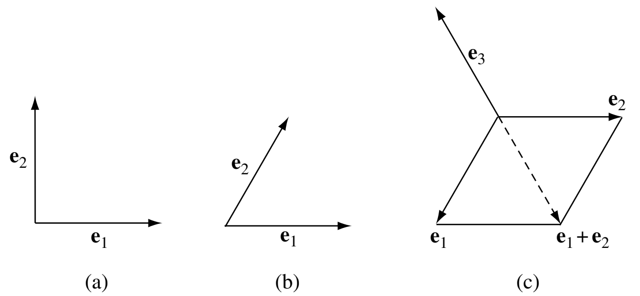


Figure 3.2. Examples, in 2-D space, of (a) an LI set of orthogonal basis vectors $\{\mathbf{e}_1\ \mathbf{e}_2\}$, (b) an LI non-orthogonal basis, and (c) a set of three basis vectors in 2-D space that are not LI because $\mathbf{e}_1 + \mathbf{e}_2 + \mathbf{e}_3 = 0$.

$\{v_1\ v_2\ \ldots\ v_n\}$. If the basis $\{\mathbf{e}_i\}$ and/or the components $\{v_j\}$ are complex, the definition of the scalar product has to be generalized. The Hermitian scalar product of two vectors **u** and **v** is defined by

$$\mathbf{u}^* \cdot \mathbf{v} = \langle \mathbf{e}|u\rangle^\dagger \cdot \langle \mathbf{e}|v\rangle, \tag{6}$$

the superscript † denoting the *adjoint* or transposed complex conjugate:

(5), (6)

$$\mathbf{u}^* \cdot \mathbf{v} = \langle u^*|\mathbf{e}^*\rangle \cdot \langle \mathbf{e}|v\rangle \tag{7a}$$

$$= \langle u^*|\mathtt{M}|v\rangle \tag{7b}$$

$$= \sum_{i,j} u_i{}^* \mathtt{M}_{ij} v_j. \tag{7c}$$

The square matrix

$$\mathtt{M} = |\mathbf{e}^*\rangle \cdot \langle \mathbf{e}| \tag{8}$$

is called the *metric* of the LVS:

$$\mathtt{M} = |\mathbf{e}_1{}^* \ \mathbf{e}_2{}^* \ \ldots \ \mathbf{e}_n{}^*\rangle \cdot \langle \mathbf{e}_1 \ \mathbf{e}_2 \ \ldots \ \mathbf{e}_n| = \begin{bmatrix} \mathbf{e}_1{}^* \cdot \mathbf{e}_1 & \mathbf{e}_1{}^* \cdot \mathbf{e}_2 & \ldots \\ \mathbf{e}_2{}^* \cdot \mathbf{e}_1 & \mathbf{e}_2{}^* \cdot \mathbf{e}_2 & \ldots \\ \vdots & \vdots & \vdots \end{bmatrix}. \tag{9}$$

Note that (i)

$$\mathtt{M}_{ij} = \mathbf{e}_i{}^* \cdot \mathbf{e}_j = \mathbf{e}_j \cdot \mathbf{e}_i{}^* = (\mathbf{e}_j{}^* \cdot \mathbf{e}_i)^* = \mathtt{M}_{ji}{}^* \tag{10}$$

so that $\mathtt{M}$ is a Hermitian matrix ($\mathtt{M} = \mathtt{M}^\dagger$). (ii) If the basis is *orthonormal* (or *unitary*)

$$\mathtt{M}_{ij} = \mathbf{e}_i{}^* \cdot \mathbf{e}_j = \delta_{ij} \tag{11}$$

and $\mathtt{M}$ is just the unit matrix with n rows and columns,

$$\mathtt{M} = \mathtt{E}_n. \tag{12}$$

In this case,

$$\mathbf{u}^* \cdot \mathbf{v} = \langle u^* | v \rangle = \sum_i u_i{}^* v_i. \tag{13}$$

In eqs. (7a) and (7b) $|v\rangle$ is a matrix of one column containing the components of $\mathbf{v}$, and $\langle u^*|$ is a matrix of one row, which is the transpose of $|u^*\rangle$, the matrix of one column containing the components of $\mathbf{u}$, complex conjugated. In eq. (6), transposition is necessary to conform with the matrix representation of the scalar product so that the row $\times$ column law of matrix multiplication may be applied. Complex conjugation is necessary to ensure that the length of a vector $\mathbf{v}$

$$v = |\mathbf{v}| = (\mathbf{v}^* \cdot \mathbf{v})^{1/2} \tag{14}$$

is real. A vector of unit length is said to be *normalized*, and any vector $\mathbf{v}$ can be normalized by dividing $\mathbf{v}$ by its length v.

3.2 Matrix representatives of operators

Suppose a basis $\langle \mathbf{e}|$ is transformed into a new basis $\langle \mathbf{e}'|$ under the proper rotation R, so that

$$R\langle \mathbf{e}| = \mathbf{e}'|, \tag{1}$$

or, in more detail,

$$R\langle \mathbf{e}_1 \ \mathbf{e}_2 \ \mathbf{e}_3| = \langle \mathbf{e}_1{}' \ \mathbf{e}_2{}' \ \mathbf{e}_3{}'|. \tag{2}$$

Then the new basis vectors $\{\mathbf{e}_j{}'\}$ can be expressed in terms of the old set by writing $\mathbf{e}_j{}'$ as the sum of its projections (cf. eq. (3.1.3)):

$$\mathbf{e}_j{}' = \sum_{i=1}^{3} \mathbf{e}_i \ \mathrm{r}_{ij}, \qquad j = 1, 2, 3; \tag{3}$$

$\mathbf{r}_{ij}$ is the component of $\mathbf{e}_j{}'$ along $\mathbf{e}_i$. In matrix form,

(3)
$$\langle \mathbf{e}_1{}' \ \mathbf{e}_2{}' \ \mathbf{e}_3{}'| = \langle \mathbf{e}_1 \ \mathbf{e}_2 \ \mathbf{e}_3|\Gamma(R), \tag{4}$$

where the square matrix

$$\Gamma(R) = [r_{ij}] = \begin{bmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \end{bmatrix} \tag{5}$$

and the r_{ij} in eq. (3) are seen to be the elements of the jth column of $\Gamma(R)$. In shorter notation,

(4)
$$\langle \mathbf{e}'| = \langle \mathbf{e}|\Gamma(R). \tag{6}$$

Equation (6), or eq. (4), is the matrix representation of the operation of deriving the new basis $\{\mathbf{e}_j{}'\}$ from the original basis $\{\mathbf{e}_i\}$, and when we carry out the matrix multiplication on the RS of eq. (6) or eq. (4) we are using eq. (3) successively for each $\mathbf{e}_j{}'$ in turn as $j = 1, 2, 3$.

(1), (6)
$$R\langle \mathbf{e}| = \langle \mathbf{e}'| = \langle \mathbf{e} \ |\Gamma(R), \tag{7}$$

which shows that $\Gamma(R)$ is the *matrix representative* (MR) of the operator R.

Example 3.2-1 When R is the identity E, $\langle \mathbf{e}'|$ is just $\langle \mathbf{e}|$ and so $\Gamma(E)$ is the 3×3 unit matrix, E_3.

Example 3.2-2 Consider a basis of three orthogonal unit vectors with $\mathbf{e}_3$ (along OZ) normal to the plane of the paper, and consider the proper rotation of this basis about OZ through an angle ϕ by the operator R (ϕ **z**) (see Figure 3.3). Any vector **v** may be expressed as the sum of its projections along the basis vectors:

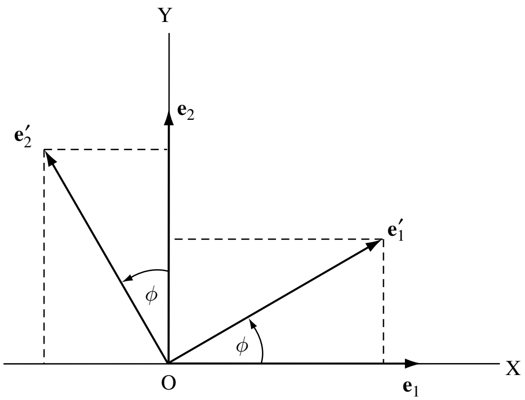


Figure 3.3. Rotation of configuration space, and therefore of all vectors in configuration space including $\{\mathbf{e}_1 \ \mathbf{e}_2 \ \mathbf{e}_3\}$, through an angle ϕ about OZ (active representation).

$$\mathbf{v} = \sum_i \mathbf{e}_i \; v_i. \tag{3.1.3}$$

To find the ith component v_i, take the scalar product of $\mathbf{e}_i$ with $\mathbf{v}$. Here the basis is real and orthonormal, so

(3.1.3)
$$\mathbf{e}_i \cdot \mathbf{v} = \mathbf{e}_i \cdot \sum_j \mathbf{e}_j \; v_j = \sum_j \delta_{ij} \; v_j = v_i. \tag{8}$$

We now represent the transformed basis vectors $\{\mathbf{e}_j{}'\}$ in terms of the original set $\{\mathbf{e}_i\}$ by expressing each as the sum of its projections, according to eq. (3). Writing each $\mathbf{e}_j{}'$ ($j = 1, 2, 3$) as the sum of their projections along $\{\mathbf{e}_i\}$ yields

$$\begin{aligned} \mathbf{e}_1{}' &= \mathbf{e}_1(\cos\phi) + \mathbf{e}_2(\sin\phi) + \mathbf{e}_3(0) \\ \mathbf{e}_2{}' &= \mathbf{e}_1(-\sin\phi) + \mathbf{e}_2(\cos\phi) + \mathbf{e}_3(0) \\ \mathbf{e}_3{}' &= \mathbf{e}_1(0) + \mathbf{e}_2(0) + \mathbf{e}_3(1) \end{aligned} \tag{9}$$

where we have used the fact that the scalar product of two unit vectors at an angle θ is $\cos\theta$, and that $\cos(\frac{1}{2}\pi - \phi) = \sin\phi$, $\cos(\frac{1}{2}\pi + \phi) = -\sin\{\phi\}$, and $\cos 0 = 1$. Because of the row × column law of matrix multiplication, eqs. (9) may be written as

$$\langle \mathbf{e}_1{}' \; \mathbf{e}_2{}' \; \mathbf{e}_3{}' \,| = \langle \mathbf{e}_1 \; \mathbf{e}_2 \; \mathbf{e}_3 | \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{10}$$

On using eq. (7), the MR of $R(\phi\ \mathbf{z})$ is seen to be

(10)
$$\Gamma(R(\phi\ \mathbf{z})) = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} c & -s & 0 \\ s & c & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{11}$$

where $c = \cos\phi$, $s = \sin\phi$. The proper rotation $R(\phi\ \mathbf{z})$ rotates a vector $\mathbf{r}$ in configuration space into the vector $\mathbf{r}'$ given by

(7)
$$\mathbf{r}' = R\ \mathbf{r} = R\langle \mathbf{e}|r\rangle = \langle \mathbf{e}'|r\rangle = \langle \mathbf{e}|\Gamma(R)|r\rangle = \langle \mathbf{e}|r'\rangle. \tag{12}$$

For $R = R\ (\phi\ \mathbf{z})$, the components of $\mathbf{r}'$ (which are the coordinates of the transformed point P′) are in

(12)
$$|r'\rangle = \Gamma(R)|r\rangle, \tag{13}$$

which provides a means of calculating the components of $|r'\rangle$ from

(13), (11)
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} c & -s & 0 \\ s & c & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}. \tag{14}$$

Example 3.2-3 Find the t ransformed components of a vector **r** when acted on by the operator $C_{4z}^{+} = R(\pi/2 \;\; \mathbf{z})$.

(14)
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} c & -s & 0 \\ s & c & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \bar{y} \\ x \\ z \end{bmatrix}. \tag{15}$$

The set of components of the vector $\mathbf{r}'$ in eq. (13) is the *Jones symbol* or Jones faithful representation of the symmetry operator R, and is usually written as $(x'\, y'\, z')$ or $x'\, y'\, z'$. For example, from eq. (15) the Jones symbol of the operator R $(\pi/2 \;\; \mathbf{z})$ is $(\bar{y}\, x\, z)$ or $\bar{y}\, x\, z$. In order to save space, particularly in tables, we will usually present Jones symbols without parentheses. A "faithful representation" is one which obeys the same multiplication table as the group elements (symmetry operators).

The inversion operator I leaves $\langle \mathbf{e}|$ invariant but changes the sign of the components of **r** (see eq. (2.1.5) and Figure 2.3):

$$I\langle \mathbf{e}|r\rangle = \langle \mathbf{e}|I|r\rangle = \langle \mathbf{e}|\Gamma(I)|r\rangle; \tag{16}$$

(16)
$$I|x\; y\; z\rangle = \Gamma(I)|x\; y\; z\rangle = |-x \;\; -y \;\; -z\rangle. \tag{17}$$

Therefore the MR of I is

(17)
$$\Gamma(I) = \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}. \tag{18}$$

It follows that if R is a proper rotation and $R|x\; y\; z\rangle = |x'\; y'\; z'\rangle$, then

(17)
$$IR|x\; y\; z\rangle = I|x'\; y'\; z'\rangle = |-x' \; -y' \; -z'\rangle. \tag{19}$$

The improper rotation $S(\phi\, \mathbf{n}) = IR(\phi \mp \pi \;\; \mathbf{n})$, for $\phi>0$ or $\phi<0$ (see eq. (2.1.9)), so that it is sometimes convenient to have the MR of $S(\phi \;\; \mathbf{n})$ as well. In the improper rotation $S(\phi\; \mathbf{z}) = \sigma_{\mathbf{z}} R(\phi\; \mathbf{z})$, $\sigma_{\mathbf{z}}|x\; y\; z\,\rangle = |x\, y\, \bar{z}\rangle$, and so the MR of $S(\phi\; \mathbf{z})$ is

(11)
$$\Gamma(S(\phi\; \mathbf{z})) = \begin{bmatrix} c & -s & 0 \\ s & c & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}. \tag{20}$$

Exercise 3.2-1 Write down the Jones symbol for the improper rotation $S_{4\mathbf{z}}^{-}$.

Exercise 3.2-2 Show that $S_n^{\pm k} = IC_n^{k \mp (n/2)}$. Find operators of the form IC_n^k that are equivalent to $S_{4\mathbf{z}}^{\pm}$ and $S_{6\mathbf{z}}^{\pm}$.

It is demonstrated in Problem 3.1 that $\Gamma(R)$ and $\Gamma(S)$ are real orthogonal matrices. An orthogonal matrix $\mathbb{A}$ has the property $\mathbb{A}^{\mathrm{T}}\mathbb{A} = \mathbb{E}$, where $\mathbb{E}$ is the unit matrix, so that $\mathbb{A}^{-1} = \mathbb{A}^{\mathrm{T}}$, which makes the calculation of $\Gamma(R)^{-1}$ and $\Gamma(S)^{-1}$ very straightforward or simple (to use space). Equations (13), (17), and (19) are of considerable importance since every point symmetry operation, apart from E and I, is equivalent to a proper or improper rotation.

Example 3.2-4 Nevertheless it is convenient to have the MR of $\sigma(\theta\ \mathbf{y})$, the operator that produces reflection in a plane whose normal **m** makes an angle θ with **y** (Figure 3.4) so that the reflecting plane makes an angle θ with the **zx** plane.

From Figure 3.4,

$$x = \cos\alpha,\ \ y = \sin\alpha, \tag{21}$$

$$x' = \cos(2\theta - \alpha) = x\cos(2\theta) + y\sin(2\theta), \tag{22}$$

$$y' = \sin(2\theta - \alpha) = x\sin(2\theta) - y\cos(2\theta). \tag{23}$$

(21)–(23)
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos 2\theta & \sin 2\theta & 0 \\ \sin 2\theta & -\cos 2\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \tag{24}$$

so that the MR of $\sigma(\theta\,\mathbf{y})$ is

(24)
$$\Gamma(\sigma(\theta\ \mathbf{y})) = \begin{bmatrix} \cos 2\theta & \sin 2\theta & 0 \\ \sin 2\theta & -\cos 2\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{25}$$

Example 3.2-5 The MR of $\sigma(\pi/3\ \ \mathbf{y})$ is

(22)
$$\Gamma(\sigma(\pi/3\quad \mathbf{y})) = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{26}$$

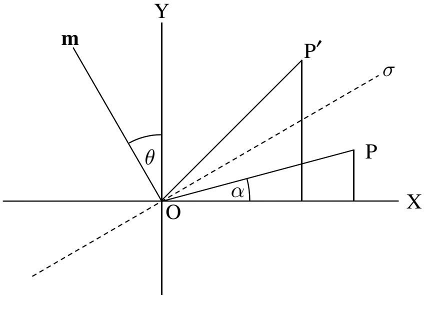


Figure 3.4. Reflection of a point $P(x\ \ y)$ in a mirror plane σ whose normal **m** makes an angle θ with **y**, so that the angle between σ and the **zx** plane is θ. OP makes an angle α with **x**. $P'(x'\ \ y')$ is the reflection of P in σ, and OP′ makes an angle $2\theta - \alpha$ with **x**.

Answers to Exercises 3.2

Exercise 3.2-1 From eqs. (15) and (19), the Jones symbol for $S_{4\mathbf{z}}^{-}$ is $y\ \bar{x}\ \bar{z}$.

Exercise 3.2-2 Let $S(\phi\ \mathbf{n}) = IC\ (\phi'\ \mathbf{n})$. Then $\phi = 2\pi k/n$ and $\phi' = 2\pi[k \mp (n/2)]/n$ so that $S_n^k = IC_n^{k \mp (n/2)}$. Therefore, $S_{4\mathbf{z}}^{\pm} = IC_{4\mathbf{z}}^{\mp}$ and $S_{6\mathbf{z}}^{\pm} = IC_{3\mathbf{z}}^{\mp}$.

