SYMMETRY in the World of Molecules

I. S DMITRIEV

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И. С. ДМИТРИЕВ

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FOREWORD

> It is the combination of rigorous symmetry arguments and qualitative or semi-quantitative physical theory that forms the basis of valence theory.
>
> R.M. Hochstrasser

This booklet is devoted to one of the most important concepts of natural science, the concept of symmetry. The beneficial impact of the symmetry theory can be traced in the theory of elementary particles, crystallography, solid state physics, space and time theory, molecular biology, quantum chemistry, the study of arts, the theory of music as well as many branches of mathematics.

Since many things are necessarily omitted even in a large monograph, this is all the more so in a small unpretentious booklet. Our narration does not cover transpositional symmetry, solid state theory and numerous problems pertaining to application of symmetry theory to organic chemistry. This booklet deals primarily with spatial symmetry of molecules.

The study of any theory is to a certain extent similar to the learning of a foreign language. While some people learn it in order to write and speak fluently, others are satisfied with the understanding of foreign texts even if using a dictionary. The same is true in the case of a theory. While some people learn it very comprehensively in order to work actively in the area, it is sufficient for others to understand the language of theorists and the substance of their conclusions. This book is intended for the latter group, who are much more numerous than the former. This booklet is intended just for them. We address it to experimental chemists, teachers, university students and even high school senior students.

The symmetry theory is usually applied to the specific problems of physics and chemistry when non-algebraic objects such as atoms, molecules, solids are studied with algebraic methods. Therefore some readers will probably need to overcome certain barriers of mathematical reasoning.

The general logical plan of the booklet is as follows. The first chapter has a narrative nature and is dedicated to the description of the major types of molecular symmetry. The second chapter may be considered as a mathematical model of the first. The next two chapters are devoted to problems of the interrelation between the composition, geometry and electronic structure of molecules (Chapter 3) and chemical reactions (Chapter 4). The final fifth chapter is of an historic and methodological character.

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Chapter Four

Chapter Five

Chapter One

SYMMETRY OF A NUCLEAR POLYHEDRON

> Symmetries might give us a certain pleasure and perhaps amazement to contemplate, even though they would not furnish new information.
>
> E. Wigner

Elements and Operations of Symmetry

Modern chemistry deals with a tremendous number of substances and creates a great variety of geometric forms. Each molecule differs not only in the kind and number of constituent atoms but also in the symmetry of its nuclear skeleton, that is the nuclear polyhedron. The symmetry of a molecule has to be taken into account when its electronic structure is considered.

How is symmetry defined? Everyone has an intuitive notion of symmetry. Symmetry, some people would

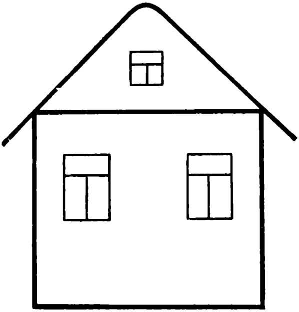


FIG. 1.

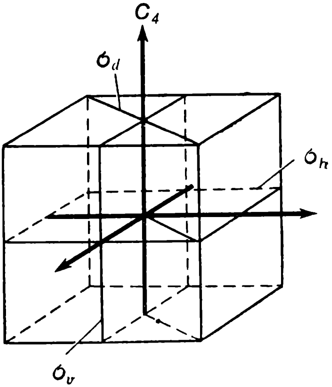


FIG. 2

say, is when one part of a geometric body is exactly the same as another, but "reflected in the mirror" (see, for example, Fig. 1). Not necessarily, the others would argue, it could be that the rotation of a figure through some angle, say 60°, does not change its appearance. Both groups of people are right but only partially. Indeed, the symmetry of a body is specified by the combination of rotations and reflections that do not change its "appearance", or, strictly speaking, match the body with itself.

TABLE 1

Symmetry elements	Symmetry operations
Plane	Reflection in a plane (σ)
Centre of symmetry, or inversion centre	Inversion of all atoms through a centre (i)
n-fold axis	One or several rotations about an axis through an angle of $2\pi/n$ (C_n)
n-fold rotation-reflection axis	Rotation through an angle of $2\pi/n$ followed by reflection in a plane perpendicular to the rotation axis (S_n)

It follows that the precondition of symmetry of a geometric body is the presence of axes and planes of symmetry (some axes and planes of symmetry in a cube are indicated in Fig. 2).

Such axes and planes are known as *symmetry elements.* Each symmetry element brings up the corresponding *symmetry transformations*, or *symmetry operations.* They are listed in Table 1.

Rotation about an axis. If a body rotating about an axis through an angle of 2π (360°) coincides with itself

n times then the axis is referred to as the n-fold symmetry axis. It is denoted by C_n (the letter "C" is derived from the Latin word "circulate").

Obviously, the least angle of rotation which brings about coincidence is equal to $2\pi/n$ (or $360°/n$). The symmetry operation is denoted by the same letter as the axis, i.e. C_n. Occasionally somewhat different symbols are used: C_n for the symmetry axis and $\hat{C}_n$ for the symmetry operation (transformation) about that axis.

If we perform several (for example, k) successive rotations of a body through an angle of $2\pi/n$, i.e. we actually rotate a body through an angle of $2\pi k/n$, the operation is denoted as C_n^k. Having been carried out n times the symmetry operation C_n brings a body (a polyhedron) back into the initial position. This is equivalent to the identity transformation E which is the same as not moving the polyhedron at all:

$$C_n^n \equiv E$$

If a body has several symmetry axes, the one with the highest n is called the *principal axis.*

Reflection in a plane. Another symmetry element is a plane bisecting a body into two parts which are mirror images of each other. A plane of this kind is the symmetry plane and the operation of reflection in it is designated by the symbol σ. It is obvious that two successive reflections in the same plane are equivalent to the identity transformation:

$$\sigma^2 \equiv E$$

The symbol σ is supplied by a subscript indicating the position of the symmetry plane relative to the principal axis. So σ_h signifies reflection in the plane perpendicular to the principal axis (h stands for "horizontal");

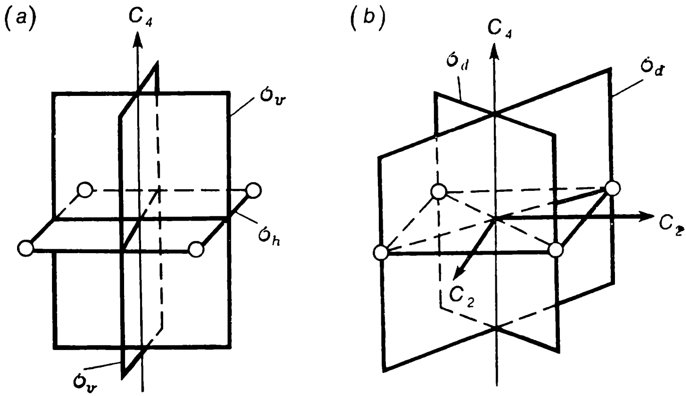


FIG. 3

σ_v, the reflection in the plane containing the principal axis (v for "vertical") and σ_d, reflection in the plane which contains the principal axis and bisects the angle between two C_2 axes (d for "diagonal") (see Fig. 3).