3.3 Mappings

When the symmetry operator $R \in$ G acts on configuration space, a vector $\mathbf{r}$ is transformed into $\mathbf{r}' = R\ \mathbf{r}$; $\mathbf{r}'$ is the *image* of $\mathbf{r}$, and the process whereby $R\{\mathbf{r}\} \rightarrow \{\mathbf{r}'\}$ is called a *mapping*. The components of $\mathbf{r}'$ are given by

(3.2.13), (3.2.19) $$|x'\ y'\ z'\rangle = \Gamma(R)|x\ y\ z\rangle, \tag{1}$$

where $\Gamma(R)$ is the MR of the *operator* R. Equation (1) will be found to be extremely useful, for it enables us to find the effect of a symmetry operator R on the coordinates of P($x\ y\ z$). (In eq. (1) R may be the identity, the inversion operator, or a proper or improper rotation.) The lengths of all vectors and the angles between them are invariant under symmetry operations and so, therefore, are scalar products. Consider the transformation of two vectors $\mathbf{u}$, $\mathbf{v}$ into $\mathbf{u}'$, $\mathbf{v}'$ under the symmetry operator R:

(3.2.12) $$\mathbf{u}' = R\ \mathbf{u} = R\langle\mathbf{e}|u\rangle = \langle\mathbf{e}|\Gamma(R)|u\rangle, \tag{2}$$

(3.2.12) $$\mathbf{v}' = R\ \mathbf{v} = R\langle\mathbf{e}|v\rangle = \langle\mathbf{e}|\Gamma(\mathrm{R})|v\rangle. \tag{3}$$

The Hermitian scalar product of $\mathbf{u}$ and $\mathbf{v}$ is

(3.1.6) $$\mathbf{u}^* \cdot \mathbf{v} = \langle\mathbf{e}|u\rangle^\dagger \cdot \langle\mathbf{e}|v\rangle$$

(3.1.7a) $$= \langle u^*|\mathtt{M}|v\rangle. \tag{4}$$

Similarly, that of $\mathbf{u}'$ and $\mathbf{v}'$ is

(2), (3) $$\mathbf{u}'^* \cdot \mathbf{v}' = \langle\mathbf{e}|\Gamma(R)|u\rangle^\dagger \cdot \langle\mathbf{e}|\Gamma(R)|v\rangle. \tag{5}$$

The adjoint of a product of matrices is the product of the adjoints in reverse order, so

(5) $$\mathbf{u}'^* \cdot \mathbf{v}' = \langle u^*|\Gamma(R)^\dagger|\mathbf{e}^*\rangle \cdot \langle\mathbf{e}|\Gamma(R)|v\rangle$$

(3.1.8) $$= \langle u^*|\Gamma(R)^\dagger \mathtt{M}\Gamma(R)|v\rangle. \tag{6}$$

Because the scalar product is invariant under R, $\mathbf{u}'^* \cdot \mathbf{v}' = \mathbf{u}^* \cdot \mathbf{v}$, and

(6), (4) $$\Gamma(R)^\dagger \mathtt{M}\Gamma(R) = \mathtt{M}. \tag{7}$$

In group theory the most important cases are those of an orthogonal or unitary basis when $\mathtt{M}$ is the 3×3 unit matrix, and consequently

(7) $$\Gamma(R)^{\dagger}\Gamma(R) = \mathbb{E}. \tag{8}$$

Equation (8) shows that $\Gamma(R)$ is a *unitary* matrix and that

$$[\Gamma(R)]^{-1} = \Gamma(R)^{\dagger} = [\Gamma(R)]^{*\mathrm{T}}, \tag{9}$$

where the superscript T denotes the transposed matrix. When the MR $\Gamma(R)$ is real,

(9) $$[\Gamma(R)]^{-1} = [\Gamma(R)]^{\mathrm{T}}. \tag{10}$$

This is a most useful result since we often need to calculate the inverse of a 3×3 MR of a symmetry operator R. Equation (10) shows that when $\Gamma(R)$ is real, $\Gamma(R)^{-1}$ is just the transpose of $\Gamma(R)$. A matrix with this property is an *orthogonal* matrix. In configuration space the basis and the components of vectors are real, so that proper and improper rotations which leave all lengths and angles invariant are therefore represented by 3×3 real orthogonal matrices. Proper and improper rotations in configuration space may be distinguished by det $\Gamma(R)$,

(10) $$\Gamma(R)\Gamma(R)^{\mathrm{T}} = \Gamma(R)^{\mathrm{T}}\Gamma(R) = \mathbb{E}. \tag{11}$$

Since

$$\det \mathbb{A}\,\mathbb{B} = \det \mathbb{A} \det \mathbb{B},$$

(11) $$\det\,\Gamma(R)^{\mathrm{T}}\Gamma(R) = \det\,\Gamma(R)^{\mathrm{T}}\,\det\,\Gamma(R) = [\det\,\Gamma(R)]^2 = 1, \tag{12}$$

(12) $$\det\,\Gamma(R) = \pm 1 \quad (\Gamma(R)\ \text{real}). \tag{13}$$

Real 3×3 orthogonal matrices with determinant +1 are called *special orthogonal* (SO) matrices and they represent proper rotations, while those with determinant −1 represent improper rotations. The set of all 3×3 real orthogonal matrices form a group called the *orthogonal group* O(3); the set of all SO matrices form a subgroup of O(3) called the *special orthogonal group* SO(3).

Exercise 3.3-1 Evaluate the matrix representative of $R(\pi/2\ \ \mathbf{z})$ by considering the rotation of the basis vectors $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ into $\{\mathbf{e}_1{}'\ \mathbf{e}_2{}'\ \mathbf{e}_3{}'\}$.

Exercise 3.3-2 The set of real 3×3 orthogonal matrices with determinant −1 does not form a group. Why?

Answers to Exercises 3.3

Exercise 3.3-1 As shown in Figure 3.5,

$$R(\pi/2\ \ \mathbf{z})\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3| = \langle \mathbf{e}_2\ -\mathbf{e}_1\ \mathbf{e}_3| = \langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3| \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

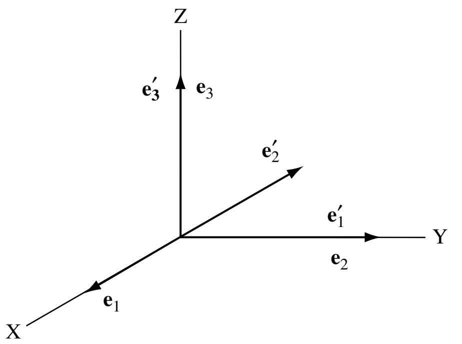


Figure 3.5. Effect of $R(\pi/2\ \mathbf{z})$ on $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$.

Exercise 3.3-2 The identity in O(3) is $\Gamma(E) = \mathrm{E}_3$, the 3×3 unit matrix with determinant $+1$. The set of all 3×3 real orthogonal matrices with determinant -1 does not contain the identity and therefore cannot form a group.

3.4 Group representations

If $\{R, S, T, \ldots\}$ form a group G, then the set of MRs $\{\Gamma(R), \Gamma(S), \Gamma(T), \ldots\}$ forms a group that is isomorphous with G called a *group representation*. Suppose that $RS = T$; then

(3.2.12) $$T\mathbf{v} = \langle \mathbf{e}|\Gamma(T)|\mathbf{v}\rangle, \tag{1}$$

$$T\mathbf{v} = RS\mathbf{v} = R\mathbf{v}' \text{ (given)}, \tag{2}$$

$$\mathbf{v}' = S\mathbf{v} \text{ (definition of } \mathbf{v}'). \tag{3}$$

(3), (3.2.13) $$|v'\rangle = \Gamma(S)|v\rangle, \tag{4}$$

(4), (3.2.12) $$R\mathbf{v}' = \langle \mathbf{e}|\Gamma(R)|v'\rangle = \langle \mathbf{e}|\Gamma(R)\ \Gamma(S)|v\rangle, \tag{5}$$

(1), (2), (5) $$\Gamma(R)\ \Gamma(S) = \Gamma(T). \tag{6}$$

Equation (6) shows that the MRs obey the same multiplication table as the operators, and so $\{\Gamma(R), \Gamma(S), \Gamma(T), \ldots\}$ forms a group that is isomorphous with $\mathrm{G} = \{R, S, T, \ldots\}$. Such a matrix group is an example of a group representation.

3.5 Transformation of functions

We have studied the transformation of vectors induced by symmetry operators, and this led us to the concept of the MR of a symmetry operator. In order to understand how atomic orbitals transform in symmetry operations, we must now study the transformation of *functions*. To say that $f(x, y, z)$ is a *function* of the set of variables $\{x\} \equiv \{x\ y\ z\}$ means that $f(\{x\})$ has a definite value at each point $P(x, y, z)$ with coordinates $\{x, y, z\}$. Note that we will be using $\{x\}$ as an abbreviation for $\{x\ y\ z\}$ and similarly $\{x'\}$ for $\{x'\ y'\ z'\}$. Now suppose that a symmetry operator R transforms $P(x\ y\ z)$ into $P'(x'\ y'\ z'\}$so that

$$R\{x\} = \{x'\}; \tag{1}$$

(3.3.3) $$|x'\rangle = \Gamma(R)|x\rangle. \tag{2}$$

$|x'\rangle$ is a matrix of one column containing the coordinates $\{x'\ y'\ z'\}$ of the transformed point P′. (Recall the correspondence between the coordinates of the point P and the components of the vector **r** that joins P to the origin O of the coordinate system, Figure 3.1.) But since a symmetry operator leaves a system in an indistinguishable configuration (for example, interchanges indistinguishable particles), the *properties* of the system are unaffected by R. Therefore R must also transform f into some new function $\hat{R}f$ in such a way that

$$\hat{R}f(\{x'\}) = f(\{x\}). \tag{3}$$

$\hat{R}$, which transforms f into a new function $f' = \hat{R}f$, is called a *function operator*. Equation (3) states that "the value of the new function $\hat{R}f$, evaluated at the transformed point $\{x'\}$, is the same as the value of the original function f evaluated at the original point $\{x\}$." Equation (3) is of great importance in applications of group theory. It is based (i) on what we understand by a function and (ii) on the invariance of physical properties under symmetry operations. The consequence of (i) and (ii) is that when a symmetry operator acts on configuration space, any function f is simultaneously transformed into a new function $\hat{R}f$. We now require a prescription for calculating $\hat{R}f$. Under the symmetry operator R, each point P is transformed into P′:

$$R\ P(x\ y\ z) = P'(x'\ \ y'\ z'). \tag{4}$$

(4) $$R^{-1}P'(x'\ y'\ z') = P(x\ y\ z); \tag{5}$$

(3), (5) $$\hat{R}f(\{x'\}) = f(\{x\}) = f(R^{-1}\{x'\}). \tag{6}$$

The primes in eq. (6) can be dispensed with since it is applicable at *any* point $P'\ (x'\ y'\ z')$:

(6) $$\hat{R}f(\{x\}) = f(R^{-1}\{x\}). \tag{7}$$

Example 3.5-1 Consider the effect of $R(\pi/2\ \ \mathbf{z})$ on the d orbital $d_{xy} = x\ y\ g(r)$, where $g(r)$ is a function of r only and the angular dependence is contained in the factor $x\ y$, which is therefore used as an identifying subscript on d.

$$(3.2.15)\qquad \Gamma(R) = \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \tag{8}$$

$$(3.3.10)\qquad [\Gamma(R)]^{-1} = [\Gamma(R)]^{\mathrm{T}} = \begin{bmatrix} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \tag{9}$$

$$(9)\qquad \begin{bmatrix} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} y \\ \bar{x} \\ z \end{bmatrix}; \tag{10}$$

$$(10)\qquad R^{-1}\{x\ y\ z\} = \{y\ \bar{x}\ z\}. \tag{11}$$

In other words, the Jones symbol for the operator R^{-1} is $y\ \bar{x}\ z$. Therefore $\hat{R}f(\{x\})$ is

$$\begin{aligned} \hat{R}\ d_{xy} &= d_{xy}(R^{-1}\{x\}) \\ &= d_{xy}(\{y\ \bar{x}\ z\}) \\ &= y\bar{x}\ g(r),\ \text{ or } -xy\ g(r), \\ &= -d_{xy}\ . \end{aligned} \tag{12}$$

The second equality states that $f(\{x\ y\ z\})$ is to become $f(\{y\ \bar{x}\ z\})$ so that x is to be replaced by y, and y by $-x$ (and z by z); this is done on the third line, which shows that the function d_{xy} is transformed into the function $-d_{xy}$ under the symmetry operator $R(\pi/2\ \ \mathbf{z})$. Figure 3.6 shows that the value of $\hat{R}d_{xy} = d'_{xy} = -d_{xy}$ evaluated at the transformed point P′ has the same numerical value as d_{xy} evaluated at P. Figure 3.6 demonstrates an important result: the effect of the function operator $\hat{R}$ on d_{xy} is *just as if* the contours of the function had been rotated by $R(\pi/2\ \mathbf{z})$. However, eq. (7) will always supply the correct result for the transformed function, and is especially useful when it is difficult to visualize the rotation of the contours of the function.

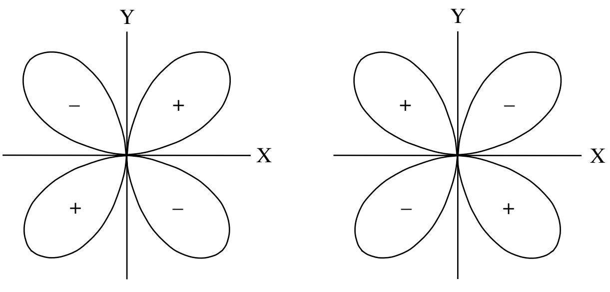


Figure 3.6. This figure shows that the effect on d_{xy} of the function operator $\hat{R}$, which corresponds to the symmetry operator $R = R(\pi/2\ \ \mathbf{z})$, is just as if the contours of the function had been rotated by R.

Exercise 3.5-1 Using $R\langle \mathbf{e}| = \langle \mathbf{e}'| = \langle \mathbf{e}|\Gamma(R)$, determine the MR $\Gamma(R)$ of the symmetry operator $R(\pi/2\ \ \mathbf{x})$. Hence find $R^{-1}\{x\ y\ z\}$ and then find how the three p orbitals transform under the symmetry operator $R(\pi/2\ \ \mathbf{x})$.

The complete set of function operators $\{\hat{R}\ \hat{S}\ \hat{T} \ldots\}$ forms a group isomorphous with the group of symmetry operators $\{R\ S\ T \ldots\}$ which transforms configuration space (and all points and vectors therein). The proof of this statement requires the inverse of the product RS. By definition, $(RS)^{-1}$ is the operator which, on multiplying RS, gives the identity E:

$$(RS)^{-1}RS = E; \tag{13}$$

$$S^{-1}R^{-1}R\ S = E \qquad (R^{-1}R = E, \forall\ R, S \ldots); \tag{14}$$

(13), (14) $$(RS)^{-1} = S^{-1}R^{-1}. \tag{15}$$

This is the anticipated result since the MRs of symmetry operators obey the same multiplication table as the operators themselves, and it is known from the properties of matrices that

$$[\Gamma(R)\Gamma(S)]^{-1} = \Gamma(S)^{-1}\Gamma(R)^{-1}. \tag{16}$$

Suppose that $RS = T$. Then,

$$\hat{S}f(\{x\}) = f(S^{-1}\{x\}) = f'(\{x\}), \tag{17}$$

where f' denotes the transformed function $\hat{S}f$.

(17), (7) $$\hat{R}\hat{S}f(\{x\}) = \hat{R}f'(\{x\}) = f'(R^{-1}\{x\}). \tag{18}$$

(17), (18) $$\hat{R}\hat{S}f(\{x\}) = f(S^{-1}R^{-1}\{x\})$$
(15) $$= f((RS)^{-1}\{x\})$$
(17) $$= f(T^{-1}\{x\})$$
(7) $$= \hat{T}f(\{x\}); \tag{19}$$

(18), (19) $$\hat{R}\hat{S} = \hat{T}. \tag{20}$$

Equation (20) verifies that the set of function operators $\{\hat{R}\ \hat{S}\ \hat{T} \ldots\}$ obeys the same multiplication table as the set of symmetry operators $G = \{R\ S\ T \ldots\}$ and therefore forms a group isomorphous with G.

Answer to Exercise 3.5-1

From Figure 3.7(a),

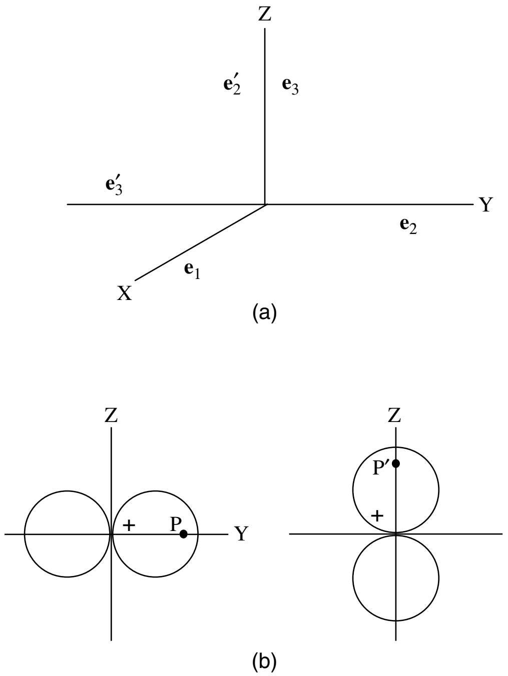


Figure 3.7. (a) Transformation of the basis set $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ under $R(\pi/2\ \mathbf{x})$. (b) Illustration of $\hat{R}p_y = p_y' = p_z$. The value of the original function p_y at P(0 a 0) is the same as that of the transformed function p_z at P′(0 0 a).

$$R\langle\mathbf{e}_1\,\mathbf{e}_2\,\mathbf{e}_3| = \langle\mathbf{e}_1{}'\,\mathbf{e}_2{}'\,\mathbf{e}_3{}'\,| = \langle\mathbf{e}_1\,\mathbf{e}_3\,\bar{\mathbf{e}}_2|$$
$$= \langle\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|\Gamma(R) = \langle\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|\begin{bmatrix}1 & 0 & 0\\ 0 & 0 & \bar{1}\\ 0 & 1 & 0\end{bmatrix};$$

$$R^{-1}\{x\ y\ z\} = \Gamma(R^{-1})\begin{bmatrix}x\\ y\\ z\end{bmatrix} = \begin{bmatrix}1 & 0 & 0\\ 0 & 0 & 1\\ 0 & \bar{1} & 0\end{bmatrix}\begin{bmatrix}x\\ y\\ z\end{bmatrix} = \begin{bmatrix}x\\ z\\ \bar{y}\end{bmatrix}. \tag{21}$$

$$\hat{R}\{p_x\ p_y\ p_z\} = \hat{R}\{x\ g(r)\ y\ g(r)\ z\ g(r)\}$$
$$= \{p_x(R^{-1}\{x\})\ p_y(R^{-1}\{x\})\ p_z(R^{-1}\{x\})\}$$

(21)

$$= \{p_x\ p_z\ {-p_y}\}, \tag{22}$$

on replacing $\{x\ y\ z\}$ by $\{x\,y\,\bar{z}\}$ in $\{p_x\ p_y\ p_z\}$. Equation (22) states that p_z is the function which, when evaluated at the transformed point $\{x\ y\ z\}$, has the same value as the original function p_y evaluated at the original point $R^{-1}\{x\,y\,z\} = \{x\,z\,\bar{y}\}$. For example, $p_z(\{0\ 0\ a\}) = p_y(\{0\ a\ 0\})$. Note from Figure 3.7(b) that the effect of R on p_y is simply to rotate the contour of the function p_y into that of p_z.

3.6 Some quantum mechanical considerations

For a quantum mechanical state function $\psi(\{x\})$, the RS of eq. (3.5.7) requires multiplication by ω, a phase factor or complex number of modulus unity. Since the choice of phase is arbitrary and has no effect on physical properties, we generally make the most convenient choice of phase, which here is $\omega = 1$. So, for the matrix representations used in Chapters 1–11, we may use eq. (3.5.7) without modification for function operators $\hat{R}$ operating on quantum mechanical state functions, as indeed we have already done in Example 3.5-1. However, there are certain kinds of representations called *projective* or *multiplier* representations for which the conventions used result in phase factors that are not always $+1$. These representations are discussed in Chapter 12.

We already know from the invariance of the scalar product under symmetry operations that spatial symmetry operators are unitary operators, that is they obey the relation $R^{\dagger}R = R\,R^{\dagger} = E$, where E is the identity operator. It follows from eq. (3.5.7) that the set of function operators $\{\hat{R}\}$ are also unitary operators.

Exercise 3.6-1 Prove that the function operators $\{\hat{R}\}$ are unitary.

In quantum mechanics the stationary states of a system are described by the state function (or wave function) $\psi(\{x\})$, which satisfies the time-independent Schrödinger equation

$$\hat{H}\psi(\{x\}) = \mathrm{E}\psi(\{x\}). \tag{1}$$

Here $\{x\}$ stands for the positional coordinates of all the particles in the system, E is the energy of the system, and $\hat{H}$ is the Hamiltonian operator. Since a symmetry operator merely rearranges indistinguishable particles so as to leave the system in an indistinguishable configuration, the Hamiltonian is invariant under any spatial symmetry operator R. Let $\{\psi_i\}$ denote a set of eigenfunctions of $\hat{H}$ so that

$$\hat{H}\psi_i = \mathrm{E}_i\psi_i. \tag{2}$$

Suppose that a symmetry operator R acts on the physical system (atom, molecule, crystal, etc.). Then ψ_i is transformed into the function $\hat{R}\psi_i$, where $\hat{R}$ is a function operator corresponding to the symmetry operator R. Physical properties, and specifically here the energy eigenvalues $\{\mathrm{E}_i\}$, are invariant under symmetry operators that leave the system in indistinguishable configurations. Consequently, $\hat{R}\psi_i$ is also an eigenfunction of $\hat{H}$ with the same eigenvalue E_i, which therefore is degenerate:

$$\text{(2)} \qquad \hat{H}\,\hat{R}\psi_i = \mathrm{E}_i\,\hat{R}\psi_i = \hat{R}\,\mathrm{E}_i\psi_i = \hat{R}\,\hat{H}\psi_i. \tag{3}$$

Because the eigenfunctions of any linear Hermitian operator form a complete set, in the sense that any arbitrary function that satisfies appropriate boundary conditions can be expressed as a linear superposition of this set, eq. (3) holds also for such arbitrary functions. Therefore,

$$\text{(3)} \qquad [\hat{R},\ \hat{H}] = 0, \tag{4}$$

and any function operator $\hat{R}$ that corresponds to a symmetry operator R therefore commutes with the Hamiltonian. The set of all function operators $\{\hat{R}\}$ which commute with the Hamiltonian, and which form a group isomorphous with the set of symmetry operators $\{R\}$, is known as the *group of the Hamiltonian* or the *group of the Schrödinger equation*.

Answer to Exercise 3.6-1

$$\begin{aligned}\hat{R}\,\hat{R}^{\dagger}\psi(\{x\}) &= \hat{R}\,\psi'(\{x\}) = \psi'(R^{-1}\{x\}) = \hat{R}^{\dagger}\psi(R^{-1}\{x\})\\ &= \psi((R^{\dagger})^{-1}R^{-1}\{x\}) = \psi((RR^{\dagger})^{-1}\{x\})\\ &= \psi(E^{-1}\{x\}) = \hat{E}\psi(\{x\}),\end{aligned}$$

where E is the identity operator, whence it follows that the function operators $\{\hat{R}\}$ also are unitary.

Problems

3.1 Show by evaluating $[\Gamma(R)]^{\mathrm{T}}\,\Gamma(R)$, where R is the proper rotation $R(\phi\ \mathbf{z})$, that $\Gamma(R)$ is an orthogonal matrix, and hence write down $[\Gamma(R)]^{-1}$. Also write down $\Gamma(R(-\phi\ \mathbf{z}))$. Is this the same matrix as $\Gamma(R(\phi\ \mathbf{z}))^{-1}$ and, if so, is this the result you would expect? Evaluate det $\Gamma(R(\phi\ \mathbf{z}))$ and det $\Gamma(S(\phi\ \mathbf{z}))$.

3.2 Find the MR $\Gamma(R)$ for $R = R(2\pi/3\ \ \mathbf{n})$ with $\mathbf{n}$ a unit vector from O along an axis that makes equal angles with OX, OY, and OZ. What is the trace of $\Gamma(R)$? Find $|x'\ y'\ z'\rangle = \Gamma(R)|x\ y\ z\rangle$ and write down the Jones symbol for this operation. [*Hints*: Consider the effect of $R(2\pi/3\ \ \mathbf{n})$ by noting the action of R on $\langle\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|$ as you imagine yourself looking down $\mathbf{n}$ towards the origin. The trace of a matrix is the sum of its diagonal elements.]

3.3 (a) Find the MR $\Gamma(R)$ of R for $R(-\pi/2\ \ \mathbf{z})$ and hence find the matrix $\Gamma(I)\ \Gamma(R)$.
(b) Using projection diagrams, find the single operator Q that is equivalent to IR; show also that I and R commute. Give the Schönflies symbol for Q.
(c) Find the MR $\Gamma(Q)$ from $Q\langle\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3| = \langle\mathbf{e}_1{}'\ \mathbf{e}_2{}'\ \mathbf{e}_3{}'| = \langle\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|\Gamma(Q)$.
(d) What can you deduce from comparing $\Gamma(Q)$ from part (c) with $\Gamma(I)\Gamma(R)$ from part (a)?

3.4 Find the MRs of the operators $\sigma_{\mathbf{a}}$, $\sigma_{\mathbf{b}}$ for the basis $\langle\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|$, where $\mathbf{a} = 2^{-1/2}[1\ 1\ 0], \mathbf{b} = 2^{-1/2}[\bar{1}\ 1\ 0]$. Evaluate $\Gamma(\sigma_a)\Gamma(\sigma_b)$. Using a projection diagram find $Q = \sigma_{\mathbf{a}}\ \sigma_{\mathbf{b}}$. Find the MR of Q and compare this with $\Gamma(\sigma_{\mathbf{a}})\ \Gamma(\sigma_{\mathbf{b}})$. What can you conclude from this comparison?

3.5 Find the MRs of the operators E, C_{4z}^{+}, C_{4z}^{-}, $\sigma_{\mathbf{x}}$, $\sigma_{\mathbf{y}}$ for the basis $\langle\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|$.

3.6 Write down the Jones symbols for $R \in C_{4\mathrm{v}}$ and then the Jones symbols for $\{R^{-1}\}$. [*Hints*: You have enough information from Problems 3.4 and 3.5 to do this very easily. Remember that the MRs of $\{R\}$ are orthogonal matrices.] Write down the angular factor in the transforms of the five d orbitals under the operations of the point group C_{4v}. [*Hint*: This may be done immediately by using the substitutions provided by the Jones symbols for R^{-1}.]

3.7 Find the MR of $R(-2\pi/3\ \ [1\ \bar{1}\ 1])$ for the basis $\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|$. Hence write down the Jones representations of R and of R^{-1}. Find the transformed d orbitals $\hat{R}d$, when d is d_{xy}, d_{yz}, or d_{zx}. [*Hint*: Remember that the unit vectors $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$ are oriented initially along OX, OY, OZ, but are transformed under symmetry operations. Observe the comparative simplicity with which the transformed functions are obtained from the Jones symbol for R^{-1} instead of trying to visualize the transformation of the contours of these functions under the configuration space operator R.]

3.8 (a) List the symmetry operators of the point group D_2. Show in a projection diagram their action on a representative point E. Complete the multiplication table of D_2 and find the classes of D_2. [*Hint*: This can be done without evaluating transforms QRQ^{-1}, $Q \in D_2$.]

(b) Evaluate the direct product $D_2 \otimes C_i = G$ and name the point group G. Study the transformation of the basis $\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|$ under the symmetry operators $R \in G = \{R\}$. Use the MRs of R^{-1} to find the Jones symbols for $\{R^{-1}\}$, and hence write down the transformed d orbitals when the symmetry operators of G act on configuration space.

3.9 Find the MRs of $R(\alpha\ \mathbf{x})$ and $R(\beta\ \mathbf{y})$.

4 Group representations

4.1 Matrix representations

If $\{A \;\; B \;\; C \ldots\}$ form a group G then any set of square matrices that obey the same multiplication table as that of the group elements is a *matrix representation* Γ of G. For example, we have already seen that the matrix representatives (MRs) $\Gamma(R)$ defined by

$$R\langle \mathbf{e}| = \langle \mathbf{e}'| = \langle \mathbf{e}|\Gamma(R), \;\; R \in \mathrm{G}, \tag{1}$$

form a representation of the group of symmetry operators. The *dimension* l of a representation is the number of rows and columns in the square matrices making up the matrix representation. In general, a matrix representation Γ is homomorphous with G, with matrix multiplication as the law of binary composition. For example, every group has a one-dimensional (1-D) representation called the *identity* representation or the *totally symmetric* representation Γ_1 for which

$$\Gamma_1(A) = 1, \;\; \forall A \in \mathrm{G}. \tag{2}$$

If all the matrices $\Gamma(A)$ are different, however, then Γ is isomorphous with G and it is called a *true* or *faithful* representation.

Exercise 4.1-1 Show that the MR of the inverse of A, $\Gamma(A^{-1})$, is $[\Gamma(A)]^{-1}$.

Example 4.1-1 Find a matrix representation of the symmetry group $\mathrm{C_{3v}}$ which consists of the symmetry operators associated with a regular triangular-based pyramid (see Section 2.2).

$\mathrm{C_{3v}} = \{E \;\; C_3^+ \;\; C_3^- \sigma_\mathbf{d} \;\; \sigma_\mathbf{e} \;\; \sigma_\mathbf{f}\}$. The MR for the two rotations, evaluated from eq. (1), is

$$\Gamma(R(\phi \;\mathbf{z})) = \begin{bmatrix} c & -s & 0 \\ s & c & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{3.2.11}$$

where $c = \cos\phi$, $s = \sin\phi$. For the three reflections,

$$\Gamma(\sigma(\theta \;\mathbf{y})) = \begin{bmatrix} c_2 & s_2 & 0 \\ s_2 & -c_2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{3.2.15}$$

with $c_2 = \cos 2\theta$, $s_2 = \sin 2\theta$. From Figure 2.10, the values of ϕ and θ are

$$\begin{array}{ccccc} C_3^+ & C_3^- & \sigma_\mathbf{d} & \sigma_\mathbf{e} & \sigma_\mathbf{f} \\ \phi = 2\pi/3 & \phi = -2\pi/3 & \theta = 0 & \theta = -\pi/3 & \theta = \pi/3 \end{array}$$

Since $\cos(2\pi/3) = -\cos(\pi/3) = \tfrac{1}{2}$, $\sin(2\pi/3) = \sin(\pi/3) = \sqrt{3}/2$, $\cos(-2\pi/3) = \cos(2\pi/3) = -\tfrac{1}{2}$, and $\sin(-2\pi/3) = -\sin(2\pi/3) = -\sqrt{3}/2$, the MRs of the elements of the symmetry group C_{3v} are as follows:

$$\begin{array}{ccc} E & C_3^+ & C_3^- \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -\sqrt{1}/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -\sqrt{1}/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ \sigma_\mathbf{d} & \sigma_\mathbf{e} & \sigma_\mathbf{f} \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & \sqrt{1}/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & \sqrt{1}/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \end{array} \qquad (3)$$

Example 4.1-2 Evaluate $\Gamma(\sigma_\mathbf{e})\Gamma(\sigma_\mathbf{f})$ and show that the result agrees with that expected from the multiplication table for the operators, Table 2.3.

$$\begin{array}{ccccc} \Gamma(\sigma_\mathbf{e}) & & \Gamma(\sigma_\mathbf{f}) & & \Gamma(C_3^+) \\ \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} & & \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} & = & \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \end{array}$$

From Table 2.3, we see that $\sigma_\mathbf{e}\sigma_\mathbf{f} = C_3^+$, so that multiplication of the matrix representations does indeed give the same result as binary combination of the group elements (symmetry operators) in this example.

Exercise 4.1-2 Evaluate $\Gamma(C_3^-)\Gamma(\sigma_\mathbf{e})$ and show that your result agrees with that expected from the multiplication table.

Answers to Exercises 4.1

Exercise 4.1-1 Since $A^{-1}A = E$, and since the matrix representations obey the same multiplication table as the group elements, $\Gamma(A^{-1})\Gamma(A) = \Gamma(E) = \mathrm{E}$, the unit matrix. Therefore, from the definition of the inverse matrix, $[\Gamma(A)]^{-1} = \Gamma(A^{-1})$. For example, $C_3^- C_3^+ = E$, and from eq. (3) $\Gamma(C_3^-) = [\Gamma(C_3^+)]^\mathrm{T} = [\Gamma(C_3^+)]^{-1}$.

Exercise 4.1-2 From eq. (3),

$$\Gamma(C_3^-)\Gamma(\sigma_\mathbf{e}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \Gamma(\sigma_\mathbf{f})$$

From Table 2.3, $C_3^- \sigma_{\mathbf{e}} = \sigma_{\mathbf{f}}$, so for this random test the multiplication of two matrix representations again gives the same result as the group multiplication table.

4.2 Irreducible representations

Suppose that $\{\Gamma(A)\,\Gamma(B)\,\ldots\}$ forms an l-dimensional matrix representation of G and define $\Gamma^{'}(A)$ by the *similarity transformation*

$$\Gamma'(A) = \mathrm{S}\ \Gamma(A)\ \mathrm{S}^{-1}, \tag{1}$$

where S is any non-singular $l \times l$ matrix. Then the set $\{\Gamma^{'}(A)\ \Gamma^{'}(B)\ \ldots\}$ also forms an l-dimensional representation of G. (Note that notation varies here, S^{-1} often being substituted for S in eq. (1).)

Proof Let AB denote the product of A and B; then

$$\begin{aligned}\Gamma'(A)\Gamma'(B) &= \mathrm{S}\Gamma(A)\mathrm{S}^{-1}\mathrm{S}\Gamma(B)\mathrm{S}^{-1} = \mathrm{S}\Gamma(A)\Gamma(B)\mathrm{S}^{-1}\\ &= \mathrm{S}\Gamma(AB)\mathrm{S}^{-1} = \Gamma'(AB),\end{aligned} \tag{2}$$

so that $\{\Gamma^{'}(A)\,\Gamma^{'}(B)\ \ldots\}$ is also a representation of G. Two representations that are related by a similarity transformation are said to be *equivalent*. We have seen that for an orthonormal or unitary basis, the matrix representations of point symmetry operators are unitary matrices. In fact, *any* representation of a finite group is equivalent to a unitary representation (Appendix A1.5). Hence we may consider only *unitary representations*. Suppose that Γ^1, Γ^2 are matrix representations of G of dimensions l_1 and l_2 and that for every $A \in \mathrm{G}$ an $(l_1 + l_2)$-dimensional matrix is defined by

$$\Gamma(A) = \begin{bmatrix} \Gamma^1(A) & 0 \\ 0 & \Gamma^2(A) \end{bmatrix}. \tag{3}$$

Then

$$\begin{aligned}\Gamma(A)\ \Gamma(B) &= \begin{bmatrix} \Gamma^1(A) & 0 \\ 0 & \Gamma^2(A) \end{bmatrix}\begin{bmatrix} \Gamma^1(B) & 0 \\ 0 & \Gamma^2(B) \end{bmatrix}\\ &= \begin{bmatrix} \Gamma^1(A)\Gamma^1(B) & 0 \\ 0 & \Gamma^2(A)\Gamma^2(B) \end{bmatrix}\\ &= \begin{bmatrix} \Gamma^1(AB) & 0 \\ 0 & \Gamma^2(AB) \end{bmatrix} = \Gamma(AB).\end{aligned} \tag{4}$$

Therefore, $\{\Gamma(A)\ \Gamma(B)\ \ldots\}$ also forms a representation of G. This matrix representation Γ of G is called the *direct sum* of Γ^1, Γ^2 and is written as

Table 4.1.

E	C_3^+	C_3^-
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$\sigma_{\mathbf{d}}$	$\sigma_{\mathbf{e}}$	$\sigma_{\mathbf{f}}$
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$$\Gamma = \Gamma^1 \oplus \Gamma^2. \tag{5}$$

Alternatively, we can regard Γ as reduced into Γ^1 and Γ^2. A representation of G is *reducible* if it can be transformed by a similarity transformation into an equivalent representation, each matrix of which has the same block-diagonal form. Then, each of the smaller representations Γ^1, Γ^2 is also a representation of G. A representation that cannot be reduced any further is called an *irreducible representation* (IR).

Example 4.2-1 Show that the matrix representation found for C_{3v} consists of the totally symmetric representation and a 2-D representation (Γ_3).

Table 4.1 shows that the MRs $\Gamma(T)$ of the symmetry operators $T \in C_{3v}$ for the basis $\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|$ all have the same block-diagonal structure so that $\Gamma = \Gamma_1 \oplus \Gamma_3$. We shall soon deduce a simple rule for deciding whether or not a given representation is reducible, and we shall see then that Γ_3 is in fact irreducible.

4.3 The orthogonality theorem

Many of the properties of IRs that are used in applications of group theory in chemistry and physics follow from one fundamental theorem called the *orthogonality theorem* (OT). If Γ^i, Γ^j are two irreducible unitary representations of G which are inequivalent if $i \neq j$ and identical if $i = j$, then

$$\sum_T \sqrt{l_i/g}\ \Gamma^i(T)^*_{pq} \sqrt{l_j/g}\ \Gamma^j(T)_{rs} = \delta_{ij}\ \delta_{pr}\ \delta_{qs}. \tag{1}$$

Note that $\Gamma^i(T)^*_{pq}$ means the element common to the pth row and qth column of the MR for the group element T in the ith IR, complex conjugated. The sum is over all the elements of the group. If the matrix elements $\Gamma^i(T)_{pq}$, $\Gamma^j(T)_{rs}$ are corresponding elements, that is from the same row $p = r$ and the same column $q = s$, and from the same IR, $i = j$, then the sum is unity, but otherwise it is zero. The proof of the OT is quite lengthy, and it is therefore given in Appendix A1.5. Here we verify eq. (1) for some particular cases.

Example 4.3-1 (a) Evaluate the LS of eq. (1) for the 2-D IR Γ_3 of C_{3v} ($i=j=3$) with $p=r=1$, $q=s=1$. (b) Repeat the procedure for $i=1, j=3$.