Rotation-reflection axes. A body can be matched with itself in another way, that is by rotation through an angle of $2\pi/n$ followed by reflection in a plane perpendicular to the rotation axis. Such a symmetry operation is called the mirror rotation and denoted by the symbol S_n. The axis of rotation is referred to as the n-fold rotation-reflection axis (Fig. 4). Inasmuch as this operation combines both rotation and reflection it can be represented as the "multiplication" of ope-

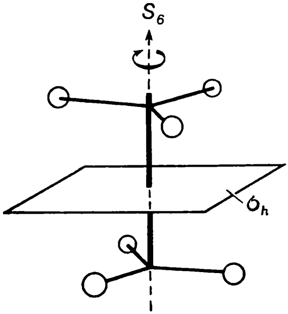
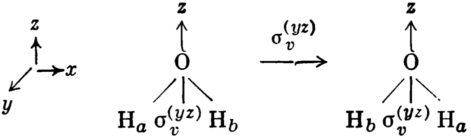


FIG. 4

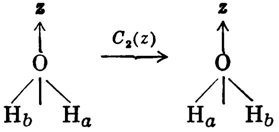
rations:

$$S_n = C_n\sigma_h = \sigma_h C_n$$

In general, the presentation of symmetry operations as the multiplication of one by another should be interpreted this way: one has to perform first the operation indicated in the right part of the "product", and then the second one. In the case of the water molecule, for example, the product of symmetry operations $C_2\sigma_v$ means that the reflection in a plane σ_v must be performed first. As a result, hydrogen atoms switch positions



Then the molecule is rotated about the C_2 axis, and the atoms come back to their initial positions



Instead of performing these two operations it is sufficient just to reflect the molecule in the $\sigma_v^{(xz)}$ plane. Therefore we may write the following:

$$C_2^{(z)}\sigma_v^{(yz)} = \sigma_v^{(xz)}$$

Frequently the order of performing symmetry transformations becomes very important. Unlike the conventional high school arithmetic the permutation of "cofactors" in the symmetry theory may occasionally alter the "product". Let us consider, for example, the

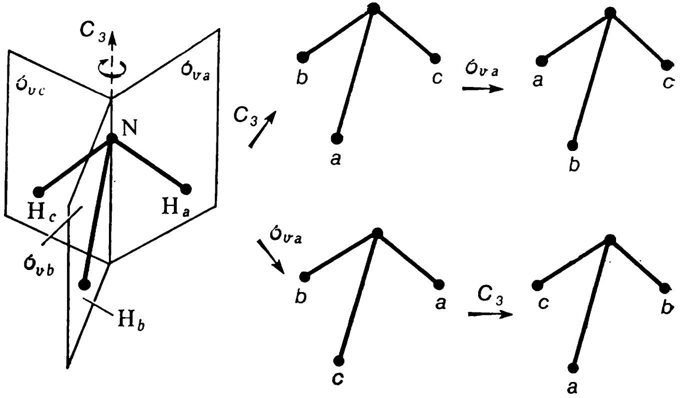


FIG. 5

ammonia molecule. In Fig. 5 one can see that the final positions of the atoms H_a, H_b and H_c depend on the sequence of operations performed.

Inversion operation. Note that a two-fold rotation-reflection axis is equivalent to the presence of a *centre of symmetry* in a body. The centre of symmetry is located in the point of intersection of the S_2 axis and the σ_h plane. The inversion operation is usually denoted by the symbol i:

$$i \equiv S_2 = C_2\sigma_h$$

Order is needed. As a rule a nuclear polyhedron of a molecule possesses not one but many symmetry elements. The definite relation between them can be established using one of the most important concepts of modern mathematics, i.e. the concept of a *group*.

Concept of a Group

What is a group? Usually, when talking of groups one implies a set of objects, notions, men, etc. Mathematicians define a group as a set of elements between which certain binary relations are specified, i.e. any two group elements are associated with a third element of the same group. For example, two integers, 4 and 5, may correspond to a third integer—9, i.e. their sum. The integer 9 belongs to the same set or group of nonnegative integers as the summands do. Here is another example. In ancient times, when money did not exist and people exchanged commodities, two lambs could be procured for, say, a sack of grain. This is also one of the ways to specify rules of correspondence between elements of the set which in this case is the set of objects to be exchanged. As any other analogy this comparison is conditional. Bartering is not always a binary operation. Indeed, a sack of grain could be exchanged for several knives....

Thus the rule bringing two group elements into correspondence with the third one may alter according to the substance of a problem. Mathematicians call such a rule for combining elements a *group product*. It should be remembered that (as we saw in the examples quoted earlier) this product is not always a conventional one.

Therefore, to convert a set of elements into a group the rule of correspondence should be specified. This could be written as

$$a \cdot b = c$$

Here a, b and c are elements of a group and the sign $\cdot$ indicates some rule or law bringing elements a and b in correspondence with the element c.

For a set of elements to constitute a group the second condition must also be satisfied, which is the associative law of group multiplication:

$$(a \cdot b) \cdot c = a \cdot (b \cdot c)$$

This law states that if the element which is the "product" of a and b is "multiplied" by c the resulting element is the same as would be obtained by multiplying the element a by the "product" of b and c.

Besides, a group must have at least one element usually denoted by the letter E and called the *identity element* which makes the following relation valid for any element a of the group:

$$a \cdot E = E \cdot a = a$$

And the final condition: every element a of a group must have an inverse element a^{-1} obeying the relation

$$a \cdot a^{-1} = a^{-1} \cdot a = E$$

Our collection of elements constitutes a group if these four conditions are met, i.e. the rule of group multiplication is defined so that the associative law is valid, an identity element is singled out and every element has its inverse which also belongs to this group.

Symmetry group. Now let us pass on from mathematical abstractions to a specific chemical example. Consider the water molecule which is known to have the following geometrical structure:

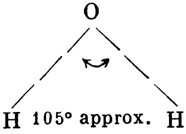


Fig. 6 illustrates the symmetry elements of the water molecule: C_2, σ_v, σ'_v.

Let us "multiply" the symmetry elements of the water molecule one by one. The results of such multiplication

TABLE 2

C_{2v}	E	C_2	σ_v	σ'_v
E	E	C_2	σ_v	σ'_v
C_2	C_2	E	σ'_v	σ_v
σ_v	σ_v	σ'_v	E	C_2
σ'_v	σ'_v	σ_v	C_2	E

are listed in Table 2. Here we denoted the operation of reflection in the *yz* plane as σ_v, in the *xz* plane as σ'_v (see Fig. 6) and the operation of rotation about the *z* axis as C_2.

Table 2 shows that the product of any two symmetry operations for the water molecule again results in a symmetry operation for the same molecule. The case discussed on page 113 may serve as an example:

$$C_2\sigma_v = \sigma'_v$$

Whatever symmetry elements are "multiplied" we shall never obtain a symmetry element which the molecule does not possess. Obviously, that is the evidence

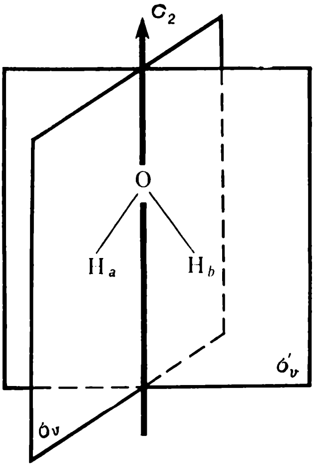


FIG. 6

that the collection of symmetry elements of the water molecule constitutes a group. One need only check:

(a) which element serves as the identity element,

(b) whether there is an inverse element for every symmetry element,

(c) whether the associative law holds.

As to the first condition, the E element serves as the identity element (see Table 2):

$$C_2E = EC_2 = C_2$$
$$\sigma_v E = E\sigma_v = \sigma_v, \text{ etc.}$$

It is now clear why we introduced the operation E into the set of symmetry operations, although it seemed "redundant" at first. Without it the collection of operations would not have had the properties of the group for there would have been no identity element.

From the group multiplication table it also becomes clear that every element has a corresponding inverse. Indeed, for the element which is the inverse of C_2, for example, the following relations must hold:

$$C_2^{-1} \cdot C_2 = C_2 \cdot C_2^{-1} = E$$

Let us have a look at Table 2 again and see which element becomes E when multiplied by C_2 (regardless of the order of multiplication). Evidently such an element is C_2, i.e. the C_2 symmetry element (as well as the other elements of our set) does not differ from the inverse element.

Again using the group multiplication table one can easily discover that the product of symmetry elements obeys the associative law.

Thus we come to the following conclusion: *the collection of symmetry operations which are intrinsic to the given molecule constitutes its symmetry point group.* (It is called the point group because whatever symmetry operations we perform on the given body at least *one* point remains stationary.)

Hierarchy of Point Groups

We shall begin the classification of symmetry point groups with the description of the simplest of them and then go on to those which possess a greater number of symmetry operations.

Minimum of symmetry. Let us start our description with symmetry groups in which the n-fold axis is the only symmetry element. Such groups are denoted by the symbol C_n. These groups possess neither mirror planes, nor rotation-reflection axes, nor centres of inversion. The simplest group C_1 has only the first-order symmetry axis. This means that a body will not change its appearance after the 360° rotation about any axis passing through that body. The formic acid molecule, for example, possesses such "degraded" symmetry (Fig. 7).