For (a), the LS $=(2/6)\times[1+¼+¼+1+¼+¼]=1$; for (b), the LS $=\sqrt{1/6}\sqrt{2/6}\times[1-½-½+1-½-½]=0$. Notice that we are multiplying together pairs of numbers as in the evaluation of the scalar product of two vectors. The Hermitian scalar product of two normalized vectors **u** and **v** in an n-dimensional linear vector space (LVS) with unitary (orthonormal) basis is

$$\begin{aligned}\mathbf{u}^*\cdot\mathbf{v} &= \sum_{i=1}^{n} u_i^* v_i = 1 \ (\mathbf{u},\ \mathbf{v}\ \text{parallel}),\\ &= 0\ (\mathbf{u},\ \mathbf{v}\ \text{orthogonal}).\end{aligned} \tag{2}$$

So we may interpret eq. (1) as a statement about the orthogonality of vectors in a g-dimensional vector space, where the components of the vectors are chosen from the elements of the l_i, l_j-dimensional matrix representations $\Gamma^i(T)$, $\Gamma^j(T)$, i.e. from the pth row and qth column of the ith IR, and from the rth row and sth column of the jth IR. If these are corresponding elements ($p=r$, $q=s$) from the same representation ($i=j$), then the theorem states that a vector whose components are $\Gamma^i(T)_{pq}$, $T\in G$, is of length $\sqrt{g/l_i}$. But if the components are not corresponding elements of matrices from the same representation, then these vectors are orthogonal. The maximum number of mutually orthogonal vectors in a g-dimensional space is g. Now p may be chosen in l_i ways ($p=1,\ldots,l_i$) and similarly q may be chosen in l_i ways ($q=1,\ldots,l_i$) so that $\Gamma^i(T)_{pq}$ may be chosen in l_i^2 from the ith IR and in $\sum_i l_i^2$ from all IRs. Therefore,

$$\sum_i l_i^2 \le g. \tag{3}$$

In fact, we show later that the equality holds in eq. (3) so that

$$\sum_i l_i^2 = g. \tag{4}$$

4.4 The characters of a representation

The character χ^i of the MR $\Gamma^i(A)$ is the trace of the matrix $\Gamma^i(A)$, i.e. the sum of its diagonal elements $\Gamma^i(A)_{pp}$,

$$\chi^i(A) = \sum_p \Gamma^i(A)_{pp} = \text{Tr}\ \Gamma^i(A). \tag{1}$$

The set of characters $\{\chi^i(A)\ \chi^i(B)\ \ldots\}$ is called the *character system* of the ith representation Γ^i.

4.4.1 Properties of the characters

(i) The character system is the same for all equivalent representations. To prove this, we need to show that $\text{Tr}\ \mathsf{M}'=\text{Tr}\ \mathsf{S}\ \mathsf{M}\ \mathsf{S}^{-1}=\text{Tr}\ \mathsf{M}$, and to prove this result we need to show first that $\text{Tr}\ \mathsf{AB}=\text{Tr}\ \mathsf{BA}$:

$$\text{Tr } \mathtt{AB} = \sum_p \sum_q a_{pq} \; b_{qp} = \sum_q \sum_p b_{qp} \; a_{pq} = \text{Tr } \mathtt{BA}; \tag{2}$$

(2)
$$\text{Tr } \mathtt{M}' = \text{Tr } (\mathtt{S} \; \mathtt{M})\mathtt{S}^{-1} = \text{Tr } \mathtt{S}^{-1}\mathtt{S} \; \mathtt{M} = \text{Tr } \mathtt{M}. \tag{3}$$

Equation (3) shows that the character system is invariant under a similarity transformation and therefore is the same for all equivalent representations. If for some $S \in$ G, $S \, R \, S^{-1} = T$, then R and T are in the same class in G. And since the MRs obey the same multiplication table as the group elements, it follows that all members of the same class have the same character. This holds too for a direct sum of IRs.

Example 4.4-1 From Table 4.1 the characters of two representations of C_{3v} are

C_{3v}	E	C_3^+	C_3^-	$\sigma_\mathbf{d}$	$\sigma_\mathbf{e}$	$\sigma_\mathbf{f}$
Γ_1	1	1	1	1	1	1
Γ_3	2	−1	−1	0	0	0

(ii) The sum of the squares of the characters is equal to the order of the group. In eq. (4.3.1), set $q = p$, $s = r$, and sum over p, r, to yield

(4.3.1)
$$\sum_T \sqrt{l_i/g} \; \chi^i(T)^* \sqrt{l_j/g} \; \chi^j(T) = \delta_{ij} \sum_{p=1}^{l_i} \sum_{r=1}^{l_j} \delta_{pr} = \delta_{ij} \sum_{p=1}^{l_i} 1 = \delta_{ij} l_i;$$

$$\sum_T \chi^i(T)^* \chi^j(T) = g\sqrt{l_i/l_j} \; \delta_{ij} = g \; \delta_{ij}. \tag{4}$$

(4)
$$\sum_T |\chi^i(T)|^2 = g \quad (i = j); \tag{5}$$

(4)
$$\sum_T \chi^i(T)^* \chi^j(T) = 0 \quad (i \neq j). \tag{6}$$

Equation (5) provides a simple test as to whether or not a representation is reducible.

Example 4.4-2 Is the 2-D representation Γ_3 of C_{3v} reducible?

$$\chi(\Gamma_3) = \{2 \quad -1 \quad -1 \;\; 0 \;\; 0 \;\; 0\},$$

$$\sum_T |\chi_3(T)|^2 = 4 + 1 + 1 + 0 + 0 + 0 = 6 = g,$$

so it is irreducible. The 3×3 representation in Table 4.1 is clearly reducible because of its block-diagonal structure, and, as expected,

Table 4.2. *General form of the character table for a group* G.

g_k is a symbol for the type of element in the class $\mathscr{C}_k$ (e.g. C_2, σ_v); c_k is the number of elements in the kth class; g_1 is E, c_1 is 1, and Γ^1 is the totally symmetric representation.

G	$c_1\, g_1$	$c_2\, g_2$	…	$c_k g_k$	…
Γ^1	$\chi^1(\mathscr{C}_1)$	$\chi^1(\mathscr{C}_2)$		$\chi^1(\mathscr{C}_k)$	
Γ^2	$\chi^2(\mathscr{C}_1)$	$\chi^2(\mathscr{C}_2)$		$\chi^2(\mathscr{C}_k)$	
⋮					
Γ^i	$\chi^i(\mathscr{C}_1)$	$\chi^i(\mathscr{C}_2)$		$\chi^i(\mathscr{C}_k)$	
Γ^j	$\chi^j(\mathscr{C}_1)$	$\chi^j(\mathscr{C}_2)$		$\chi^j(\mathscr{C}_k)$	

$$\sum_T |\chi(T)|^2 = 3^2 + 2(0)^2 + 3(1)^2 = 12 \neq g.$$

Generally, we would take advantage of the fact that all members of the same class have the same character and so perform the sums in eqs. (4), (5), and (6) over classes rather than over group elements.

(iii) First orthogonality theorem for the characters. Performing the sum over classes

(4) $$\sum_{k=1}^{N_c} \sqrt{c_k/g}\; \chi^i(\mathscr{C}_k)^* \sqrt{c_k/g}\; \chi^j(\mathscr{C}_k) = \delta_{ij}, \tag{7}$$

where N_c is the number of classes and c_k is the number of elements in the kth class, $\mathscr{C}_k$ Equation (7) states that the vectors with components $\sqrt{c_k/g}\; \chi^i(\mathscr{C}_k)$, $\sqrt{c_k/g}\; \chi^j(\mathscr{C}_k)$ are orthonormal. If we set up a table of characters in which the columns are labeled by the elements in that class and the rows by the representations – the so-called *character table* of the group (see Table 4.2) – then we see that eq. (7) states that the rows of the character table are orthonormal. The normalization factors $\sqrt{c_k/g}$ are omitted from the character table (see Table 4.2) so that when checking for orthogonality or normalization we use eq. (7) in the form

$$g^{-1} \sum_{k=1}^{N_c} c_k\; \chi^i(\mathscr{C}_k)^* \chi^j(\mathscr{C}_k) = \delta_{ij}. \tag{8}$$

It is customary to include c_k in the column headings along with the symbol for the elements in $\mathscr{C}_k$ (e.g. $3\sigma_v$ in Table 4.3). Since E is always in a class by itself, $E = \mathscr{C}_1$ is placed first in the list of classes and $c_1 = 1$ is omitted. The first representation is always the totally symmetric representation Γ_1.

Example 4.4-3 Using the partial character table for C_{3v} in Table 4.3, show that the character systems $\{\chi_1\}$ and $\{\chi_3\}$ satisfy the orthonormality condition for the rows.

$$g^{-1} \sum_k c_k\; |\chi_1(\mathscr{C}_k)|^2 = (1/6)[1(1)^2 + 2(1)^2 + 3(1)^2] = 1;$$

Table 4.3. *Partial character table for* C_{3v} *obtained from the matrices of the IRs* Γ_1 *and* Γ_3 *in Table 4.1.*

$\mathscr{C}_1 = \{E\}, \mathscr{C}_2 = \{C_3^+ \; C_3^-\}$, and $\mathscr{C}_3 = \{\sigma_{\mathbf{d}} \; \sigma_{\mathbf{e}} \; \sigma_{\mathbf{f}}\}$, and so in C_{3v}, $c_1 = 1$, $c_2 = 2$, and $c_3 = 3$.

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_3	2	−1	0

$$g^{-1}\sum_k c_k \, |\chi_3(\mathscr{C}_k)|^2 = (1/6)[1(2)^2 + 2(-1)^2 + 3(0)^2] = 1;$$

$$g^{-1}\sum_k c_k \, \chi_1(\mathscr{C}_k)^* \, \chi_3(\mathscr{C}_k) = (1/6)[1(1)(2) + 2(1)(-1) + 3(1)(0)] = 0.$$

In how many ways can these vectors be chosen? We may choose the character $\chi^i(\mathscr{C}_k)$ from any of the N_r IRs. Therefore the number of mutually orthogonal vectors is the number of IRs, N_r and this must be $\leq N_c$ the dimension of the space. In fact, we shall see shortly that the number of IRs is equal to the number of classes.

(iv) Second orthogonality theorem for the characters. Set up a matrix Q and its adjoint $\mathrm{Q}^\dagger$ in which the elements of Q are the characters as in Table 4.2 but now including normalization factors, so that typical elements are

$$\mathrm{Q}_{ik} = \sqrt{c_k/g} \; \chi^i(\mathscr{C}_k), \;\; (\mathrm{Q}^\dagger)_{kj} = \mathrm{Q}_{jk}^* = \sqrt{c_k/g} \; \chi^j(\mathscr{C}_k)^*. \qquad (9)$$

(9) $$(\mathrm{Q}\,\mathrm{Q}^\dagger)_{ij} = \sum_k \mathrm{Q}_{ik}(\mathrm{Q}^\dagger)_{kj} = \sum_k \sqrt{c_k/g} \; \chi^i(\mathscr{C}_k) \; \sqrt{c_k/g} \; \chi^i(\mathscr{C}_k)^* = \delta_{ji}. \qquad (10)$$

(10) $$\mathrm{Q}\,\mathrm{Q}^\dagger = \mathrm{E} \quad (\mathrm{Q} \text{ a unitary matrix}); \qquad (11)$$

(11) $$\mathrm{Q}^\dagger\,\mathrm{Q} = \mathrm{E}; \qquad (12)$$

(12) $$\begin{aligned}(\mathrm{Q}^\dagger\mathrm{Q})_{kl} &= \sum_i (\mathrm{Q}^\dagger)_{ki}\mathrm{Q}_{il} = \sum_i \mathrm{Q}_{ik}^*\mathrm{Q}_{il} \\ &= \sum_{i=1}^{N_r} \sqrt{c_k/g} \; \chi^i(\mathscr{C}_k)^* \sqrt{c_l/g} \; \chi^i(\mathscr{C}_l) = \delta_{kl}.\end{aligned} \qquad (13)$$

Equation (13) describes the orthogonality of the columns of the character table. It states that vectors with components $\sqrt{c_k/g} \; \chi^i(\mathscr{C}_k)$ in an N_r-dimensional space are orthonormal. Since these vectors may be chosen in N_c ways (one from each of the N_c classes),

(13) $$N_c \leq N_r. \qquad (14)$$

But in eq. (7) the vectors with components $\sqrt{c_k/g}\,\chi^i(\mathscr{C}_k)$ may be chosen in N_r ways (one from each of N_r representations), and so

(7) $$N_r \leq N_c. \tag{15}$$

(14), (15) $$N_r = N_c. \tag{16}$$

The number of representations N_r is equal to N_c, the number of classes. In a more practical form for testing orthogonality

(13) $$\sum_{i=1}^{N_r} \chi^i(\mathscr{C}_k)^* \chi^i(\mathscr{C}_l) = (g/c_k)\delta_{kl}. \tag{17}$$

These orthogonality relations in eqs.(8) and (17), and also eq.(16), are very useful in setting up character tables.

Example 4.4-4 In C_{3v} there are three classes and therefore three IRs. We have established that Γ_1 and Γ_3 are both IRs, and, using $\sum_i l_i^2 = g$, we find $1 + l_2^2 + 4 = 6$, so that $l_2 = 1$. The character table for C_{3v} is therefore as given in Table 4.4(a).

From the orthogonality of the rows,

$$1(1)(1) + 2(1)\chi_2(C_3) + 3(1)\chi_2(\sigma) = 0,$$
$$1(2)(1) + 2(-1)\chi_2(C_3) + 3(0)\chi_2(\sigma) = 0,$$

so that $\chi_2(C_3) = 1$, $\chi_2(\sigma) = -1$. We check for normalization of the character system of Γ_2:

$$\sum_k c_k |\chi(\mathscr{C}_k)|^2 = 1(1)^2 + 2(1)^2 + 3(-1)^2 = 6 = g.$$

Exercise 4.4-1 Check the orthogonality of the columns in the character table for C_{3v} which was completed in Example 4.4-4.

(v) Reduction of a representation. For Γ to be a reducible representation, it must be equivalent to a representation in which each matrix $\Gamma(T)$ of T has the same block-diagonal structure. Suppose that the jth IR occurs c^j times in Γ; then

$$\chi(T) = \textstyle\sum_j c^j \chi_j(T). \tag{18}$$

Multiplying by $\chi_i(T)^*$ and summing over T yields

(18), (4) $$\sum_T \chi_i(T)^* \chi(T) = \sum_j c^j \sum_T \chi_i(T)^* \chi_j(T) = \sum_j c^j\ g\ \delta_{ij} = g\ c^j; \tag{19}$$

(19) $$c^i = g^{-1} \sum_T \chi_i(T)^* \chi(T) = \sum_{k=1}^{N_c} c_k\ \chi_i(\mathscr{C}_k)^* \chi(\mathscr{C}_k). \tag{20}$$

Table 4.4(a) *Character table for* C_{3v}.

C_{3v}	E	$2C_3$	3σ
Γ_1	1	1	1
Γ_2	1	$\chi_2(C_3)$	$\chi_2(\sigma)$
Γ_3	2	-1	0

Table 4.4(b).

C_3	E	C_3^+	C_3^-
E	E	C_3^+	C_3^-
C_3^+	C_3^+	C_3^-	E
C_3^-	C_3^-	E	C_3^+

Table 4.4(c).

C_3	E	C_3^+	C_3^-
E	E	C_3^-	C_3^+
C_3^+	C_3^+	E	C_3^-
C_3^-	C_3^-	C_3^+	E

Normally we would choose to do the sum over classes rather than over group elements. Equation (20) is an extremely useful relation, and is used frequently in many practical applications of group theory.

(vi) The celebrated theorem. The number of times the ith IR occurs in a certain reducible representation called the *regular representation* Γ^r is equal to the dimension of the representation, l_i. To set up the matrices of Γ^r arrange the columns of the multiplication table so that only E appears on the diagonal. Then $\Gamma^r(T)$ is obtained by replacing T by 1 and every other element by zero (Jansen and Boon (1967)).

Example 4.4-5 Find the regular representation for the group C_3. $C_3 = \{E\ C_3^+\ C_3^-\}$. Interchanging the second and third columns of Table 4.4(b) gives Table 4.4(c).

Therefore, the matrices of the regular representation are

$$\begin{matrix} \Gamma^r(E) & \Gamma^r(C_3^+) & \Gamma^r(C_3^-) \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} & \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \end{matrix}$$

The group C_3 is Abelian and has three classes; there are therefore three IRs and each IR occurs once in Γ^r. (But note that the matrices of Γ^r are not block-diagonal.)

Proof of the celebrated theorem

(20)
$$\begin{aligned} c^i &= g^{-1}\sum_T \chi_i(T)^* \ \chi_r(T) \\ &= g^{-1}\chi_i(E)\ \chi_r(E), (\chi_r(T) = 0, \forall\, T \neq E) \\ &= g^{-1}\ l_i\ g = l_i. \end{aligned} \tag{21}$$

The dimension of Γ^r is g; it is also $\sum_i l_i^2$. Therefore

$$\sum_i l_i^2 = g, \tag{22}$$

as promised earlier.

Answer to Exercise 4.4-1

Normalization of the class $2C_3$: $1^2+1^2+(-1)^2=3=6/2$, and of the class 3σ: $1^2+(-1)^2+(0)^2=2=6/3$. Orthogonality of E and $2C_3$: $1(1)+1(1)+2(-1)=0$; orthogonality of E and 3σ: $1(1)+1(-1)+2(0)=0$; orthogonality of $2C_3$ and 3σ: $1(1)+1(-1)+1(-1)(0)=0$.

4.5 Character tables

Character tables are tabulations by classes of the characters of the IRs of the point groups. They are used constantly in practical applications of group theory. As an example, the character table for the point group C_{3v} (or $3m$) is given in Table 4.5. The name of the point group in either Schönflies or International notation (or both) is in the top left-hand corner. The headings to the columns are the number of elements c_k in each class $\mathscr{C}_k$ and a symbol describing the type of elements in that class. For example, the heading for the column of characters for the class $\{C_3^+ C_3^-\}$ in C_{3v} is $2C_3$. Usually Schönflies symbols are used, but some authors use other notation. Each row is labeled by the symbol for an IR; usually either Bethe or Mulliken notation is used, but sometimes one encounters other notations and examples of these will be introduced later. In Bethe's notation, the IRs are labeled

Table 4.5. *Character table for the point group* C_{3v}.

The IRs are labeled using both Bethe and Mulliken notation.

C_{3v}	E	$2C_3$	$3\sigma_v$	
Γ_1, A_1	1	1	1	z, x^2+y^2, z^2
Γ_2, A_2	1	1	−1	R_z
Γ_3, E	2	−1	0	$(x\ y)$, $(R_x\ R_y)$, $(x^2-y^2\ \ xy)$, $(yz\ \ zx)$

Table 4.6. *Mulliken notation for the IRs of the point groups.*

The entry + or − signifies a positive or negative integer, respectively.

l	Notation used for IR	$\chi(C_n)$[a]	$\chi(C_2{}')$ or $\chi(\sigma_v)$[b]	$\chi(\sigma_h)$	$\chi(I)$
1	A	+1			
	B	−1			
	subscript 1		+1		
	subscript 2		−1		
2	E[c]				
3	T				
1, 2, or 3	superscript ′			+	
	superscript ″			−	
	subscript *g*				+
	subscript *u*				−

[a] Or $\chi(S_n)$ if the principal axis is an S_n axis. In D_2 the four 1-D IRs are usually designated A, B_1, B_2, B_3, because there are three equivalent C_2 axes.
[b] If no $C_2{}'$ is present then subscripts 1 or 2 are used according to whether $\chi(\sigma_v)$ is +1 or −1.
[c] The symbol E for a 2-D IR is not to be confused with that used for the identity operator, *E*.

$\Gamma_1, \Gamma_2, \Gamma_3, \ldots$ successively; Γ_1 is always the totally symmetric representation. The remaining representations are listed in order of increasing l. Mulliken notation, which is generally used in molecular symmetry, is explained in Table 4.6. Thus, the totally symmetric representation is A_1 in C_{3v}. The second IR is labeled A_2 since $\chi(\sigma_v) = -1$, there being no C_2' axes in this group. The third IR is labeled E because $l = 2$. The dimension of any representation is given by $\chi(E)$ since the identity operator E is always represented by the unit matrix. In addition to the characters, the table includes information about how the components of a vector $\mathbf{r} = \mathbf{e}_1 x + \mathbf{e}_2 y + \mathbf{e}_3 z$ transform (or how linear functions of x, y, or z, transform) and how quadratic functions of x, y, and z transform. This information tells us to which representations p and d orbitals belong. For example, the three p orbitals and the five d orbitals are both degenerate in spherical symmetry (atoms), but in C_{3v} symmetry the maximum degeneracy is two and

$$\Gamma_p = \Gamma_1 \oplus \Gamma_3 = A_1 \oplus E,$$
$$\Gamma_d = \Gamma_1 \oplus 2\ \Gamma_3 = A_1 \oplus 2\ E.$$

We say that "z forms a *basis* for A_1," or that "z belongs to A_1," or that "z transforms according to the totally symmetric representation A_1." The s orbitals have spherical symmetry and so always belong to Γ_1. This is taken to be understood and is not stated explicitly in character tables. R_x, R_y, R_z tell us how rotations about **x**, **y**, and **z** transform (see Section 4.6). Table 4.5 is in fact only a partial character table, which includes only the *vector representations*. When we allow for the existence of electron spin, the state function $\psi(x\ y\ z)$ is replaced by $\psi(x\ y\ z)\chi(m_s)$, where $\chi(m_s)$ describes the electron spin. There are two ways of dealing with this complication. In the first one, the introduction of a new operator $\overline{E} = R(2\pi\ \mathbf{n}) \neq E$ results in additional classes and representations, and the point groups are then called *double groups*. The symbols for these new representations include information about the total angular momentum quantum number J. Double groups will be introduced in Chapter 8, and until then we shall use simplified point group character tables, like that for C_{3v} in Table 4.5, which are appropriate for discussions of the symmetry of functions of position, $f(x\ y\ z)$. The second way of arriving at the additional representations, which are called *spinor representations* (because their bases correspond to half-integral J), will be introduced in Chapter 12. This method has the advantages that the size of G is unchanged and no new classes are introduced.

Special notation is required for the complex representations of cyclic groups, and this will be explained in Section 4.7. The notation used for the IRs of the axial groups $C_{\infty v}$ and $D_{\infty h}$ is different and requires some comment. The states of diatomic molecules are classified according to the magnitude of the z component of angular momentum, L_z, using the symbols

$$\text{according to} \qquad \begin{array}{rcccc} & \Sigma & \Pi & \Delta & \Phi \\ \Lambda = |L_z| = & 0 & 1 & 2 & 3 \end{array}$$

All representations except Σ are two-dimensional. Subscripts g and u have the usual meaning, but a superscript + or − is used on Σ representations according to whether $\chi(\sigma_v) = \pm 1$. For $L_z > 0$, $\chi(C_2')$, and $\chi(\sigma_v)$ are zero. In double groups the spinor representations depend on the total angular momentum quantum number and are labeled accordingly.

4.6 Axial vectors

Polar vectors such as $\mathbf{r} = \mathbf{e}_1 x + \mathbf{e}_2 y + \mathbf{e}_3 z$ change sign on inversion and on reflection in a plane normal to the vector, but do not change sign on reflection in a plane that contains the vector. *Axial vectors* or *pseudovectors* do not change sign under inversion. They occur as vector products, and in symmetry operations they transform like *rotations* (hence the name axial vectors). The vector product of two polar vectors

$$\mathbf{r}_1 \times \mathbf{r}_2 = \mathbf{R} \tag{1}$$

is a pseudovector, or axial vector, of magnitude $r_1\ r_2 \sin\theta$, where θ is the included angle, $0 \leq \theta \leq \pi$ (see Figure 4.1(a)). The orientation of the axis of rotation is that it coincides with that of a unit vector $\mathbf{n}$ in a direction such that $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{n}$ form a right-handed system. However, $\mathbf{R}$ is *not* a polar vector because its transformation properties under inversion and reflection are quite different to those of the polar vector $\mathbf{r}$. In Figure 4.1 the directed line segment symbols used for $\mathbf{r}_1$, $\mathbf{r}_2$ are the conventional ones for polar vectors, but the curved arrow symbol used for $\mathbf{R}$ indicates a rotation about the axis $\mathbf{n}$. The direction of rotation is that of the first-named vector $\mathbf{r}_1$ into $\mathbf{r}_2$, and the sign of $\mathbf{R}$ is positive because the direction

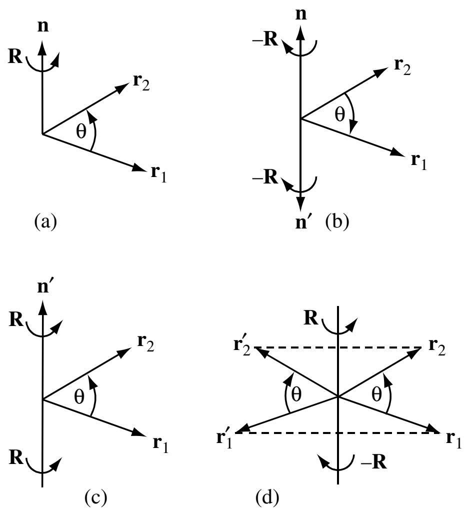


Figure 4.1. (a) The axial vector, or pseudovector, $\mathbf{r}_1 \times \mathbf{r}_2 = \mathbf{R}$. The curved arrow symbol used for **R** expresses the idea that the sense of rotation (which is that of a right-handed screw advancing along **n**, where **n**, $\mathbf{r}_1$, and $\mathbf{r}_2$ form a right-handed system) is from $\mathbf{r}_1$ into $\mathbf{r}_2$, i.e. from the first vector into the second one. (b) Reversing the order of the vectors in a vector product reverses the direction of rotation and so reverses its sign. (c) Invariance of the pseudovector $\mathbf{r}_1 \times \mathbf{r}_2 = \mathbf{R}$ under reflection in a plane normal to the axis of rotation. This figure shows why **R** must not be represented by a directed line segment normal to the plane of $\mathbf{r}_1, \mathbf{r}_2$ because such an object would change sign on reflection in the plane of $\mathbf{r}_1, \mathbf{r}_2$, whereas the sense of rotation of $\mathbf{r}_1$ into $\mathbf{r}_2$, as expressed by the curved arrow, is unchanged under this symmetry operation. (d) Reversal of the direction of rotation occurs on reflection in a plane that contains the axis of rotation.

of rotation appears anticlockwise on looking down the axis towards the origin. Reversing the order of the vectors in a vector product reverses its sign:

$$\mathbf{r}_2 \times \mathbf{r}_1 = -(\mathbf{r}_1 \times \mathbf{r}_2) \tag{2}$$

(Figure 4.1(b)). One can see in Figure 4.1(c) that reflection in a plane normal to the axis of rotation does not change the direction of rotation, but that it is reversed (Figure 4.1(d)) on reflection in a plane that contains the axis of rotation. Specification of a rotation requires a statement about both the axis of rotation and the amount of rotation. We define *infinitesimal* rotations about the axes OX, OY, and OZ by (note the cyclic order)

$$R_x = \phi(\mathbf{e}_2 \times \mathbf{e}_3), \tag{3}$$

$$R_y = \phi(\mathbf{e}_3 \times \mathbf{e}_1), \tag{4}$$

$$R_z = \phi(\mathbf{e}_1 \times \mathbf{e}_2). \tag{5}$$

Under a symmetry operator T, R_x transforms into $R_x' = \phi(\mathbf{e}_2' \times \mathbf{e}_3')$ and similarly, so that

Table 4.7. *Transformation of the basis* $\{R_x \ R_y \ R_z\}$ *under the operators in the first column.*

T	$\mathbf{e}_1{}'$	$\mathbf{e}_2{}'$	$\mathbf{e}_3{}'$	$R_x{}'$	$R_y{}'$	$R_z{}'$
E	$\mathbf{e}_1$	$\mathbf{e}_2$	$\mathbf{e}_3$	R_x	R_y	R_z
$R(\pi/2\ \mathbf{z})$	$\mathbf{e}_2$	$-\mathbf{e}_1$	$\mathbf{e}_3$	R_y	$-R_x$	R_z
$R(\pi\ \mathbf{z})$	$-\mathbf{e}_1$	$-\mathbf{e}_2$	$\mathbf{e}_3$	$-R_x$	$-R_y$	R_z
$R(\pi\ \mathbf{x})$	$\mathbf{e}_1$	$-\mathbf{e}_2$	$-\mathbf{e}_3$	R_x	$-R_y$	$-R_z$
$R(\pi\ [\bar{1}\ 1\ 0])$	$-\mathbf{e}_2$	$-\mathbf{e}_1$	$-\mathbf{e}_3$	$-R_y$	$-R_x$	$-R_z$
I	$\mathbf{e}_1$	$\mathbf{e}_2$	$\mathbf{e}_3$	R_x	R_y	R_z
$R(\phi\ \mathbf{z})$	$c\ \mathbf{e}_1 + s\ \mathbf{e}_2$	$-s\ \mathbf{e}_1 + c\ \mathbf{e}_2$	$\mathbf{e}_3$	$c\ R_x + s\ R_y$	$-s\ R_x + c\ R_y$	R_z

$$T\langle R_x\ R_y\ R_z| = \langle R_x{}'\ R_y{}'\ R_z{}'| = \langle R_x\ R_y\ R_z \mid \Gamma^{(\mathbf{R})}(T), \tag{6}$$

where

$$R_x{}' = \phi(\mathbf{e}_2{}' \times \mathbf{e}_3{}'),\ R_y{}' = \phi(\mathbf{e}_3{}' \times \mathbf{e}_1{}'),\ R_z{}' = \phi(\mathbf{e}_1{}' \times \mathbf{e}_2{}'). \tag{7}$$

$\Gamma^{(\mathbf{R})}(T)$ is not usually the same as the MR $\Gamma^{(\mathbf{r})}(T)$ for the basis $\langle\ \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|$ (previously called just $\Gamma(T)$, since there was no need then to specify the basis). With this refinement in the notation,

$$T\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3| \ = \ \langle \mathbf{e}_1{}'\ \mathbf{e}_2{}'\ \mathbf{e}_3{}'| \ = \ \langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3|\Gamma^{(\mathbf{r})}(T). \tag{8}$$

The transformation properties of $\{R_x\ R_y\ R_z\}$ are then readily worked out from eq. (6) using the primed equations (7) with $\{\mathbf{e}_1{}'\ \mathbf{e}_2{}'\ \mathbf{e}_3{}'\}$ obtained from eq. (8) with the use, when necessary, of eq. (2), which simply states that reversing the order of the terms in a vector product reverses its sign.

Example 4.6-1 Find how the rotations $\{R_x\ R_y\ R_z\}$ transform under the symmetry operators: $E, R(\pi/2\ \mathbf{z}),\ R(\pi\ \mathbf{z}),\ R(\pi\ \mathbf{x}),\ R(\pi\ [\bar{1}\ 1\ 0]),\ I,\ R(\phi\ \mathbf{z})$. The solution is summarized in Table 4.7. Figure 4.2 will be found helpful in arriving at the entries in columns 2, 3, and 4.

Exercise 4.6-1 Verify in detail (from eq. (7)) the entries in columns 5, 6, and 7 of Table 4.7 for $R(\phi\ \mathbf{z})$.

The MRs of the operators in the rows 2 to 6 for the basis $\langle\ R_x\ R_y\ R_z|$ are

$$\underset{E}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}} \quad \underset{R(\pi/2\ \mathbf{z})}{\begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}} \quad \underset{R(\pi\ \mathbf{z})}{\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}} \quad \underset{R(\pi\ \mathbf{x})}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}} \quad \underset{R(\pi\ [\bar{1}\ 1\ 0])}{\begin{bmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}}.$$

This is a matrix representation of the group $D_4 = \{E\ 2C_4\ C_2\ 2C_2{}'\ 2C_2{}''\}$ and it is clearly reducible. The character systems of the two representations in the direct sum $\Gamma^{(\mathbf{R})} = \Gamma_2 \oplus \Gamma_5$ are

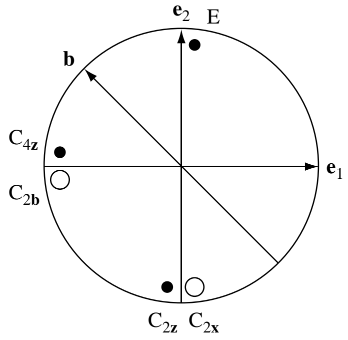


Figure 4.2. Projection in the **xy** plane of the unit sphere in configuration space, showing the initial orientation of the unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$ before applying the symmetry operator T. Note that $\mathbf{e}_3$ is normal to the plane of the paper and points upwards towards the reader. Also shown are the positions of the representative point E after applying to configuration space the symmetry operators in rows 2 to 6 of Table 4.6. The unit vector **b** lies along the direction $[\bar{1}\ 1\ 0]$.

$$\begin{array}{rcllllll} & & E & 2C_4 & C_2 & 2C_2{}' & 2C_2{}'' \\ \Gamma_2 & = & \{1 & 1 & 1 & -1 & -1\} \\ \Gamma_5 & = & \{2 & 0 & -2 & 0 & 0\}. \end{array}$$

Exercise 4.6-2 Show that Γ_5 is an IR of D_4. How many IRs are there in the character table of D_4? Give the names of Γ_2 and Γ_5 in Mulliken notation.

Answers to Exercises 4.6

Exercise 4.6-1 From eq. (7) and columns 2–4 of Table 4.7,

$$\mathbf{e}_2{}' \times \mathbf{e}_3{}' = (-s\ \mathbf{e}_1 + c\ \mathbf{e}_2) \times \mathbf{e}_3 = -s(\mathbf{e}_1 \times \mathbf{e}_3) + c(\mathbf{e}_2 \times \mathbf{e}_3)$$
$$= s(\mathbf{e}_3 \times \mathbf{e}_1) + c(\mathbf{e}_2 \times \mathbf{e}_3).$$

Therefore, $R_x{}' = c\ R_x + s\ R_y$.

$$\mathbf{e}_3{}' \times \mathbf{e}_1{}' = \mathbf{e}_3 \times (c\ \mathbf{e}_1 + s\ \mathbf{e}_2) = c(\mathbf{e}_3 \times \mathbf{e}_1) + s(\mathbf{e}_3 \times \mathbf{e}_2)$$
$$= c(\mathbf{e}_3 \times \mathbf{e}_1) - s(\mathbf{e}_2 \times \mathbf{e}_3).$$

Therefore, $R_y{}' = -s\ R_x + c\ R_y$.

$$\mathbf{e}_1{}' \times \mathbf{e}_2{}' = (c\ \mathbf{e}_1 + s\ \mathbf{e}_2) \times (-s\ \mathbf{e}_1 \times c\ \mathbf{e}_2) = c^2(\mathbf{e}_1 \times \mathbf{e}_2) + (-s^2)(\mathbf{e}_2 \times \mathbf{e}_1)$$
$$= (\mathbf{e}_1 \times \mathbf{e}_2).$$

Therefore $R_z{}' = R_z$.

Exercise 4.6-2 If Γ is an IR, the sum of the squares of the characters is equal to the order of the group. For Γ_5, $1(2)^2 + 1(-2)^2 + 2(0)^2 = 8 = g$, so Γ_5 is an IR. There are five classes and therefore five IRs. From $\sum_i l_i^2 = 8$ four are 1-D and one is 2-D. Since Γ_5 is the only IR with

$l = 2$, it is named E; Γ_2 is a 1-D IR, and in Mulliken notation it is called A_2 because $\chi(C_4) = +1$ *and* $\chi(C_2') = -1$.

4.7 Cyclic groups

If $A^n = E$, then the sequence $\{A^k\}$, with $k = 1, 2, \ldots, n$,

$$\{A\ A^2\ A^3 \ldots A^n = E\}, \tag{1}$$

is a cyclic group of order n. All pairs of elements $A^k, A^{k'}$ commute and so $\{A^k\}$ is an Abelian group with n classes and therefore n 1-D IRs. If A is a symmetry operator then, in order to satisfy $A^n = E$, A must be either E $(n = 1)$, I $(n = 2)$, or a proper or an improper rotation, and if it is an improper rotation then n must be even. Writing the n classes in their proper order with $E = A^n$ first, a representation of

$$\{A^n = E \quad A \quad A^2 \ \ldots \ A^{n-1}\} \tag{1$'$}$$

is given by

$$\{\varepsilon^n = 1 \quad \varepsilon \quad \varepsilon^2 \ \ldots \ \varepsilon^{n-1}\}, \tag{2}$$

where the MRs

$$\varepsilon^k = \exp(-2\pi i k/n), \ k = 1, \ldots, n \tag{3}$$

are the n complex roots of unity. Note that

$$\varepsilon^{n-k} = \exp(-2\pi i(n-k)/n) = \exp(2\pi i k/n) = (\varepsilon^*)^k. \tag{4}$$

A second representation is

$$\{(\varepsilon^*)^n = 1 \quad \varepsilon^* \quad (\varepsilon^*)^2 \ \ldots \ (\varepsilon^*)^{n-1}\}, \tag{5}$$

so that the IRs occur in complex conjugate pairs generated from

$$\chi(A) = \exp(-2\pi i p/n), \ p = \pm 1, \pm 2, \ldots \tag{6}$$

$p = 0$ gives the totally symmetric representation

$$\Gamma_1 \text{ or } A = \{1 \ 1 \ 1 \ \ldots \ 1\}. \tag{7}$$

If n is odd, $p = 0, \pm 1, \pm 2, \ldots, \pm(n-1)/2$ generates all the representations which consist of Γ_1 and $(n-1)/2$ conjugate pairs. If n is even, $p = 0, \pm 1, \pm 2, \ldots, \pm(n-2)/2, n/2$. When $p = n/2$, $\chi(A^k) = (\varepsilon^{n/2})^k = [\exp(-i\pi)]^k = (-1)^k$, which is a representation

$$\Gamma_2 \text{ or } B = \{1 \ \ -1 \ \ 1 \ \ -1 \ \ldots \ -1\} \tag{8}$$

from $k = n\ 1\ 2\ 3 \ldots n-1$. The character table of C_3 is given in Table 4.8.

To study the transformation of functions of $\{x\ y\ z\}$ under $R(\phi\ \mathbf{z})$ we make use of $\hat{R} f(\{x\ y\ z\}) = f(R^{-1}\{x\ y\ z\})$:

Table 4.8. *Character table for* C_3.

The form of this table with real basis functions ($E = {}^1E \oplus {}^2E$) given below the dashed line is seen in many compilations of character tables, but in practical applications the form with 1-D representations and complex basis functions should be used. If making comparisons with other compilations, note that we use the Condon and Shortley (1967) phase conventions, whereas Lax (1974) uses the Fano and Racah (1959) choice of phase (which for $j = 1$ would introduce an additional factor of i in the complex bases).