S_{2n} groups. These groups possess one rotation-reflection axis S_{2n}. The order of symmetry of a rotation-reflection axis may be only even. As an S_2 group is nothing else but the combination of operations E and i, it is often denoted as C_i. Molecules possessing

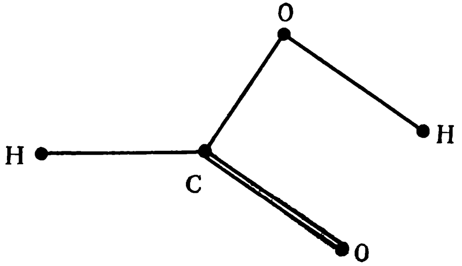
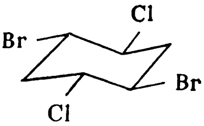
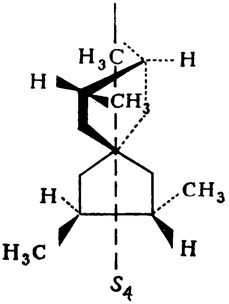


FIG. 7

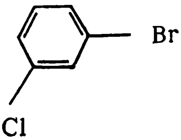
this kind of symmetry are very rare. Here is one of the few examples:



And here is the molecule belonging to the S_4 group:



C_{nh} groups. We have already seen how prosaic are the C_n groups. However, the addition of only one element—the horizontal symmetry plane σ_h—carries a molecule over into the group (denoted by the symbol C_{nh}) that is more entertaining, so to say. Some chloroderivatives of ethylene may serve as an example (Fig. 8). The molecules $SOCl_2$ or m-C_6H_4ClBr



belong to the C_{1h} group* which is the simplest of the C_{nh} groups. It is sometimes denoted by C_S.

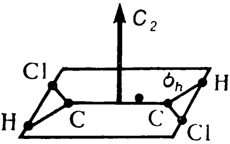
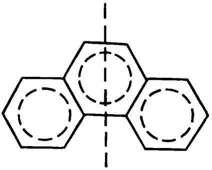
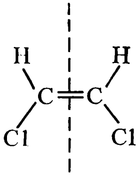


FIG. 8

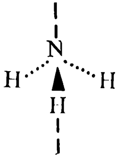
C_{nv} groups. The C_{nv} groups have the *n*-fold symmetry axis and *n* symmetry planes containing this axis. Such well-known molecules as H_2O, H_2S, SO_2, NO_2, $C_{14}H_{10}$, *trans*-$C_2H_2Cl_2$, etc. belong to the C_{2v} group while PCl_3, NH_3, $(C_6H_6)Cr(CO)_3$, etc. belong to the C_{3v} group:



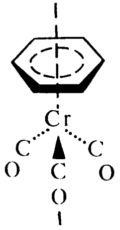
C_{2v}



C_{2v}



C_{3v}



C_{3v}

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* The C_{1h} group is identical to the S_1 group.

As to the number of symmetry elements these groups are medium rich. Like C_{nh} groups they may be constructed from C_n groups but this time it is not a horizontal plane but n vertical ones that are added. Besides, only several of those belong to the σ_v type when n is even, all other planes being diagonal (σ_d). For example, the C_{4v} group includes the molecules having the shape of the tetragonal (Egyptian) pyramid ($[Cu(NH_3)_5]^{2+}$) as well as systems originating as a result of the asymmetric distortion of the octahedron whose two *trans*-positional apices cease to be equivalent because of the presence of different atoms.

D_{nh} groups. In all foregoing cases molecules had only the vertical n-fold symmetry axis and the reflection planes passing through it. However, there are many molecules possessing also horizontal symmetry planes which are perpendicular to the principal axis. Such groups are designated by the symbol D_{nh}. The benzene molecule belonging to the D_{6h} group is an example (Fig. 9*a*). Almost all plane molecules of the AX_3 composition constructed in the form of a regular triangle (BF_3, CO_3^{2-}, NO_3^-, etc.) belong to the D_{3h} group.

The D_{4h} symmetry group is of particular significance for inorganic chemistry. Such symmetry is inherent in square complexes of the MX_4 composition that are typical for M = Pt(II), Pd(II), Ni(II), etc. and compounds of the *trans*-MX_4Y_2 type, such as, for example, the intraspherical fragment of *trans*-dichlorotetrammineplatinum chloride $[Pt(NH_3)_4Cl_2]Cl_2$. The D_{4h} group is derived from the C_{4v} group via an addition of a horizontal plane σ_h perpendicular to the fourfold axis and of the products of σ_h by the rest of C_{4v} group symmetry operations: $i = \sigma_h C_2$, $S_4 = C_4\sigma_h$, etc.

The D_{5h} point group was formerly thought to be of no importance to inorganic chemistry. It is now known, however, that such symmetry is typical for some biscyclopentadienyls of transitional metals, for example, $Fe(C_5H_5)_2$, $Ru(C_5H_5)_2$, uranyl ion (UO_2^{2+}) compounds constructed in the form of a pentagonal pyramid with the O—U—O group along the five-fold axis (e.g. UO_2F_5).

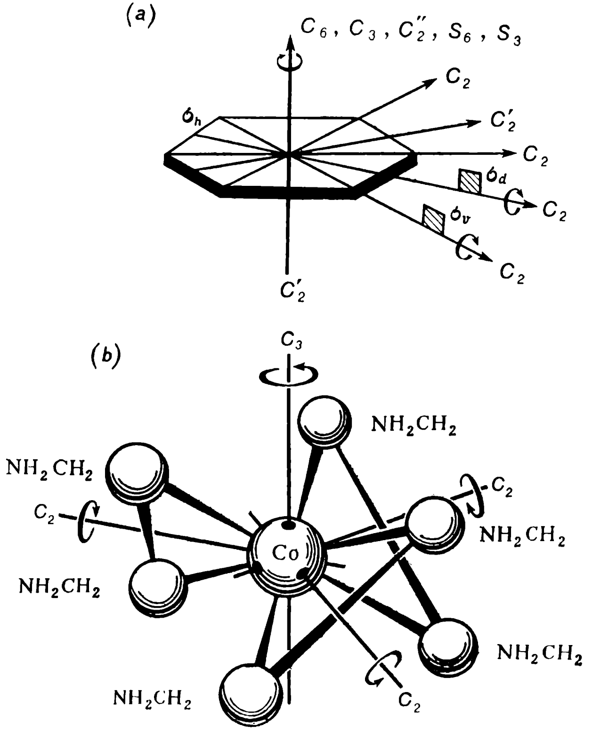

FIG. 9

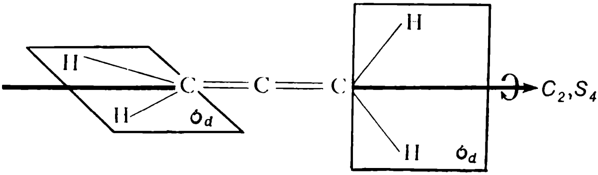

FIG. 10

D_n groups. This is a fairly rare symmetry to be met in chemistry. If the nuclear polyhedron of a molecule has this type of symmetry, the molecule possesses n C_2 axes, in addition to the C_n axis, which are perpendicular to the C_n axis, but has no symmetry planes. The Co·en_3^+ ion ("en" stands for ethylene diamine $NH_2CH_2CH_2NH_2$) is an example (Fig. 9*b*). Due to the absence of symmetry planes such molecule exhibits an optical activity.

D_{nd} groups. If the system of D_n group axes is supplemented with n symmetry planes containing the C_n axis and bisecting the angle between the neighbouring two-fold axes, the resulting group is denoted by the symbol D_{nd}.

The allene molecule is an example of a molecule possessing the D_{2d} group symmetry (Fig. 10).

Cubic groups (Plato's bodies). Cubic groups possess the largest number of symmetry elements. They are so called because every group has the symmetry elements characteristic of a cube. Why they are called Plato's bodies, the reader will learn later, in Chapter 5. Here we should point out that only regular polyhedrons may be regarded as Plato's bodies, and not any geometric figure possessing the cubic point group symmetry. The characteristic feature of cubic groups is the presence of several axes of the order higher than 2.

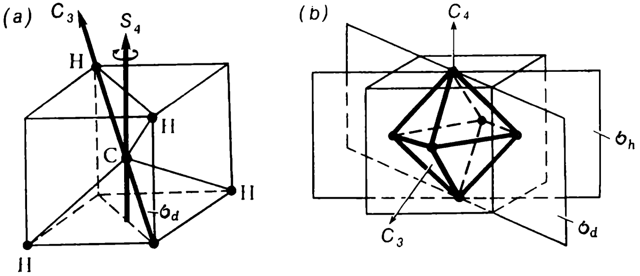

FIG. 11

We shall dwell on three cubic groups: the tetrahedron group (T_d), octahedron group (O_h) and icosahedron group (I_h). Molecules belonging to these groups are highly symmetric.

The characteristic elements of the tetrahedron are: four C_3 axes, three S_4 axes and six σ_d planes (Fig. 11*a*)*. The octahedron has four C_3 axes, three C_4 axes, three σ_h and six σ_d planes (Fig. 11*b*). As distinct from the T_d group the O_h group possesses the inversion centre *i*. Molecules belonging to the icosahedron symmetry group possess six C_5 axes. For example, CH_4, CCl_4 and P_4 molecules belong to the T_d group. UF_6 or SF_6 molecules as well as many complex ions (see Chapter 3) are the examples of the O_h symmetry molecules. Some boron compounds ($B_{12}H_{12}^{2-}$, $B_{12}Cl_{12}^{2-}$) provide examples of molecules belonging to the icosahedron symmetry.

Continuous symmetry point groups. In linear molecules the line along which nuclei are located is the symmetry axis of an infinite order since there are innumerable angles of rotation carrying the molecules into themselves. When the linear molecule also has a symmetry

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* For the sake of simplicity Fig. 11*a* and *b* illustrates only one characteristic symmetry element of each kind.

plane perpendicular to its axis, the molecule is said to belong to the $D_{\infty h}$ symmetry point group (Fig. 12*a*). Such are, for example, all biatomic homonuclear molecules (H_2, N_2, O_2, F_2, etc.), C_2H_2, CO_2 and other molecules. When a molecule has no plane of that kind the symmetry group is denoted by the symbol $C_{\infty v}$. Such are the molecules HCl, NO, HCN, etc. (Fig. 12*b*).

There is still another group to be mentioned, that is the $O(3)$ group. The symmetry transformations of this group represent combinations of rotations around any axis passing through the origin of coordinates and the inversion centre. The $O(3)$ group is the symmetry point group of an atom.

We have got to know the basic symmetry point groups of molecules. These groups are usually subdivided into four types:

(1) isotropic groups: $O(3)$, I_h, O_h, T_d;

(2) dihedral groups, containing n mutually perpendicular symmetry axes: D_n, D_{nh}, D_{nd} (where $n = 2, 3, \ldots, \infty$);

(3) axial groups, possessing only one n-fold symmetry axis: C_n, C_{nh}, C_{nv} ($n = 1, 2, \ldots, \infty$);

(4) improper axial groups, or "alternating" groups: S_n ($n = 1, 2, \ldots, \infty$), S_1 being denoted by the symbol C_s and S_2 by the symbol C_i.

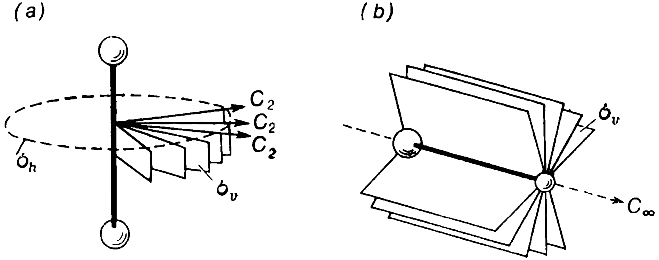
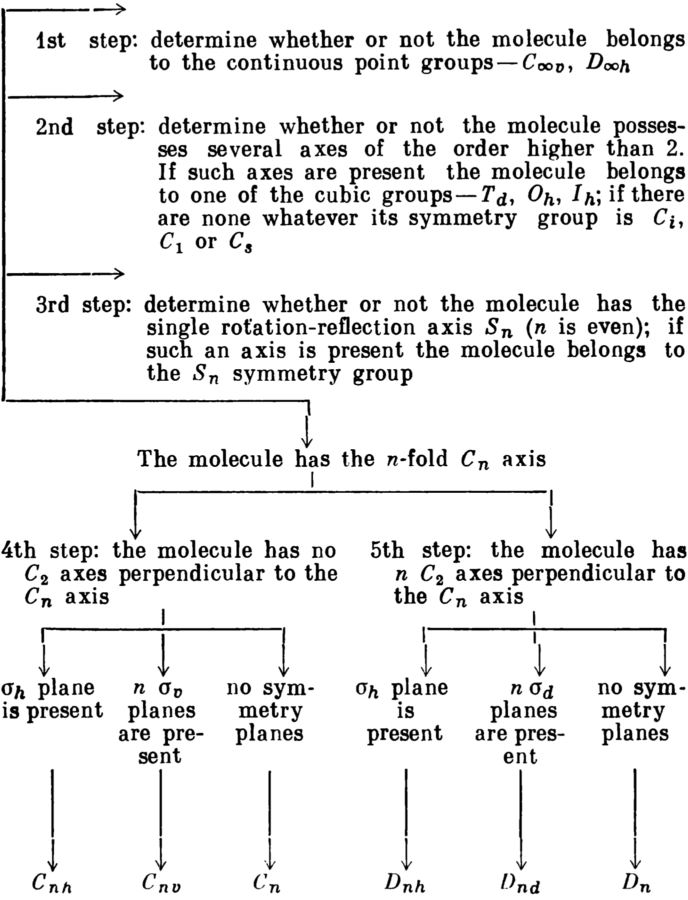


FIG. 12

TABLE 3 *



1st step: determine whether or not the molecule belongs to the continuous point groups—$C_{\infty v}$, $D_{\infty h}$

2nd step: determine whether or not the molecule possesses several axes of the order higher than 2. If such axes are present the molecule belongs to one of the cubic groups—T_d, O_h, I_h; if there are none whatever its symmetry group is C_i, C_1 or C_s

3rd step: determine whether or not the molecule has the single rotation-reflection axis S_n (n is even); if such an axis is present the molecule belongs to the S_n symmetry group

The molecule has the n-fold C_n axis

4th step: the molecule has no C_2 axes perpendicular to the C_n axis

5th step: the molecule has n C_2 axes perpendicular to the C_n axis

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* Only the basic point groups are shown in the table.

Now let us learn to determine the symmetry of a molecule when its geometry is known. Table 3 shows how to classify molecules into one or another group. Let us illustrate the method of determining the symmetry group by the example of the ferrocene molecules $Fe(C_5H_5)_2$.

Symmetry of the sandwich with a Fe atom. Ferrocene is the compound which was synthesized in 1951 simultaneously by two research groups in Great Britain and the United States of America. Its structure resembles a double-decked sandwich with the Fe atom in the centre (Fig. 13). Substances with the structure of this kind are appropriately called the "sandwich" compounds. In the crystal state the ferrocene molecule has the so-called *hindered conformation*, i.e. carbon atoms (when observed along the S_{10} axis) are arranged in a chessboard order in contrast to the analogous ruthenium compound in which atoms are arranged one under another.

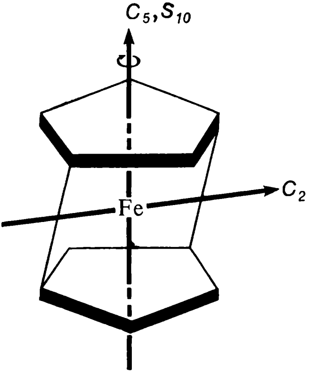

FIG. 13

Let us determine the point group of the ferrocene molecule in the hindered conformation following the procedure specified in Table 3.

The first two steps are easy to make. Since the ferrocene molecule is nonlinear it cannot belong to either a $C_{\infty v}$ or a $D_{\infty h}$ group. It does not belong to cubic groups either for it possesses only one axis of the order higher than 2, that is the C_5 axis.

The third step is to determine whether any S_n axes are present (where n is an even integer). There is such an axis in the ferrocene molecule (see Fig. 13). In addition to it, however, other symmetry elements are present in this molecule so that we should not classify it into the S_{10} group.