C_3	E	C_3^+	C_3^-	$\varepsilon = \exp(-\,i2\pi/3)$
A_1	1	1	1	z, R_z, $(x+iy)(x-iy)$, z^2
${}^1E$	1	ε	ε^*	$-(x+iy)$, $R_x + iR_y$, $z(x+iy)$, $(x-iy)^2$
${}^2E$	1	ε^*	ε	$x - iy$, $R_x - iR_y$, $z(x-iy)$, $(x+iy)^2$
A_1	1	1	1	z, R_z, x^2+y^2, z^2
E	2	-1	-1	$(x\ y)$, $(R_x\ R_y)$, $(yz\ zx)$, $(xy\ x^2-y^2)$

$$\Gamma(R^{-1}) = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} c & s & 0 \\ -s & c & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} c\,x + s\,y \\ -s\,x + c\,y \\ z \end{bmatrix}. \tag{9}$$

Thus a proper (or improper) general rotation about $\mathbf{z}$ mixes the functions x and y. This is why $(x\ \ y)$ forms a basis for the 2-D representation E in C_{3v} while z, which transforms by itself under both $2C_3$ and $3\sigma_v$, forms a basis for the 1-D representation A_1. In C_3 there are, in addition to A, two more 1-D IRs. Since

$$R^{-1}(x \pm iy) \;=\; (c\,x + s\,y) \pm i(-s\,x + c\,y) = (c \mp is)(x \pm iy), \tag{10}$$

$-(x+iy)$ and $(x-iy)$ form 1-D bases, that is transform into themselves under $R(\phi\ \mathbf{z})$ rather than into a linear combination of functions. (The negative sign in $-(x+iy)$ comes from the Condon and Shortley phase conventions (see Chapter 11).) From eq. (10), the character for $-(x+iy)$ is $\varepsilon = \exp\,(-i\phi)$ for a general rotation through an angle ϕ, which becomes $\exp(-2\pi i/3)$ for a C_3^+ rotation, in agreement with eq. (6) for $p = 1$. For the basis $(x - iy)$ the character is $\exp(i\phi) = \varepsilon^*$, or $\exp(2\pi i/3)$ when $n = 3$, corresponding to $p = -1$ in eq. (6). In character tables of cyclic groups the complex conjugate (CC) representations are paired and each member of the pair is labeled by ${}^1E$, ${}^2E$ (with the addition of primes or subscripts g or u when appropriate). Because the states p and $-p$ are degenerate under time-reversal symmetry (Chapter 13), the pairs ${}^1E_p$ and ${}^2E_p$ are often bracketed together, each pair being labeled by the Mulliken symbol E, with superscripts and subscripts added when necessary. The character table for C_3 is given in Table 4.8 in both forms with complex and real representations. Complex characters should be used when reducing representations or when using projection operators (Chapter 5). However, in character tables real bases are usually given, and this practice is followed in Appendix A3.

4.8 Induced representations

Remark The material in this section is not made use of in this book until Section 16.5, in the chapter on space groups. Consequently, readers may choose to postpone their study of Section 4.8 until they reach Section 16.5.

Let $G = \{g_j\}$ be a group of order g with a subgroup $H = \{h_l\}$ of order h. The left coset expansion of G on H is

$$G = \sum_{r=1}^{t} g_r \text{ H}, \; t = g/h, \; g_1 = E, \tag{1}$$

where the coset representatives g_r for $r = 2, \ldots, t$, are $\in$ G but $\notin$ H. By closure in G, $g_j\, g_s$ ($g_s \in \{g_r\}$) is $\in$ G (g_k say) and thus a member of one of the cosets, say g_r H. Therefore, for some $h_l \in$ H,

$$g_j \; g_s = g_k = g_r \; h_l. \tag{2}$$

(2) $$g_j \; g_s \text{ H} = g_r \; h_l \text{ H} = g_r \text{ H}; \tag{3}$$

(3) $$g_j \langle g_s \text{ H}| = \langle g_r \text{ H}| = \langle g_s \text{ H}| \; \Gamma^{\text{g}}(g_j). \tag{4}$$

In eq. (4) the cosets themselves are used as a basis for G, and from eq. (3) g_s H is transformed into g_r H by g_j. Since the operator g_j simply re-orders the basis, each matrix representation in the *ground representation* Γ^{g} is a permutation matrix (Appendix A1.2). Thus the sth column of Γ^{g} has only one non-zero element,

(4), (2) $$\begin{aligned}[\Gamma^{\text{g}}(g_j)]_{us} &= 1, \text{ when } u = r, \; g_j \; g_s = g_r \; h_l \\ &= 0, \text{ when } u \neq r.\end{aligned} \tag{5}$$

Because binary composition is unique (rearrangement theorem) the same restriction of only one non-zero element applies to the rows of Γ^{g}.

Exercise 4.8-1 What is the dimension of the ground representation?

Example 4.8-1 The multiplication table of the permutation group S(3), which has the cyclic subgroup H = C(3), is given in Table 1.3. Using the coset representatives $\{g_s\} = \{P_0 \; P_3\}$, write the left coset expansion of S(3) on C(3). Using eq. (2) find $g_r \; h_l$ for $\forall \; g_j \in$ G. [*Hint*: $g_r \in \{g_s\}$ and h_l are determined uniquely by g_i, g_s.] Hence write down the matrices of the ground representation.

The left coset expansion of S(3) on C(3) is

$$G = \sum_{s=1}^{t} g_s \text{ H} = P_0 \text{ H} \oplus P_3 \text{ H} = \{P_0 \; P_1 \; P_2\} \oplus \{P_3 \; P_4 \; P_5\}, \tag{6}$$

with g_r and h_l, determined from $g_j \;\; g_s = g_k = g_r \;\; h_l$, given in Table 4.9. With the cosets as a basis,

$$g_j \langle P_0 \text{ H}, P_3 \text{ H}| = \langle P_0{'} \text{ H}, P_3{'} \text{ H}| = \langle P_0 \text{ H}, P_3 \text{ H}| \; \Gamma^{\text{g}}(g_j). \tag{7}$$

Table 4.9. *The values of g_k and h_l determined from eq. (4.8.2) for* G = S(3) *and* H = C(3).

$g_s = P_0$					$g_s = P_3$				
g_j	g_s	g_k	g_r	h_l	g_j	g_s	g_k	g_r	h_l
P_0	P_0	P_0	P_0	P_0	P_0	P_3	P_3	P_3	P_0
P_1	P_0	P_1	P_0	P_1	P_1	P_3	P_5	P_3	P_2
P_2	P_0	P_2	P_0	P_2	P_2	P_3	P_4	P_3	P_1
P_3	P_0	P_3	P_3	P_0	P_3	P_3	P_0	P_0	P_0
P_4	P_0	P_4	P_3	P_1	P_4	P_3	P_2	P_0	P_2
P_5	P_0	P_5	P_3	P_2	P_5	P_3	P_1	P_0	P_1

Table 4.10. *The ground representation Γ^g determined from the cosets P_0* H, P_3 H *by using the cosets as a basis, eq. (4.8.4).*

g_j	P_0	P_1	P_2	P_3	P_4	P_5
$P_0{}', P_3{}'$	P_0, P_3	P_0, P_3	P_0, P_3	P_3, P_0	P_3, P_0	P_3, P_0
$\Gamma^g(g_j)$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$

The matrices of the ground representation are in Table 4.10. Each choice of g_j and g_s in eq. (2) leads to a particular h_l so that eq. (2) describes a mapping of G on to its subgroup H in which h_l is the image of g_j.

Example 4.8-2 Write a left coset expansion of S(3) on H = $\{P_0\ P_3\}$. Show that for $g_s = P_1$, $g_r \in \{g_s\}$ and $h_l \in$ H are determined uniquely for each choice of $g_j \in$ G.

Using Table 1.3,

$$S(3) = P_0\{P_0\ P_3\} \oplus P_1\{P_0\ P_3\} \oplus P_2\{P_0\ P_3\}. \tag{8}$$

The g_r and h_l that satisfy eq. (2) are given in Table 4.11, where $\{g_r\} = \{P_0\ P_1\ P_2\}$ and $h_l \in \{P_0\ P_3\}$. Table 4.11 verifies the homomorphous mapping of G → H by $\{P_0\ P_1\ P_2\} \to P_0$ and $\{P_3\ P_4\ P_5\} \to P_3$. When necessary for greater clarity, the *subelement* h_l can be denoted by h_{sl} or by $h_{sl}(g_j)$, as in

$$g_j\ g_s = g_r\ h_{sl}(g_j). \tag{9}$$

(9), (5)
$$h_{sl}(g_j) = g_r^{-1} g_j\ g_s = \sum_u g_u^{-1} g_j\ g_s\ [\Gamma^g(g_j)]_{us}. \tag{10}$$

The purpose of this section is to show how the representations of G may be constructed from those of its subgroup H. Let $\{\mathbf{e}_q\}$, $q = 1, \ldots, l_i$, be a subset of $\{\mathbf{e}_q\}$, $q = 1, \ldots, h$, that is an irreducible basis for H. Then

Table 4.11. *This table confirms that for $g_s = P_1$, g_r and h_l are determined by the choice of g_j, where $g_j\, g_s = g_k = g_r\, h_l$.*

g_j	g_s	g_k	g_r	h_l
P_0	P_1	P_1	P_1	P_0
P_1	P_1	P_2	P_2	P_0
P_2	P_1	P_0	P_0	P_0
P_3	P_1	P_4	P_2	P_3
P_4	P_1	P_5	P_1	P_3
P_5	P_1	P_3	P_0	P_3

$$h_l\ \mathbf{e}_q = \sum_{p=1}^{l_i} \mathbf{e}_p\ \tilde{\Gamma}_i(h_l)_{pq}, \tag{11}$$

where $\tilde{\Gamma}_i$ is the ith IR of the subgroup H. Define the set of vectors $\{\mathbf{e}_{rq}\}$ by

$$\mathbf{e}_{rq} = g_r\ \mathbf{e}_q,\ \ r = 1, \ldots, t;\ \ q = 1, \ldots, l_i. \tag{12}$$

Then $\langle \mathbf{e}_{rq}|$ is a basis for a representation of G:

(2), (5) $$g_j\ \mathbf{e}_{sq} = g_j\ g_s\ \mathbf{e}_q = g_r\ h_l\ \mathbf{e}_q = \sum_u g_u\ [\Gamma^{\mathrm{g}}(g_j)]_{us}\ h_l\ \mathbf{e}_q. \tag{13}$$

In eq. (13) g_r has been replaced by

$$\sum_u g_u\ [\Gamma^{\mathrm{g}}(g_j)]_{us} = g_r \tag{14}$$

since the sth column of Γ^{g} consists of zeros except $u = r$.

(13), (11) $$g_j\ \mathbf{e}_{sq} = \sum_u g_u\ [\Gamma^{\mathrm{g}}(g_j)]_{us} \sum_p \mathbf{e}_p\ \tilde{\Gamma}_i(h_{sl})_{pq} \tag{15}$$

$$= \sum_u \sum_p \mathbf{e}_{up}\ (\Gamma(g_j)_{[u\ s]})_{pq}. \tag{16}$$

In the supermatrix Γ in eq. (16) each element $[u\ s]$ is itself a matrix, in this case $\tilde{\Gamma}_i(h_{sl})$ multiplied by $\Gamma^{\mathrm{g}}(g_j)_{us}$.

(16), (15) $$\Gamma(g_j)_{up,\ sq} = \Gamma^{\mathrm{g}}(g_j)_{us}\ \tilde{\Gamma}_i(h_{sl})_{pq}, \tag{17}$$

in which u, p label the rows and s, q label the columns; $\Gamma(g_j)$ is the matrix representation of g_j in the *induced representation* $\Gamma = \tilde{\Gamma}_i \uparrow \mathrm{G}$. Because Γ^{g} is a permutation matrix, with $\Gamma^{\mathrm{g}}(g_j)_{us} = 0$ unless $u = r$, an alternative way of describing the structure of Γ is as follows:

(15), (16), (5), (10) $$\Gamma(g_j)_{up,\ sq} = \tilde{\Gamma}_i(g_u^{-1} g_j\ g_s)_{pq}\ \delta_{ur}. \tag{18}$$

$\tilde{\Gamma}_i(g_u^{-1} g_j\ g_s)$ is the matrix that lies at the junction of the uth row and the sth column of $\Gamma_{[u\ s]}$, and the Kronecker δ in eq. (18) ensures that $\tilde{\Gamma}_i$ is replaced by the null matrix except for $\Gamma_{[r\ s]}$.

Table 4.12. *Character table of the cyclic group* C(3) *and of the permutation group* S(3).

$\varepsilon = \exp(-2i\pi/3)$.

C(3)	P_0	P_1	P_2	S(3)	P_0	P_1, P_2	P_3, P_4, P_5
Γ_1, A	1	1	1	Γ_1, A_1	1	1	1
Γ_2, ${}^1E$	1	ε	ε^*	Γ_2, A_2	1	1	−1
Γ_3, ${}^2E$	1	ε^*	ε	Γ_3, E	2	−1	0

Table 4.13. *Subelements* $h_{sl}(g_j)$ *and MRs* $\Gamma(g_j)$ *of two representations of* S(3), $\tilde{\Gamma}\uparrow G$, *obtained by the method of induced representations.*

The third and fourth rows contain the subelements $h_{sl}(g_j)$ as determined by the values of g_s (in row 2), g_j, and g_r (in the first column). The $\Gamma^g(g_j)$ matrices were taken from Table 4.9. $\varepsilon = \exp(-i2\pi/3)$. Using Table 4.11, we see that the two representations of S(3) are $\tilde{\Gamma}_1\uparrow G = A_1 \oplus A_2$ and $\tilde{\Gamma}_2\uparrow G = E$.

g_j	P_0	P_1	P_2	P_3	P_4	P_5
g_r, g_s	P_0, P_3	P_0, P_3	P_0, P_3	P_0, P_3	P_0, P_3	P_0, P_3
P_0	P_0	P_1	P_2	P_0	P_2	P_1
P_3	P_0	P_2	P_1	P_0	P_1	P_2
$\tilde{\Gamma}_1\uparrow G$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$
$\tilde{\Gamma}_2\uparrow G$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\varepsilon & 0\\0 & \varepsilon^*\end{bmatrix}$	$\begin{bmatrix}\varepsilon^* & 0\\0 & \varepsilon\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & \varepsilon^*\\\varepsilon & 0\end{bmatrix}$	$\begin{bmatrix}0 & \varepsilon\\\varepsilon^* & 0\end{bmatrix}$
$\chi(\tilde{\Gamma}_1\uparrow G)$	2	2	2	0	0	0
$\chi(\tilde{\Gamma}_2\uparrow G)$	2	−1	−1	0	0	0

Example 4.8-3 Construct the induced representations of S(3) from those of its subgroup C(3).

The cyclic subgroup C(3) has three 1-D IRs so that $\tilde{\Gamma}_i(h_{sl})$ has just one element ($p = 1$, $q = 1$). The character table of C(3) is given in Table 4.13, along with that of S(3), which will be needed to check our results. The subelements h_{sl} and coset representatives g_r depend on g_j and g_s, and our first task is to extract them from Table 4.8. They are listed in Table 4.13. Multiplying the $[\tilde{\Gamma}_i(h_{sl})]_{11} = \tilde{\chi}_i(h_{sl})$ by the elements of $\Gamma^g(g_j)$ in Table 4.12 gives the representations of S(3). An example should help clarify the procedure. In Table 4.13, when $g_j = P_4$, $g_s = P_3$, and $g_r = P_0$, the subelement $h_{sl}(g_j) = P_2$. (In rows 3 and 4 of Table 4.13 the subelements are located in positions that correspond to the non-zero elements of $\Gamma^g(g_j)$.) From Table 4.10, $[\Gamma^g(P_4)]_{12} = 1$, and in Table 4.12 $\tilde{\chi}_2(P_2) = \varepsilon^*$, so that $[\tilde{\Gamma}_2\uparrow G]_{12} = \varepsilon^*$, as entered in the sixth row of Table 4.13.

From the character systems in Table 4.13 we see that for the IRs of S(3), $[\tilde{\Gamma}_1\uparrow G] = A_1 \oplus A_2$ and $[\tilde{\Gamma}_2\uparrow G] = E$. We could continue the table by finding $\tilde{\Gamma}_3\uparrow G$, but since we already have all the representations of S(3), this could only yield an equivalent representation. Note that while this procedure $\tilde{\Gamma} \uparrow$ G does not necessarily yield IRs, it does give all the IRs of G, after reduction. A proof of this statement may be found in Altmann (1977).

4.8.1 Character system of an induced representation

We begin with

$$g_j = g_r\ h_l\ g_s^{-1}. \tag{19}$$

When $s = r$,

(19) $$g_j = g_r\ h_l\ g_r^{-1}. \tag{20}$$

Define

$$\{g_r\ h_l\ g_r^{-1}\} = \mathrm{H}^r,\ \forall\ h_l \in \mathrm{H}, \tag{21}$$

where H^r is the subgroup conjugate to H by g_r.

Exercise 4.8-2 Verify closure in H^r. Is this sufficient reason to say that H^r is a group?

The character of the matrix representation of g_j in the representation Γ induced from $\tilde{\Gamma}_i$ is

(20) $$\chi(g_j) = \sum_r \chi_r(g_j), \tag{22}$$

where the trace of the rth diagonal block $(s = r)$ of Γ is

(5), (17) $$\begin{aligned} \chi_r(g_j) &= \tilde{\chi}_i\ (h_l),\ g_j \in \mathrm{H}^r \\ &= 0,\ g_j \notin \mathrm{H}^r. \end{aligned} \tag{23}$$

A representation Γ of $\mathrm{G} = \{g_j\}$ is irreducible if

(4.4.5) $$\sum_j \chi(g_j)^* \chi(g_j) = g. \tag{24}$$

(24), (22) $$\sum_r \sum_j |\chi_r(g_j)|^2 + \sum_s \sum_{r \neq s} \sum_j \chi_r(g_j)^*\ \chi_s(g_j) = g. \tag{25}$$

The first term in eq. (25) is

(25), (23) $$\sum_r \sum_l |\tilde{\chi}_r(h_l)|^2 = \sum_{r=1}^{t} h = t\,h = g, \tag{26}$$

and so the second term in eq. (25) must be zero if Γ is irreducible. The irreducibility criterion eq. (25) thus becomes

(25), (23) $$\sum_{\{g_k\}} \chi_r(g_k)^*\ \chi_s(g_k) = 0,\ \forall\ r \neq s,\ \{g_k\} = \mathrm{H}^r \cap \mathrm{H}^s. \tag{27}$$

Equation (27) is known as *Johnston's irreducibility criterion* (Johnston (1960)).