Next we look for two-fold axes perpendicular to the C_5 axis (steps 4 and 5). Indeed, there are such axes in ferrocene. One of those is shown in Fig. 13. Thus the only thing that is left to be done is to define which of three groups—D_{nh}, D_{nd} or D_n—the molecule in question belongs to. Inasmuch as a vertical plane σ_d can be drawn between any two two-fold axes, the ferrocene molecule in hindered conformation belongs to the D_{5d} symmetry point group.

As you see the classification of a molecule into one of the symmetry groups does not amount to much of a trouble providing, of course, its geometry is known.

Chapter Two

SYMMETRY IN MATHEMATICAL TERMS

> The most recent authors in the fashion of the ancient ones try to subject the natural phenomena to the laws of mathematics.
>
> I. Newton

In the Footsteps of Descartes

Statement of the problem. The French scientist R. Descartes is justly called "the father of analytical geometry". While before him algebra and geometry were fairly separated he elaborated a method which brought them together into a single whole. According to Descartes any geometric result can be expressed in algebraic terms. Indeed, if points of geometric figures are put over the coordinate grid, the position of each of them is determined by a pair of numbers (x, y). The value of Descartes' idea consists in the fact that one can change from the language of geometry to the language of algebra and back so that geometric properties of figures, including the properties of symmetry, acquire the quantitative or analytical expression. Besides, having related rotations, reflections and other operations of symmetry with a coordinate system we get rid of superfluous use of words, for figures speak for themselves. But to take advantage of blessings of Descartes' method one has to define the law governing the transformation of coordinates of points of geometric figures in symmetry operations. Since in our case these points are the nuclei of atoms constituting a molecule we may put the question differently: what is the transformation law for the coordinates of nuclei in symmetry point group operations for a molecule?

Rotations. We start with the specific example by considering the water molecule again (C_{2v} symmetry). Suppose it is placed in the xy-plane of an arbitrary Cartesian system of coordinates so that the oxygen atom coincides with the origin (Fig. 14). For the sake of lucidity the hydrogen atoms are labelled and the coordinates of H_1 atom are designated by (x_1, y_1) and those of H_2 atom by (x_2, y_2).

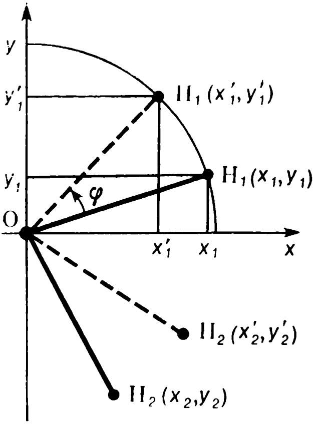

FIG. 14

Now let us rotate the molecule the way it is shown in Fig. 14, i.e. keeping it in the xy-plane. Of course, this is not a symmetry operation but it is of no importance to us as we consider now the more general case, which is the rotation of a molecule through an angle φ. After the rotation the coordinates of the molecule change. The new coordinates are denoted by a stroke: (x'_1, y'_1) and (x'_2, y'_2) for H_1 and H_2 atoms respectively.

Then we must solve a fairly simple geometric task, that is express the "new" coordinates in terms of the "old" ones (Fig. 14 will help you make it on your own). Finally we obtain:

$$x' = \cos\varphi \cdot x - \sin\varphi \cdot y$$
$$y' = \sin\varphi \cdot x + \cos\varphi \cdot y$$

Class register from mathematical viewpoint. And now we shall write these equations down in a somewhat different, "nonscholastic" manner. It is easy to see that these equations are alike. Indeed, in both equations the variable x in the first addendum is multiplied by the trigonometric function—only in the first case it is cos φ and in the second sin φ—while in the second addendum the variable y is multiplied by —sin φ or cos φ. Thus, in order to find the relation between the "old" and the "new" coordinates one has, first, to calculate sin φ and cos φ and, second, to determine what trigonometric functions are to be multiplied by the variables x and y.

If we write out the trigonometric functions in the same order as they appear in the equations we obtain the following table:

$$\begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix}$$

From this table we get, in fact, the law of the coordinate transformation of hydrogen atoms for the rotation of a molecule since the order of variables in the equations is the same: first x and then y. Such a table consisting of functions or numbers is called a *matrix*.

In mathematics a matrix is defined as a square or rectangular table of numbers or functions (real or complex):

$$A = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ a_{m1} & a_{m2} & \cdots & a_{mn} \end{pmatrix}$$

where the first subscript denotes the row number (in the matrix A there are m rows) and the second one, the column number (n columns).

We deal with matrices more often than it seems. As an example we may take ... a class register in which marks form a matrix. Empty squares may be interpreted as zero elements. Student names correspond to the rows and dates to the columns of such a matrix. The rows and columns are strictly ordered. Imagine what would happen if a schoolmaster confused columns or still worse rows and put a mark into the wrong square!

When $m = n$ a matrix is referred to as a square matrix. The number of rows (or columns) in a square matrix is called a matrix *dimension*.

In some cases $n = 1$ and $m > 1$. Such an array is called a column matrix:

$$\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_m \end{pmatrix}$$

In our example this is the state of a class register after the first test work, i.e. one column of marks. An array with $m = 1$ and $n > 1$ is referred to as a row matrix:

$$(a_1 a_2 \dots a_n)$$

This corresponds to the uncommon situation when only one student attends lessons.

Eulogy to matrix. Matrices possess a number of remarkable properties. The addition, multiplication and many other operations may be performed on them. Matrices turn out to be very useful not only in studies of rotations, reflections and other transformations of geometric bodies, they are also used for the description of deformations of bodies which makes them important in structural mechanics. We come across matrices in the theory of relativity, hydrodynamics and quantum mechanics as well.

Now we shall learn one of the methods of matrix multiplication. It should be pointed out that depending on the physical nature of the problem one may employ different methods.

Matrix multiplication

Matrices are multiplied by the "row-by-column" rule. The matrix

$$C=\begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix}$$

is called the product of matrices

$$A=\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad \text{and} \quad B=\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}$$

if its any element $c_{ij} = \sum\limits_{k=1}^{k=2} a_{ik}b_{kj}$, where $\sum$ is the summation symbol, and k is the number of columns of the matrix A or the number of rows of the matrix B. The multiplication rule is valid only in the case when both numbers are equal. Since in our case $k = 1, 2$, then

$$c_{11} = \sum_{k=1}^{k=2} a_{1k}b_{k1} = a_{11}b_{11} + a_{12}b_{21}$$

$$c_{21} = \sum_{k=1}^{k=2} a_{2k}b_{k1} = a_{21}b_{11} + a_{22}b_{21}, \text{ etc.}$$

Thus, *to calculate an element* c_{ij} *the elements of the ith row of the matrix A are multiplied by the corresponding elements of the jth column of the matrix B and the products obtained are summed up.*

Example

$$A=\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad B=\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$C = A\cdot B = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\cdot\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0\cdot1+1\cdot0 & 0\cdot0+1\cdot(-1) \\ 1\cdot1+0\cdot0 & 1\cdot0+0\cdot(-1) \end{pmatrix} =$$

$$= \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

Note that the matrix product as well as the product of group elements do not obey the commutative law, i.e.

$$A \cdot B \neq B \cdot A$$

So

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & 2 \\ -1 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 2 \\ 1 & -1 \end{pmatrix}$$

But

$$\begin{pmatrix} 0 & 2 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & -2 \\ -1 & -1 \end{pmatrix} \neq \begin{pmatrix} 0 & 2 \\ 1 & -1 \end{pmatrix}$$

Atoms in a mirror. Matrices can describe not only rotations but other symmetry operations as well. Let us consider, for example, how the reflection operation is expressed in a mathematical form.

If the water molecule is located in respect of coordinate axes the way Fig. 15 shows, the xy-plane turns into the σ_{xy} symmetry plane of the molecule. The oxygen atom does not change its position when reflected in this plane while the hydrogen atom H_1 with references (x_1, y_1, z_1) switches places with the hydrogen atom H_2.