The number of times c^i that the IR Γ_i occurs in the reducible representation $\Gamma = \sum_i c^i\ \Gamma_i$ of a group $\mathrm{G} = \{g_k\}$, or *frequency* of Γ_i in Γ, is

(4.4.20) $$c^i = g^{-1}\sum_k \chi_i(g_k)^* \ \chi(g_k), \tag{28}$$

where $\chi(g_k)$ is the character of the matrix representation of g_k in the reducible representation Γ. If Γ_i is a reducible representation, we may still calculate the RS of eq. (28), in which case it is called the *intertwining number* I of Γ_i and Γ,

$$\mathrm{I}(\Gamma_i, \Gamma) = g^{-1}\sum_k \chi_i(g_k)^* \ \chi(g_k), \ \ \Gamma_i, \Gamma \text{ not IRs.} \tag{29}$$

Since I (Γ_i, Γ) is real, eq. (29) is often used in the equivalent form

$$\mathrm{I}(\Gamma_i, \Gamma) = g^{-1}\sum_k \chi_i(g_k) \ \chi(g_k)^*, \ \ \Gamma_i, \Gamma \text{ not IRs.} \tag{30}$$

If Γ_i, Γ have no IRs in common, it follows from the OT for the characters that I $(\Gamma_i, \Gamma) = 0$.

4.8.2 *Frobenius reciprocity theorem*

The frequency c^m of an IR Γ_m of G in the induced representation $\tilde{\Gamma}_i \uparrow$ G with characters $\chi_m(g_j)$ is equal to the frequency $\tilde{c}^i$ of $\tilde{\Gamma}_i$ in the *subduced* $\Gamma_m \downarrow$ H. The tilde is used to emphasize that the $\tilde{\Gamma}_i$ are representations of H. It will not generally be necessary in practical applications when the Mulliken symbols are usually sufficient identification. For example the IRs of S(3) are A_1, A_2, and E, but those of its subgroup C(3) are A, ^{1}E, and ^{2}E. *Subduction* means the restriction of the elements of G to those of H (as occurs, for example, in a lowering of symmetry). Normally this will mean that an IR Γ_m of G becomes a direct sum of IRs in H,

$$\Gamma_m = \sum_p \tilde{c}^p \ \tilde{\Gamma}_p, \quad \chi_m = \sum_p \tilde{c}^p \ \tilde{\chi}_p\,, \tag{31}$$

although if this sum contains a single term, only re-labeling to the IR of the subgroup is necessary. For example, in the subduction of the IRs of the point group T to D_2, the IR T becomes the direct sum of three 1-D IRs $B_1 \oplus B_2 \oplus B_3$ in D_2, while A_1 is re-labeled as A.

Proof

$$c^m = g^{-1}\sum_k \chi_m(g_j)^* \chi(g_j) \tag{28$'$}$$

(22) $$= g^{-1}\sum_r\sum_j \chi_m(g_j)^* \ \chi_r(g_j)$$

(20), (23) $$= g^{-1}\sum_r\sum_l \chi_m(g_r \ h_l \ g_r^{-1})^* \ \tilde{\chi}_i(h_l) \tag{32}$$

$$(31) \qquad = h^{-1}\sum_l \sum_p \tilde{c}^{\,p} \tilde{\chi}_p(h_l)^* \ \tilde{\chi}_i(h_l) \qquad (33)$$

$$= \tilde{c}^i. \qquad (34)$$

The tildes are not standard notation and are not generally needed in applications, but are used in this proof to identify IRs of the subgroup. In writing eq. (32), the sum over j is restricted to a sum over l (subduction) because the elements $g_r \ h_l \ g_r^{-1}$ belong to the class of h_l. In substituting eq. (31) in eq. (32) we use the fact that $\{c^p\}$ is a set of real numbers. Equation (34) follows from eq. (33) because of the OT for the characters. When H is an invariant subgroup of G, $\mathrm{H}^r = \mathrm{H}^s = \mathrm{H}$, $\forall\ r, s$. Then

$$(27), (22) \qquad \sum_l \chi_r(h_l)^* \ \chi_s(h_l) = 0, \ \forall \ r, \ s, r \neq s\,, \qquad (35)$$

where Γ^r, Γ^s are representations of H but are not necessarily IRs.

$$(29) \qquad \sum_l \chi_r(h_l)^* \ \chi_s(h_l) = h \ \mathrm{I}(\Gamma_r\,, \Gamma_s). \qquad (36)$$

Therefore, when H is an invariant subgroup of G,

$$(35), (36) \qquad \mathrm{I}(\Gamma_r, \Gamma_s) = 0; \qquad (37)$$

that is, the representations Γ_r, Γ_s of H have, when reduced, no IRs in common.

Exercise 4.8-3 Test eq. (27) using the representations $\tilde{\Gamma}_1 \uparrow \mathrm{G}$ and $\tilde{\Gamma}_2 \uparrow \mathrm{G}$ of S(3), induced from C(3).

Answers to Exercises 4.8

Exercise 4.8-1 The dimension of the ground representation is equal to the number of cosets, $t = g/h$.

Exercise 4.8-2 Since $\{h_l\} = \mathrm{H}$ is closed, $h_l \, h_m \in \mathrm{H}$, say h_n. Then

$$g_r \ h_l \ g_r^{-1} \ g_r \ h_m \ g_r^{-1} = g_r \ h_l \ h_m \ g_r^{-1} = g_r \ h_n \ g_r^{-1} \in \mathrm{H}^r,$$

verifying that H^r is closed; h_l, h_m, h_n are $\in$ G, and therefore $\{g_r \ h_l \ g_r^{-1}\}$ satisfies the group properties of associativity and each element having an inverse. Moreover, $g_r \ E \ g_r^{-1} = E$, so that H^r does have all the necessary group properties.

Exercise 4.8-3 $\mathrm{H}^r = g_r \ \mathrm{H} \ g_r^{-1} = P_0\{P_0 \ P_1 \ P_2\}P_0^{-1} = \{P_0 \ P_1 \ P_2\} = \mathrm{H}$. $\mathrm{H}^s = P_3\{P_0 \ P_1 \ P_2\}P_3^{-1} = \{P_0 \ P_2 \ P_1\} = \mathrm{H}$. Therefore H is invariant and $\{g_k\} = \mathrm{H}^r \cap \mathrm{H}^s = \ \mathrm{H} = \{P_0 \ P_1 \ P_2\}$. Remember that r, s refer to different diagonal blocks. For $\tilde{\Gamma}_1 \uparrow \mathrm{G}$, $\sum_{\{g_k\}} \chi_r(g_k)^* \ \chi_s(g_k) = 1 + 1 + 1 = 3 \neq 0$, and therefore it is reducible. For $\tilde{\Gamma}_2 \uparrow \mathrm{G}$, $\sum_{\{g_k\}} \chi_r(g_k)^* \ \chi_s(g_k) = 1 + (\varepsilon^*)^2 + \varepsilon^2 = 0$, and therefore it is irreducible. This confirms the character test made in Table 4.12.

Problems

4.1 The point group of allene is $D_{2d} = \{E\ 2S_4\ C_2\ 2C_2'\ 2\sigma_d\}$ (see Problem 2.3). Choose a right-handed system of axes so that the vertical OZ axis points along the principal axis of symmetry.

(a) With the basis $\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3 |$, determine MRs of all eight symmetry operators of this group. Write down the character system of this matrix representation. This representation is reducible and is the direct sum of two IRs. Write down the character systems of these two IRs and check for normalization of the characters. Name these IRs using Mulliken notation.

(b) Determine how R_z transforms under the group operations. You now have sufficient information to arrange the elements of D_{2d} into classes.

(c) How many IRs are there? What are the dimensions of the IRs not yet found? From orthogonality relations find the character systems of these IRs and name them according to the Mulliken conventions. Summarize your results in a character table for D_{2d}.

(d) Find the character system of the DP representation $\Gamma_5 \otimes \Gamma_5$, where Γ_5 is the 2-D representation found in (a). Decompose this DP representation into a direct sum of IRs. [*Hint*: The characters of the DP representation are the products of the characters of the representations in the DP. Here, then, the character system for the DP representation is $\{\chi_5(T)\ \chi_5(T)\}$.]

4.2 Show that (a) $(x - iy)^2$, (b) $R_x + iR_y$, and (c) $R_x - iR_y$ form bases for the IRs of C_3, as stated in Table 4.7.

4.3 Find the character table of the improper cyclic group S_4.

4.4 Explain why the point group $D_2 = \{E\ C_{2\mathbf{z}}\ C_{2\mathbf{x}}\ C_{2\mathbf{y}}\}$ is an Abelian group. How many IRs are there in D_2? Find the matrix representation based on $\langle \mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3 |$ for each of the four symmetry operators $R \in D_2$. The Jones symbols for R^{-1} were determined in Problem 3.8. Use this information to write down the characters of the IRs and their bases from the set of functions $\{z\,x\,y\}$. Because there are three equivalent C_2 axes, the IRs are designated A, B_1, B_2, B_3. Assign the bases R_x, R_y, R_z to these IRs. Using the result given in Problem 4.1 for the characters of a DP representation, find the IRs based on the quadratic functions x^2, y^2, z^2, xy, yz, zx.

4.5 Show that

$$\sum_k c_k\ \chi_k{}^j = g\ \delta_{j1}, \tag{1}$$

where j labels the IRs of G. (Since eq. (1) is based on the orthogonality of the rows, it is not an independent relation.) Verify eq. (1) for the group C_{3v}. (b) Use eq. (1) to deduce the character table of C_{2v}. [*Hint*: Is C_{2v} an Abelian group?]

4.6 (a) Show that the induction of $\tilde{\Gamma}_3 \uparrow G$, where H is C(3) and G is S(3), yields a representation equivalent to $\tilde{\Gamma}_1 \uparrow G$ in Table 4.12. (b) Show that the reducible representation $\tilde{\Gamma}_1 \uparrow G$ in Table 4.12 can be reduced into a direct sum $\Gamma_1 \oplus \Gamma_2$ by a similarity transformation using the matrix

$$S = 2^{-1/2} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}.$$

5 Bases of representations

5.1 Basis functions

The group of the Hamiltonian, or the group of the Schrödinger equation, is the set of function operators $\{\hat{A}\ \hat{B}\ \ldots\ \hat{T}\ \ldots\}$ isomorphous with the symmetry group $(A\ B\ \ldots\ T\ \ldots\}$ (Section 3.5). The function operators commute with the Hamiltonian operator $\hat{H}$ (Section 3.6). We will now show that the eigenfunctions of $\hat{H}$ form a basis for the group of the Hamiltonian. We make use of the fact that if $\{\phi_s\}$ is a set of degenerate eigenfunctions then a linear combination of these eigenfunctions is also an eigenfunction with the same eigenvalue. (A familiar example is the construction of the real eigenfunctions of $\hat{H}$ for the one-electron atom with $l = 1$, p_x, and p_y, from the complex eigenfunctions p_{+1}, p_{-1}; p_0, which corresponds to $m = 0$, is the real eigenfunction p_z.) The property of a basis that we wish to exploit is this. If we have a set of operators that form a group, then a basis is a set of objects, each one of which, when operated on by one of the operators, is converted into a linear combination of the same set of objects. In our work, these objects are usually a set of vectors, or a set of functions, or a set of quantum mechanical operators. For example, for the basis vectors of an n-dimensional linear vector space (LVS)

$$T\langle\mathbf{e}| = \langle\mathbf{e}'| = \langle\mathbf{e}|\Gamma(T), \tag{1}$$

or, in greater detail,

$$T\langle\mathbf{e}_1 \ldots \mathbf{e}_i \ldots| = \langle\mathbf{e}'_1 \ldots \mathbf{e}'_j \ldots| = \langle\mathbf{e}_1 \ldots \mathbf{e}_i \ldots|\Gamma(T), \tag{2}$$

where

$$\mathbf{e}'_j = \sum_{i=1}^{l} \mathbf{e}_i\ \Gamma(T)_{ij}, \quad j = 1, \ldots, l. \tag{3}$$

The $\Gamma(T)_{ij}$ in eq. (3) are the elements of the jth column of the matrix representative $\Gamma(T)$ of the symmetry operator T. A realization of eq. (3) in 3-D space was achieved when the matrix representative (MR) of $R(\phi\ \mathbf{z})$ was calculated in Section 3.2. The MRs form a group representation, which is either an irreducible representation (IR) or a direct sum of IRs. Let $\{\phi_s\}$ be a set of degenerate eigenfunctions of $\hat{H}$ that corresponds to a particular eigenvalue E, so that

$$\hat{H}\ \phi_s = \mathrm{E}\ \phi_s, \quad s = 1, \ldots, l. \tag{4}$$

Because $\hat{H}$ and its eigenvalues are invariant when a symmetry operator T acts on the physical system, $\hat{T}\ \phi_s$ is also an eigenfunction of $\hat{H}$ with the same eigenvalue E, and therefore it is a linear combination of the $\{\phi_s\}$,

$$\hat{T}\phi_s = \sum_{r=1}^{l} \phi_r\, \Gamma(T)_{rs}, \quad s = 1, \ldots, l. \tag{5}$$

In matrix form,

$$\hat{T}\langle\phi_1 \ldots \phi_s \ldots| = \langle\phi'_1 \ldots\ \phi'_s \ldots| = \langle\phi_1 \ldots \phi_r \ldots\ |\Gamma(T). \tag{6}$$

Equation (6) can be written more compactly as

$$\hat{T}\langle\phi| = \langle\phi'| = \langle\phi|\Gamma(T), \tag{7}$$

where $\langle\phi|$ implies the whole set $\langle\phi_1\ \ldots\ \phi_s\ \ldots\ |$. Equations (7) and (1) show that the $\{\phi_s\}$ are a set of basis functions in an l-dimensional LVS, called a *function space*, which justifies the use of the alternative, equivalent, terms "eigenfunction" and "eigenvector." Because of eqs. (5)–(7), every set of eigenfunctions $\{\phi_s\}$ that corresponds to the eigenvalue E forms a basis for one of the IRs of the symmetry group G = $\{T\}$. Consequently, every energy level and its associated eigenfunctions may be labeled according to one of the IRs of $\{T\}$. The notation $\{\phi_s^k\}$, E^k means that the eigenfunctions $\{\phi_s^k\}$ that correspond to the eigenvalue E^k form a basis for the kth IR. Although the converse is not true – a set of basis functions is not necessarily a set of energy eigenfunctions – there are still advantages in working with sets of basis functions. Therefore we shall now learn how to construct sets of basis functions which form bases for particular IRs.

5.2 Construction of basis functions

Just as any arbitrary vector is the sum of its projections,

$$\mathbf{v} = \sum_i \mathbf{e}_i\, \mathbf{v}_i, \tag{1}$$

where $\mathbf{e}_i\ \mathbf{v}_i$ is the projection of $\mathbf{v}$ along $\mathbf{e}_i$, so any arbitrary function

$$\phi = \sum_k \sum_{s=1}^{l_k} \phi_s^k\, b_s^k, \tag{2}$$

where $\sum_k$ is over the IRs, and $\sum_{s=1}^{l_k}$ is a sum of projections within the subspace of the kth IR. The problem is this: how can we generate $\{\phi_p^j\}$, $p = 1,\ \ldots,\ l_j$, the set of l_j orthonormal functions which form a basis for the jth IR of the group of the Schrödinger equation? We start with any *arbitrary* function ϕ defined in the space in which the set of function operators $\{\hat{T}\}$ operate. Then

(2) $$\phi = \sum_k \sum_{s=1}^{l_k} \phi_s^k\, b_s^k = \sum_k \phi^k, \tag{3}$$

where $\phi_s^k\ b_s^k$ is the projection of ϕ along ϕ_s^k. Because ϕ_s^k is a basis function,

(3)
$$\hat{T}\phi_s^k = \sum_{r=1}^{l_k} \phi_r^k\ \Gamma^k(T)_{rs}. \tag{4}$$

(3), (4)
$$\begin{aligned}&(l_j/g)\sum_T \Gamma^j(T)_{pp}^*\ \hat{T}(\phi)\\ &= (l_j/g)\sum_T \Gamma^j(T)_{pp}^* \sum_k\sum_s\sum_r \phi_r^k\ \Gamma^k(T)_{rs}\ b_s^k\\ &= (l_j/g)\sum_k\sum_s\sum_r\left[\sum_T \Gamma^j(T)_{pp}^*\ \Gamma^k(T)_{rs}\right]\phi_r^k\ b_s^k.\end{aligned} \tag{5}$$

By the orthogonality theorem, the sum in brackets in eq. (5) is $(g/l_j)\delta_{jk}\delta_{pr}\delta_{ps}$, and consequently the triple sum yields unity if $k=j$, $r=p$, and $s=p$; otherwise it is zero. Therefore,

(5)
$$(l_j/g)\sum_T \Gamma^j(T)_{pp}^*\ \hat{T}(\phi) = \phi_p^j\ b_p^j, \tag{6}$$

and so we have ϕ_p^j apart from a constant which can always be fixed by normalization. The operator

$$(l_j/g)\sum_T \Gamma^j(T)_{pp}^*\ \hat{T} = \hat{P}_{pp}^j \tag{7}$$

is a *projection operator* because it projects out of ϕ that part which transforms as the pth column of the jth IR,

(7), (6)
$$\hat{P}_{pp}^j\ \phi = \phi_p^j\ b_p^j. \tag{8}$$

By using all the $\hat{P}_{pp}^j$, $p=1, \ldots, l_j$, in turn, that is all the diagonal elements of $\Gamma^j(T)$, we can find all the l_j functions $\{\phi_p^j\}$ that form a basis for Γ^j.

(8), (2)
$$\hat{P}^j\ \phi = \sum_p \hat{P}_{pp}^j\ \phi = \sum_{p=1}^{l_j} \phi_p^j\ b_p^j = \phi^j. \tag{9}$$

The RS side of eq. (9) is a linear combination of the l_j functions that forms a basis for Γ^j. The operator in eq. (9) is

(9), (7)
$$\hat{P}^j = \sum_p (l_j/g)\sum_T \Gamma^j(T)_{pp}^*\ \hat{T} = (l_j/g)\sum_T \chi^j(T)^*\ \hat{T}. \tag{10}$$

It projects out from ϕ in one operation the sum of all the parts of ϕ that transform according to Γ^j. Being a linear combination of the l_j linearly independent (LI) basis functions $\{\phi_p^j\}$, ϕ^j is itself a basis function for Γ^j. Equation (9) is preferable to eq. (8), that is $\hat{P}^j$ is preferred to $\hat{P}_{pp}^j$ because it requires only the characters of $\Gamma^j(T)$ and not all its diagonal elements $\sum_T \Gamma^j(T)_{pp}$. If Γ^j is 1-D, then ϕ^j is the basis function for Γ^j. But if Γ^j is not 1-D (i.e. l_j is not equal to unity) the procedure is repeated with a new ϕ to obtain a second ϕ^j, and so on, until l_j LI functions have been obtained.

5.3 Direct product representations

The *direct product* (DP) of two matrices $\mathbb{A} \otimes \mathbb{B}$ is defined in Section A1.7. If Γ is the DP of two representations Γ^i, Γ^j, then

$$\Gamma(T) = \Gamma^i(T) \otimes \Gamma^j(T), \quad \forall\ T \in G. \tag{1}$$

But is $\Gamma(T)$ also a representation?