We shall denote the new references of the atom H_1 by x_1', y_1' and z_1' as before and

$$x_1' = x_1, \quad y_1' = y_1, \quad z_1' = -z_1$$

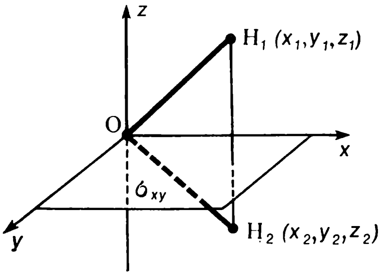

FIG. 15

The unabridged version of these equations is as follows:

$$x_1' = 1 \cdot x_1 + 0 \cdot y_1 + 0 \cdot z_1$$
$$y_1' = 0 \cdot x_1 + 1 \cdot y_1 + 0 \cdot z_1$$
$$z_1' = 0 \cdot x_1 + 0 \cdot y_1 + (-1) \cdot z_1$$

It is easy to see that these equations resemble very much the initial ones (page 31), only the variables here are multiplied by numbers and not by trigonometric functions. Consequently we can readily draw up the matrix corresponding to the operation of reflection in the σ_{xy}-plane:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Similarly, for the operation of inversion through the origin of coordinates we have:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

More complex case. Let us complicate our task. Suppose we have several functions of coordinates $\Psi_1(x, y, z)$, $\Psi_2(x, y, z)$, $\Psi_3(x, y, z)$, etc. If one of these functions, say Ψ_1, undergoes a symmetry transformation we obtain a new function:

$$(\text{Symmetry transformation } R) \longrightarrow \Psi_1(x, y, z) \longrightarrow \Psi_1'(x', y', z')$$

The mechanism of conversion of one function into another is as follows in this case: by converting the coordinate system (for example, by rotation) we transform the arguments (x, y, z) of the Ψ_1 function and consequently change the function itself.

And what is Ψ_1'? So we have obtained a new function Ψ_1'. Is it somehow possible to express it through the "old" functions Ψ_1, Ψ_2, Ψ_3, etc.? It turns out to be possible. Often a new function can be expressed through the "old" ones quite simply—as their linear combination:

$$\Psi_1' = c_1\Psi_1 + c_2\Psi_2 + \ldots + c_N\Psi_N$$

where c_1, c_2, etc. are numerical factors.

It is customary to write this expression in the abbreviated form:

$$\Psi_1' = \sum_{i=1}^{i=N} c_i\Psi_i$$

The symbol $\sum_{i=1}^{i=N}$ means the summation with respect to the index i running from 1 to N.

Now let us take another function from our set, Ψ_k, and perform the transformation in the same coordinates which corresponds to the analogous symmetry operation. This way we obtain the similar result:

$$(\text{Symmetry operation } R) \ggg\!\!\longrightarrow \Psi_k \longrightarrow \Psi_k' = \sum_{i=1}^{i=N} c_{ki}\Psi_i$$

The coefficient c_{ki} has two subscripts: i is the summation index and k signifies the fact that the summation produces the function Ψ_k' which originated from the function Ψ_k. Thus, if we write this sum in full we obtain the following expression:

$$\Psi_k' = c_{k1}\Psi_1 + c_{k2}\Psi_2 + \ldots + c_{kN}\Psi_N$$

The similar treatment of all N functions of the original set gives the following equations:

$$\begin{aligned}
\Psi_1' &= c_{11}\Psi_1 + c_{12}\Psi_2 + \ldots + c_{1N}\Psi_N \\
\Psi_2' &= c_{21}\Psi_1 + c_{22}\Psi_2 + \ldots + c_{2N}\Psi_N \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
\Psi_N' &= c_{N1}\Psi_1 + c_{N2}\Psi_2 + \ldots + c_{NN}\Psi_N
\end{aligned}$$

In such cases mathematicians would declare: "In symmetry transformations the functions of the original set transform linearly one from another".

Transformation matrix. One can arrange the square matrix from the c_{ki} coefficients

$$\begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1N} \\ c_{21} & c_{22} & \cdots & c_{2N} \\ \cdot & \cdot & \cdot & \cdot \\ c_{N1} & c_{N2} & \cdots & c_{NN} \end{pmatrix}$$

which corresponds to the definite symmetry transformation. Such matrix is called the *transformation matrix.*

The corresponding matrix can be arranged the same way for any other symmetry operation.

Group representation. Thus the following conclusion can be drawn: *each symmetry operation of the given point group may be associated with a square matrix.* For example, the C_{3v} group consists of six symmetry elements: E, C_3, C_3^2, $\sigma_v^{(1)}$, $\sigma_v^{(2)}$ and $\sigma_v^{(3)}$. Each of these elements has the corresponding square matrix:

$$\begin{aligned} E &\longrightarrow A_E \\ C_3 &\longrightarrow A_{C_3} \\ C_3^2 &\longrightarrow A_{C_3^2} \\ \sigma_v^{(1)} &\longrightarrow A_{\sigma_v^{(1)}} \\ \sigma_v^{(2)} &\longrightarrow A_{\sigma_v^{(2)}} \\ \sigma_v^{(3)} &\longrightarrow A_{\sigma_v^{(3)}} \end{aligned}$$

This fact in itself would not have been of particular importance had it not been for one circumstance. As a matter of fact one can compose a set of remarkable matrices that would copy or reproduce the table of group multiplication.

If, for example,

$$\sigma_v^{(1)} \cdot C_3 = \sigma_v^{(2)}$$

the analogous relation is also valid for matrices:

$$A_{\sigma_v^{(1)}} \cdot A_{C_3} = A_{\sigma_v^{(2)}}$$

Although special methods of finding such matrices have been developed in group theory, we shall not dwell on them here and shall limit ourselves to one example taken from the monograph *Valence Theory* by J.N. Murrell, S. A. Kettle and G.M. Tedder (J. Wiley and Sons, London, N.Y., Sidney, 1965).

The following set of square matrices may be brought into correspondence with the elements of the C_{3v} group:

$$\begin{array}{ccc} E & C_3 & C_3^2 \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \times \end{array}$$

$$\begin{array}{cccc} & \sigma_v^{(1)} & \sigma_v^{(2)} & \sigma_v^{(3)} \\ \times & \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \end{array}$$

It is easy to make sure that:

$$A_{\sigma_v^{(1)}} \cdot A_{C_3} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} =$$

$$= \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = A_{\sigma_v^{(2)}}$$

Any collection of matrices obeying the table of group multiplication is called the *representation of a group*. In other words, the representation of a group is the collection of matrices specifying how functions (or a set of functions) are transformed under operations of a group.

The above-mentioned property of matrices is of great importance for the symmetry theory. Each point group possesses the inherent set of symmetry elements and its own multiplication table. Differing from symmetry operations by their mathematical nature matrices reproduce and imitate the most important property of a point group which is the table of group multiplication, i.e. the rule relating group elements. It is a kind of a description of a group, only matrices do it in their own language, the language of matrix calculus. Now it becomes clear why mathematicians use the term "the representation of the given symmetry group" when talking of a set of square matrices repeating the basic properties of a group.*

Each group may have an infinite number of representations which may differ from one another by both the dimensions of their matrices and the type of matrix elements. Often a group is represented by a set of ordinary numbers each of which may be considered as the square single-dimensional matrix.

Irreducible representations. How is that?! some readers may exclaim. All was going so well, we have ascertained that the definite set of square matrices may embody the group multiplication table and all of a sudden in the end it turns out that there is an infinite number of such sets... . Then how to use them and which set to prefer?

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* This implies that the set of matrices discussed constitutes a group as well.

Maybe one can choose some "privileged" sets? others would ask.

Yes, one can. Physicists and mathematicians do it in exactly this way. They call these "privileged" representations of one or another group *irreducible*. The meaning of this word is rather difficult to explicate in simple terms here. In general outlines the situation is this. There are certain rules (transformations) making it possible to convert one representation, i.e. one set of square matrices, into another. Sometimes one can find a representation leading to "simpler" matrices possessing a lesser dimension compared with the initial matrices. If we can simplify matrices of a given representation by choosing the relevant algebraic transformation, such a representation is referred to as a *reducible* one. If we find no transformation simplifying initial matrices the representation consisting of such matrices is called an *irreducible* one.

Often, as a result of a consecutive reduction of the representation whose matrices have the high dimension of 6 or 7, for example, we may come to three- or two-dimensional matrices, or even single-dimensional matrices (i.e. numbers) that are much easier to work with as compared to initial "Brobdingnagian" matrices. But convenience is not the only point. The study of irreducible representations (IR, in abbreviated form) showed that they possessed some properties making them useful for applications in physics and chemistry. Besides, the number of IRs is finite for all symmetry groups with a finite number of elements.

One may approach the concept of irreducible representation somewhat differently. We should recall that matrices constituting the representation of a group were defined with a set of functions. Suppose there were *m* such functions. What is more, we have ascertained (see p. 37) that under symmetry transformations the functions of that set transform into one another linearly. It may so happen that symmetry transformations will break up m functions of the initial set into separate families (subsets) of m_1, m_2, ... functions each. Of course, the total number of functions will not change, i.e. $m_1 + m_2 + \ldots = m$. The breaking up into families will be accomplished in such a way that all symmetry operations transform the functions within a subset into one another and do not affect the functions of neighbouring subsets. In this case it is customary to say that the representation in question is reducible. But if it is impossible to decrease the number of the initial functions transforming into one another, i.e. if the initial set of functions cannot be disjoined or decomposed, the representation engendered by this initial set is called irreducible.

Symmetry and Molecular Orbitals

Having got familiar in a general way with certain concepts of symmetry theory we have to answer now the following question: what has all this to do with quantum chemistry?

Concept of orbital. In quantum mechanics electron states of one or another micro-object (an atom or a molecule) are described by the wave function which depends on the coordinates of all electrons of the system

$$\Psi\ (x_1,\ x_2,\ \ldots,\ x_N)$$

where x_i denotes the set of three spatial coordinates of the ith particle.* The wave function contains all

---

* The wave function may also depend on spin characteristics of particles, but we do not take this into account here.

the information about the state of a quantum mechanical system that can be experimentally verified, and permits computing the probabilities of possible results of any measurements of the system. For example, the square of the absolute value of the wave function

$$|\Psi(x_1, x_2, \ldots, x_N)|^2$$

describes the probability of simultaneous location of the first particle at the point x_1, the second at the point x_2, etc.

This distribution of probabilities is often depicted graphically as the electron cloud of one or another shape.

Strictly speaking, in the case of a system with many electrons the wave function can describe only the state of the system viewed as a whole (i.e. the state of the whole atom or the whole molecule), but not the states of individual electrons. The latter is impossible because electrons are "not indifferent" to each other and the Coulomb repulsion forces acting between them are considerable. When we write down the electronic formula of some atom, for example, nitrogen: $1s^2 2s^2 2p^3$, i.e. describe each electron by its own wave function (and attribute to each electron its own set of quantum numbers), we diverge from the rigorous treatment. The approach we employ here is called the *one-electron approximation.*

The methods of description of atoms, molecules and solids in terms of the one-electron wave functions (such functions are called *orbitals*) have found a wide application in modern quantum chemistry, one of its most popular methods being the *method of molecular orbitals* (MO method). The principal idea of the method involves the assumption that the electrons in a molecule are located at one-electron levels (molecular orbitals) just like electrons in atoms are located in atomic orbitals, i.e. in accordance with the Pauli principle, the filling of orbitals being effected in the order of the increase of MO's energies.

Usually molecular orbitals are made up as the *linear combination of atomic orbitals* (LCAO) of atoms comprising the system.

It often happens that one value of energy is associated with several one-electron wave functions, that is several, for example, f, orbitals. In this case the state is said to be degenerate, the order of degeneracy being f. For example, all three p-states in an isolated atom have the same energy, or, in other words, are triply degenerate. The order of degeneracy of d-orbitals is five.

In terms of symmetry theory... In terms of symmetry theory the most important circumstance is that *under transformations of the symmetry groups the wave functions corresponding to the same energy are expressed through one another. The matrices obtained in these transformations produce the irreducible representation of the given group, their dimension being equal to the order of degeneracy.*

This may be depicted in a schematic form ($\backsim$ sign means correspondence; R_1, R_2, etc. are symbols for symmetry operations):

$$E\left\{\begin{array}{l} \rule{3em}{0.4pt} \\ \rule{3em}{0.4pt} \\ \rule{3em}{0.4pt} \\ \cdots\cdots \\ \cdots\cdots \end{array}\right. \backsim \{\Psi_1,\ \Psi_2,\ \ldots,\ \Psi_f\} \backsim \mathrm{IR}\left\{\begin{array}{l} \text{matrix of dimension} \\ f \backsim R_1; \\ \text{matrix of dimension} \\ f \backsim R_2 \\ \cdots\cdots\cdots \\ \text{etc.} \end{array}\right.$$

Molecular energy level with the order of degeneracy f.

f molecular orbitals

This relation *permits bringing every energy level E of a molecule into correspondence with a certain irreduc-*

ible representation of its symmetry group. (Incidentally it is not necessary to assume only one-electron levels of energy. A certain IR of symmetry group of the system may be brought into correspondence with each "true" atomic or molecular energy level.) This result is very important. Symmetry may be one and the same for quite different molecules both in terms of the composition and the nature of chemical bonds, and group theory, due to its abstract character, makes it possible to obtain some general but precise data on the structure and properties of diverse molecular systems.

Water again... As an example illustrating the aforesaid let us take the water molecule again. Its symmetry point group C_{2v} has four IRs of single dimension. From this one can conclude that the water molecule has no degenerate levels. Note the beauty of the result obtained: we knew only the geometry of the molecule and even then not all the details as we were not interested in either the length of the H—O bond or the precise HOH angle, and still we could draw certain conclusions about the structure of energy levels. It should be pointed out that this result will be valid for any molecule possessing C_{2v} symmetry (H_2S, SO_2, etc.) regardless of the method of calculation.

In the next chapter we shall elaborate in more detail the results that could be derived on the basis of "symmetry considerations".

See the table. Well, it's O.K., some readers might say, but to get even those general results one must know how many and what kind of IRs each symmetry group possesses.

Quite true, one must know it. To the chemists' benefit mathematicians have already done this work a long time ago. They have worked out special tables—the "character tables", as they are called—from which one can get a great deal of diverse information about the irreducible representations, for example, what IRs are there in the given group and how many. Forasmuch as we do not intend to teach the reader how to employ group theory in specific calculations, there is no need to reproduce these tables here in the form they are presented in scientific publications. We shall only show how many and what kind of IRs one or another symmetry group has. In Table 4 only the most frequent groups are listed. But let us first get acquainted with the IR notation. The most common is the notation proposed by R.S. Mulliken* in the early thirties.

TABLE 4

Group	Irreducible representations
C_2	A, B
C_{2v}	A_1, A_2, B_1, B_2
C_{3v}	A_1, A_2, E
C_{2h}	A_g, B_g, A_u, B_u
D_{2h}	A_g, B_{1g}, B_{2g}, B_{3g}, A_u, B_{1u}, B_{2u}, B_{3u}
D_{4h}	A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_g, A_{1u}, A_{2u}, B_{1u}, B_{2u}, E_u
T_d	A_1, A_2, E, T_1, T_2
O_h	A_{1g}, A_{2g}, E_g, T_{1g}, T_{2g}, A_{1u}, A_{2u}, E_u, T_{1u}, T_{2u}

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* Robert Sanderson Mulliken, born 1896, American scientist, creator of the method of molecular orbitals. Nobel Prize winner. Also known for his work in the field of molecular spectroscopy.

Mulliken's notation. 1. All the single-dimensional representations ($f = 1$) are denoted by either the symbol A or B; the two-dimensional ($f = 2$) by the symbol E, and the three-dimensional ($f = 3$) by T.

2. If after rotation through an angle of $360°/n$ about the principal axis C_n the function transforming according to the single-dimensional representation does not change sign, the single-dimensional representation is denoted by the letter A, if the sign changes, i.e.

$$\text{Operation } C_n \longrightarrow \Psi \longrightarrow -\Psi$$

the IR is denoted by the letter B.

3. Besides, if a molecule possesses C_2 axes perpendicular to the principal axis or σ_v (and σ_d) planes, the function Ψ may either change sign after corresponding rotations and reflections or not. If the function changes sign the letter A or B is supplemented with the subscript 1 (A_1 or B_1), if not, with the subscript 2 (A_2 or B_2).

Similar subscripts may be seen with the symbols E and T, but in that case the notation rules are more complicated. For our purpose it is sufficient to regard these subscripts as some labels making it possible to discern one IR from another.

4. The subscripts g and u by the IR symbol indicate how the function Ψ behaves in the inversion operation, whether it changes sign (subscript u for "ungerade", German for "odd") or not (g for "gerade", German for "even").