(1), (A1.7.7)

$$\begin{aligned} \Gamma(T_1)\ \Gamma(T_2) &= (\Gamma^i(T_1) \otimes \Gamma^j(T_1))(\Gamma^i(T_2) \otimes \Gamma^j(T_2)) \\ &= (\Gamma^i(T_1)\ \Gamma^i(T_2)) \otimes (\Gamma^j(T_1)\ \Gamma^j(T_2)) \\ &= \Gamma^i(T_1 T_2) \otimes \Gamma^j(T_1 T_2) \\ &= \Gamma(T_1 T_2),\ \text{or}\ \Gamma^{ij}(T_1 T_2), \end{aligned} \tag{2}$$

which shows that the DP of the two representations Γ^i and Γ^j is also a representation. The second notation in eq. (2) stresses that the representation Γ^{ij} is derived from the DP of Γ^i and Γ^j. So we conclude that *the direct product of two representations is itself a representation*.

If $\{\phi_q^i\}, q = 1, \ldots, m$, is a set of functions that form a basis for Γ^i, and $\{\phi_s^j\}, s = 1, \ldots, n$, is a set of functions that form a basis for Γ^j, then the *direct product set* $\{\phi_q^i\ \phi_s^j\}$, which contains mn functions, forms a basis for the DP representation Γ^{ij}.

$$\begin{aligned} \hat{T}\ \phi_q^i\ \phi_s^j &= \phi_q^i(T^{-1}\{x\})\phi_s^j(T^{-1}\{x\}) \\ &= (\hat{T}\ \phi_q^i)(\hat{T}\ \phi_s^j) \\ &= \sum_{p=1}^{m} \phi_p^i\ \Gamma^i(T)_{pq} \sum_{r=1}^{n} \phi_r^j\ \Gamma^j(T)_{rs} \\ &= \sum_p \sum_r \phi_p^i\ \phi_r^j\ \Gamma^i(T)_{pq}\ \Gamma^j(T)_{rs} \\ &= \sum_p \sum_r \phi_p^i\ \phi_r^j\ \Gamma^{ij}(T)_{pr,\,qs}, \end{aligned} \tag{3}$$

since the product of the pqth element from the MR $\Gamma^i(T)$, and the rsth element of the MR $\Gamma^j(T)$, is the pr,qsth element of the DP matrix $\Gamma^{ij}(T)$. Therefore, *the direct product set* $\{\phi_q^i\ \phi_s^j\}$ *is a basis for the direct product representation* $\Gamma^i \otimes \Gamma^j$. The characters of the MRs in the DP representation

$$\begin{aligned} \chi_{ij}(T) &= \sum_p \sum_r \Gamma^{ij}(T)_{pr,pr} \\ &= \sum_p \sum_r \Gamma^i(T)_{pp}\ \Gamma^j(T)_{rr} \\ &= \chi_i(T)\ \chi_j(T). \end{aligned} \tag{4}$$

Therefore, the character of an MR in the DP representation is the product of the characters of the MRs that make up the DP. Direct product representations may be reducible or irreducible.

Table 5.1. *Some direct product representations in the point group* C_{3v}.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
$E \otimes A_1$	2	−1	0
$E \otimes A_2$	2	−1	0
$E \otimes E$	4	1	0

Example 5.3-1 Find the DPs of E with all three IRs of the point group C_{3v}. The characters of the IRs of C_{3v} and their DPs with E are given in Table 5.1.

By inspection, or by using

$$c^j = g^{-1} \sum_T \chi_j(T)^* \ \chi(T),$$

we find $E \otimes A_1 = E$, $E \otimes A_2 = E$, and $E \otimes E = A_1 \oplus A_2 \oplus E$.

5.3.1 Symmetric and antisymmetric direct products

With $j = i$, we introduce the symbols ϕ_q^i, ψ_s^i $(q, s = 1, \ldots, m)$ to designate basis functions from two bases γ, γ' of the ith IR. (The possibility that γ and γ' might be the same basis is not excluded.) Since there is only one representation under consideration, the superscript i may be suppressed. The DP of the two bases is

$$\langle \phi_q | \otimes \langle \psi_s | = \langle \phi_q \psi_s | = ½\langle \phi_q \psi_s + \phi_s \psi_q | \oplus ½\langle \phi_q \psi_s - \phi_s \psi_q |. \tag{5}$$

The first term on the RS of eq. (5) is symmetric and the second term is anti-symmetric, with respect to the exchange of subscripts q and s. These two terms are called the symmetrical ($\overline{\otimes}$) and antisymmetrical ($\underline{\otimes}$) DP, respectively, and eq. (5) shows that the DP of the two bases is the direct sum of the symmetrical and antisymmetrical DPs,

$$\langle \phi_q | \otimes \langle \psi_s | = (\langle \phi_q | \overline{\otimes} \langle \psi_s |) \oplus (\langle \phi_q | \underline{\otimes} \langle \psi_s |). \tag{6}$$

If the two bases are identical, then the antisymmetrical DP vanishes and the only DP is the symmetrical one.

(3) $$\hat{T} \ \phi_q \ \psi_s = \sum_p \sum_r \phi_p \ \psi_r \ \Gamma(T)_{pq} \ \Gamma(T)_{rs}; \tag{7}$$

(3) $$\hat{T} \ \phi_s \ \psi_q = \sum_p \sum_r \phi_p \ \psi_r \ \Gamma(T)_{ps} \ \Gamma(T)_{rq}; \tag{8}$$

$$(5),(7),(8) \qquad \hat{T}\ \phi_q\ \psi_s = \tfrac{1}{2}\sum_p\ \sum_r \phi_p\ \ \psi_r[\Gamma(T)_{pq}\ \Gamma(T)_{rs} + \Gamma(T)_{ps}\ \Gamma(T)_{rq}]$$

$$+\tfrac{1}{2}\left[\sum_p\sum_r \phi_p\ \ \psi_r[\Gamma(T)_{pq}\ \Gamma(T)_{rs} - \Gamma(T)_{ps}\ \Gamma(T)_{rq}]\right]. \tag{9}$$

Restoring the index i on Γ for greater clarity,

$$(9) \qquad \hat{T}\ \ \phi_q\ \ \psi_s = \sum_p\sum_r \phi_p\ \ \psi_r[\Gamma^{i\overline{\otimes}i}(T)_{pr,\,qs} + \Gamma^{i\underline{\otimes}i}(T)_{pr,\,sq}]. \tag{10}$$

$$(9),(10) \qquad \Gamma^{i\overline{\underline{\otimes}}i}(T)_{pr,\,qs} = \tfrac{1}{2}[\Gamma^i(T)_{pq}\ \Gamma^i(T)_{rs} \pm \Gamma^i(T)_{ps}\ \Gamma^i(T)_{rq}], \tag{11}$$

where $i\overline{\underline{\otimes}}i$ means either the symmetrical or antisymmetrical DP according to whether the positive sign or the negative sign is taken on the RS of eq. (11). To find the characters, set $q = p$, $s\ = r$, and sum over p and r:

$$(11) \qquad \chi^{i\overline{\underline{\otimes}}i}(T) = \tfrac{1}{2}\left[\sum_p\sum_r \Gamma^i(T)_{pp}\ \Gamma^i(T)_{rr} \pm \Gamma^i(T)_{pr}\ \Gamma^i(T)_{rp}\right]$$

$$= \tfrac{1}{2}\left[\sum_p\sum_r \Gamma^i(T)_{pp}\ \Gamma^i(T)_{rr} \pm \sum_p \Gamma^i(T^2)_{pp}\right]$$

$$= \tfrac{1}{2}[(\chi^i(T))^2 \pm \chi^i(T^2)]. \tag{12}$$

Example 5.3-2 Show that for the point group C_{3v}, $E\overline{\otimes}E = A_1 \oplus E$ and $E\underline{\otimes}E = A_2$. Using the character table for C_{3v} in Example 5.3-1, eq. (12) yields

C_{3v}	E	$2C_3$	3σ
$\chi^E(T)$	2	−1	0
$\chi^E(T^2)$	2	−1	2
$\chi^{E\overline{\otimes}E}(T)$	3	0	1
$\chi^{E\underline{\otimes}E}(T)$	1	1	−1

Therefore, $E\overline{\otimes}E = A_1 \oplus E$, $E\underline{\otimes}E = A_2$. The sum of the symmetrical and antisymmetrical DPs is $E \otimes E$, as expected from eq. (11). (See Example 5.3-1.)

5.4 Matrix elements

5.4.1 Dirac notation

In quantum mechanics, an integral of the form

$$\int \psi_u^*\ \ \hat{Q}\ \ \psi_q\ \ \mathrm{d}\tau = \int (\hat{Q}^\dagger\ \ \psi_u)^*\ \ \psi_q\ \ \mathrm{d}\tau \tag{1}$$

is called a *matrix element*. $\hat{Q}^\dagger$ is the adjoint of the operator $\hat{Q}$, and the definition of $\hat{Q}^\dagger$ is that it is the operator which satisfies eq. (1). In Dirac notation this matrix element is written as

$$\langle \psi_u | \hat{Q} | \psi_q \rangle = \langle \psi_u | \hat{Q}\, \psi_q \rangle = \langle \hat{Q}^\dagger\, \psi_u | \psi_q \rangle. \tag{2}$$

In matrix notation $\langle u^* | v \rangle$ describes the matrix representation of the Hermitian scalar product of the two vectors **u, v**, in an LVS with unitary basis ($\mathtt{M} = |\mathbf{e}^*\rangle\langle \mathbf{e}| = \mathtt{E}$). The second and third expressions in eq. (2) are *scalar products* in an LVS in which the basis vectors are the functions $\{\psi_q\}$ and the scalar product is defined to be an integral over the full range of the variables. Thus, the second equality in eq. (2) conveys precisely the same information as eq. (1). The first part of the complete bracket in eq. (2), $\langle \psi_u |$, is the bra-vector or *bra*, and the last part, $|\psi_q\rangle$, is the ket-vector or *ket*, and the complete matrix element is a *bra*(c)*ket* expression. Notice that in Dirac notation, complex conjugation of the function within the bra is part of the definition of the scalar product. The ket $|\psi_q\rangle$ represents the function ψ_q, in the matrix element integral. When $\hat{Q}$ operates on the function ψ_q, it produces the new function $\hat{Q}\psi_q$ so that when $\hat{Q}$ operates to the right in eq. (2) it gives the new ket $|\hat{Q}\psi_q\rangle$. But because eqs. (2) and (1) state the same thing in different notation, when $\hat{Q}$ operates to the left it becomes the adjoint operator, $\langle \psi_u | \hat{Q} = \langle \hat{Q}^\dagger \psi_u |$. Some operators are self-adjoint, notably the Hamiltonian $\hat{H} = \hat{H}^\dagger$.

5.4.2 *Transformation of operators*

Suppose that $\hat{Q}\ f = g$ and that when a symmetry operator T acts on the physical system $\hat{\mathrm{T}}\ f = f'$, $\hat{\mathrm{T}}\ g = g'$. Now,

$$g' = \hat{T}\, g = \hat{T}\ \hat{Q}\ f = \hat{T}\ \hat{Q}\ T^{-1}\ T f = \hat{T}\ \hat{Q}\ T^{-1}\ f'. \tag{3}$$

Comparing this with $g = \hat{Q} f$, we see that the effect of T has been to transform the operator from $\hat{Q}$ into a new operator $\hat{Q}'$, where

(3)
$$\hat{Q}' = \hat{T}\ \hat{Q}\ \hat{T}^{-1}. \tag{4}$$

Operators may also form bases for the IRs of the group of the Hamiltonian, for if $\hat{Q}$ is one of the set of operators $\{\hat{Q}_s^j\}$, and if

$$\hat{T}\ \hat{Q}_s^j\ T^{-1} = \sum_r \hat{Q}_r^j\ \hat{\Gamma}^j(T)_{rs} \tag{5}$$

then the $\{\hat{Q}_s^j\}$ form a basis for the jth IR.

5.4.3 *Invariance of matrix elements under symmetry operations*

In quantum mechanics, matrix elements (or scalar products) represent physical quantities and they are therefore invariant when a symmetry operator acts on the physical system. For example, the expectation value of the dynamical variable Q when the system is in the state described by the state function f is

$$\langle Q \rangle = \langle f|\hat{Q}|f\rangle = \langle f|g\rangle. \tag{6}$$

It follows that the function operators $\hat{T}$ are unitary operators. For

(6) $$\langle f|g\rangle = \langle \hat{T} f|\hat{T}\, g\rangle = \langle \hat{T}^{\dagger}\, \hat{T}\, f|g\rangle \tag{7}$$

(7) $$\hat{T}^{\dagger}\, \hat{T} = \hat{E}, \tag{8}$$

(8) $$\Gamma(T)^{\dagger}\, \Gamma(T) = \mathrm{E}, \tag{9}$$

so that the MRs of the function operators are unitary matrices. An important question which can be answered using group theory is: "Under what conditions is a matrix element zero?" Provided we neglect spin–orbit coupling, a quantum, mechanical state function (spin orbital) can be written as a product of a spatial part, called an orbital, and a spinor, $\boldsymbol{\Psi}(\mathbf{r}, m_s) = \psi(\mathbf{r})\chi(m_s)$. Since $\hat{Q}_s^j$ acts on space and not spin variables, the matrix element $\langle \boldsymbol{\Psi}_u^k|\hat{Q}_s^j|\boldsymbol{\Psi}_q^i\rangle$ factorizes as

$$\langle \boldsymbol{\Psi}_u^k|\hat{Q}_s^j|\boldsymbol{\Psi}_q^i\rangle = \langle \psi_u^k|\hat{Q}_s^j|\psi_q^i\rangle\langle \chi_u|\chi_q\rangle. \tag{10}$$

It follows from the orthogonality of the spin functions that $\langle \chi_u|\chi_q\rangle = 0$ unless χ_u, χ_q have the same spin quantum number. Hence the matrix element in eq. (10) is zero unless $\Delta S = 0$. When the matrix element describes a transition probability, this gives *the spin selection rule*. Spin–orbit coupling, although often weak, is not zero, and so the spin selection rule is not absolutely rigid. Nevertheless it is a good guide since transitions between states with $\Delta S \neq 0$ will be weaker than those for which the spin selection rule is obeyed. Now consider what happens to a matrix element under symmetry operator T. Its value is unchanged, so

$$\langle \psi_u^k|\hat{Q}_s^j|\psi_q^i\rangle = \langle \hat{T}\, \psi_u^k|\hat{T}\, \hat{Q}_s^j\, \hat{T}^{-1}|\hat{T}\, \psi_q^i\rangle. \tag{11}$$

The LS of eq. (11) is invariant under $\{T\}$ and so it belongs to the totally symmetric representation Γ_1. The function $\hat{Q}_s^j\, \psi_q^i$ transforms according to the DP representation $\Gamma^i \otimes \Gamma^j$. To see this, consider what happens when a symmetry operator T acts on configuration space: $\hat{Q}_s^j|\psi_q^i\rangle$ becomes

$$\begin{aligned}\hat{T}\, \hat{Q}_s^j\, \hat{T}^{-1}|\hat{T}\;\; \psi_q^i\rangle &= \sum_p \sum_r \Gamma^i(T)_{pq}\; \Gamma^j(T)_{rs}\; \hat{Q}_r^j|\psi_p^i\rangle \\ &= \sum_p \sum_r [\Gamma^i(T) \otimes \Gamma^j(T)]_{pr,qs}\; \hat{Q}_r^j|\psi_p^i\rangle.\end{aligned} \tag{12}$$

Therefore under T, $\hat{Q}_s^j|\psi_q^i\rangle$ transforms according to the DP representation $\Gamma^i(T) \otimes \Gamma^j(T)$. The integrand in eq. (11) is the product of two functions, $(\psi_u^k)^*$ and $\hat{Q}_s^j|\psi_q^i\rangle$, and it therefore transforms as the DP $\Gamma^{k*} \otimes \Gamma^i \otimes \Gamma^j$ or $\Gamma^{k*} \otimes \Gamma^{ij}$. What is the condition that $\Gamma^{a*} \otimes \Gamma^b \supset \Gamma^1$? This DP contains Γ^1 if

$$c^1 = g^{-1} \sum_T \chi_1(T)\, \chi^{a*b}(T) = g^{-1} \sum_T \chi^a(T)^* \, \chi^b(T) \neq 0, \tag{13}$$

which will be so if and only if $a = b$ (from the orthogonality theorem for the characters). Therefore the matrix element $\langle \psi_u^k | \hat{Q}_s^j | \psi_q^i \rangle$ is zero unless the DP $\Gamma^i \otimes \Gamma^j \supset \Gamma^k$. But $\Gamma^k \otimes \Gamma^k \supset \Gamma^1$, and so the matrix element is zero unless $\Gamma^i \otimes \Gamma^j \otimes \Gamma^k \supset \Gamma^1$. *Therefore, the matrix element is zero unless the DP of any two of the representations contains the third one*.

5.4.4 Transition probabilities

The probability of a transition being induced by interaction with electromagnetic radiation is proportional to the square of the modulus of a matrix element of the form $\langle \psi^k | \hat{Q}^j | \psi^i \rangle$, where the state function that describes the initial state transforms as Γ^i, that describing the final state transforms as Γ^k, and the operator (which depends on the type of transition being considered) transforms as Γ^j. The strongest transitions are the E1 transitions, which occur when $\hat{Q}$ is the electric dipole moment operator, $-e\mathbf{r}$. These transitions are therefore often called "electric dipole transitions." The components of the electric dipole operator transform like x, y, and z. Next in importance are the M1 transitions, for which $\hat{Q}$ is the magnetic dipole operator, which transforms like R_x, R_y, R_z. The weakest transitions are the E2 transitions, which occur when $\hat{Q}$ is the electric quadrupole operator which, transforms like binary products of x, y, and z.

Example 5.4-1 The absorption spectrum of benzene shows a strong band at 1800 Å, two weaker bands at 2000 Å and 2600 Å, and a very weak band at 3500 Å. As we shall see in Chapter 6, the ground state of benzene is $^1A_{1g}$, and there are singlet and triplet excited states of B_{1u}, B_{2u}, and E_{1u} symmetry. Given that in D_{6h}, (x, y) form a basis for E_{1u} and z transforms as A_{2u}, find which transitions are allowed.

To find which transitions are allowed, form the DPs between the ground state and the three excited states and check whether these contain the representations for which the dipole moment operator forms a basis:

$$A_{1g} \otimes B_{1u} = B_{1u},$$
$$A_{1g} \otimes B_{2u} = B_{2u},$$
$$A_{1g} \otimes E_{1u} = E_{1u}.$$

Only one of these (E_{1u}) contains a representation to which the electric dipole moment operator belongs. Therefore only one of the three possible transitions is symmetry allowed, and for this one the radiation must be polarized in the (x, y) plane (see Table 5.2).

The strong band at 1800 Å is due to the $^1A_{1g} \rightarrow {}^1E_{1u}$ transition. The two weaker bands at 2000 Å and 2600 Å are due to the $^1A_{1g} \rightarrow {}^1B_{1u}$ and $^1A_{1g} \rightarrow {}^1B_{2u}$ transitions becoming allowed through *vibronic coupling*. (We shall analyze vibronic coupling later.) The very weak transition at 3500 Å is due to $^1A_{1g} \rightarrow {}^3E_{1u}$ becoming partly allowed through spin–orbit coupling.