As an example we shall consider the tetrahedron group T_d, especially as we are supposed to deal with the molecules belonging to this group many times in the future. This group has five IRs of which two are single-dimensional, one two-dimensional and two three-dimensional. Let us first examine the single-dimensional IRs. The tetrahedron has eight C_3 axes, all of which are principal. The wave function transforming according to any of the single-dimensional IRs does not change at all when it undergoes the C_3 operation:

$$C_3 \ggg\!\!\longrightarrow \Psi \rightarrow \Psi$$

Therefore both single-dimensional IRs ought to be denoted by the letter A. The difference between them may be observed when the C_3 operation is replaced by the σ_d operation. In this case some functions, those which are transformed according to the single-dimensional IR, do not change sign:

$$\sigma_d \ggg\!\!\longrightarrow \Psi \rightarrow \Psi$$

and some do:

$$\sigma_d \ggg\!\!\longrightarrow \Psi \rightarrow -\Psi$$

The former functions are classified under the irreducible representation A_1 and the latter under A_2.

5. As to the C_s group as well as the D_{nh} and C_{nh} groups with an odd h, their IRs of the same dimension are denoted by one or two strokes over the letter symbol, depending on whether the Ψ function changes sign under the σ_h operation or not.

For example, four IRs of the C_{3h} group are denoted by the symbols A', E' if the function does not change sign under the σ_h reflection, and A'', E'' if it does.

6. As a rule different notation is used for the continuous groups $D_{\infty h}$ and $C_{\infty v}$. Single-dimensional IRs are designated by the letter Σ, two-dimensional IRs by the letters Π, Δ, Φ, etc. Besides, the symbols are supplemented with a superscript $+$ or $-$ which specifies the function behaviour in operations of reflection in σ_v planes. The number of such planes in these groups is infinite. The IR designations of the $D_{\infty h}$ group also have the parity subscripts g and u.

In scientific publications the same designations are sometimes used both for these groups and for the finite groups. Strictly speaking, this notation is not good enough but we shall be using it all the same. The relationship between two notations—"strict" and "nonstrict"—is presented below for the $D_{\infty h}$ group:

$$\Sigma_g^+ \backsim A_{1g};\quad \Sigma_u^+ \backsim A_{1u};\quad \Pi_g \backsim E_{1g};\quad \Delta_g \backsim E_{2g}$$

$$\Sigma_g^- \backsim A_{2g};\quad \Sigma_u^- \backsim A_{2u};\quad \Pi_u \backsim E_{1u};\quad \Delta_u \backsim E_{2u},\ \text{etc.}$$

Symmetry of atomic orbitals. In the one-electron approximation the motion of electrons is described by means of the concept of atomic orbitals (AOs), i.e. functions dependent on three spatial coordinates (x, y, z) of an electron or, in spherical coordinates, (r, θ, φ) (Fig. 16*b*). We shall denote such a function by $\Phi(r, \theta, \varphi)$. Assuming, as it is common practice to do, that the field of force in an atom is spherically symmetrical, atomic orbitals can be represented as

$$\Phi_{nlm}(r, \theta, \varphi) = R_{nl}(r)\, Y_l^m(\theta, \varphi)$$

where $R_{nl}(r)$ is the function dependent only on the distance between the electron and the nucleus and called the *radial* function, $Y_l^m(\theta, \varphi)$ is the so-called spherical function dependent only on the angles θ and φ. The angular momentum quantum number l $(l = 0, 1, 2, \ldots)$ determines the square of the one-electron angular momentum $\hbar^2 l(l+1)$. The magnetic quantum number m $(m = 0, \pm 1, \pm 2, \ldots, \pm l)$ describes the projection of the one-electron angular momentum on the quantization axis. And, finally, the principal quantum number n labels the orbital energy levels E_{nl}, corresponding to the same l, in the order of their increase, with positive integers starting from $(l+1)$. The AOs are denoted by the letters s, p, d, f, g, . . . corresponding to the values of the quantum

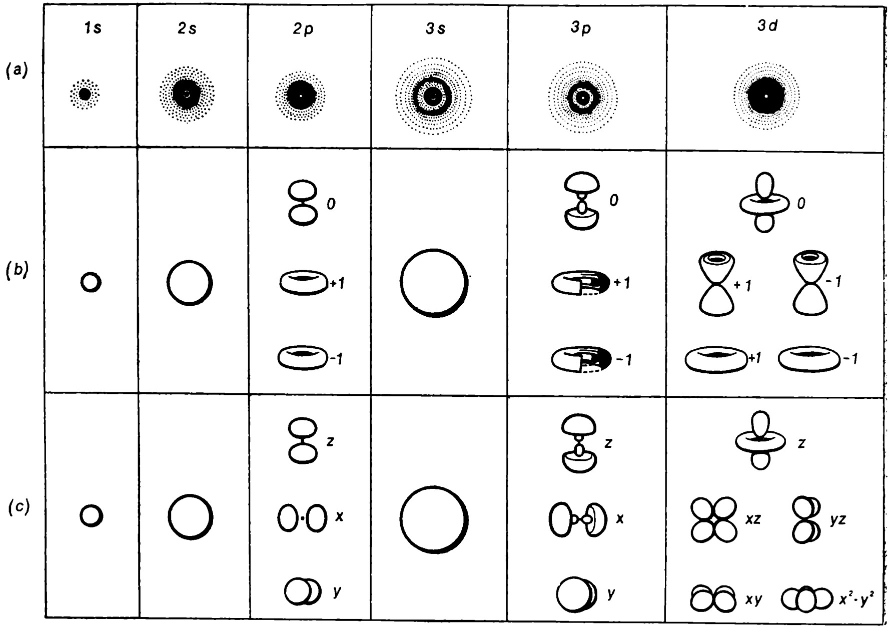

FIG. 16

number $l = 0, 1, 2, 3, 4, \ldots$. The value of n is written before the letter, the value of m being shown as the subscript, for example, $2p_0$, $2p_{\pm 1}$, etc. Depending on the absolute value of the quantum number m the orbitals may be of the type σ ($|m| = 0$), π ($|m| = 1$) and δ ($|m| = 2$).

The expression $\rho_{nl}(r) \equiv r^2 R_{nl}^2(r)$ characterizes the probability of electron localization at the distance r from the nucleus while $r(\theta) \equiv |Y_l^m(\theta, \varphi)|^2$ is the probability distribution along the directions defined by the angles θ and φ*. The "total" distribution of the orbital electron density in an atom is given by the function

$$\rho_{nlm}(r, \theta, \varphi) = |\Phi_{nlm}(r, \theta, \varphi)|^2$$

(see Fig. 16*b*).

The AOs discussed earlier include the imaginary number $i = \sqrt{-1}$, i.e. they are complex. However, wider application has been gained by the real AOs which are linear combinations of the complex AOs (Fig. 16*c*).

The real AOs $\tilde{\Phi}_{nl\mu}$ can be obtained from the complex AOs Φ_{nlm} via the following expressions:

$$\tilde{\Phi}_{nl\mu} = 1/\sqrt{2}\,[\Phi_{nlm} + (-1)^m \Phi_{nl,-m}]$$

$$\tilde{\Phi}_{nl,-\mu} = 1/\sqrt{2}\,[\Phi_{nlm} - (-1)^m \Phi_{nl,-m}]$$

where $\mu = |m|$.

The real AOs have no corresponding states with the definite quantum number m, and the symmetry of diagrams representing these AOs may be nonaxial.

We have already mentioned that the continuous $O(3)$ group is the point group of symmetry of an atom. The group includes every possible rotation about the axis passing through the atom's nucleus

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* Note that the $r(\theta)$ function does not depend on the angle φ so that the corresponding distribution of electron density possesses an axial symmetry (Fig. 16*b*).

regarded as a point and reflections in all innumerable planes containing the nucleus. Like any other group, $O(3)$ has the irreducible representations, although in this case there are an infinite number of them. The IRs of the $O(3)$ group are usually denoted by the symbol $D^{(l)}$ where l is the angular momentum quantum number. Thus, in terms of group theory the quantum number l labels the IRs of the $O(3)$ group.

For every value of l there are $(2l + 1)$ different values of the so-called magnetic quantum number m which defines the projection of the orbital angular momentum onto any z axis. The number of possible values of m, that is $(2l + 1)$, is equal to the dimension $D^{(l)}$ of the IR.

Thus, for example, $D^{(0)}$ is the single-dimensional $(2l + 1 = 2 \cdot 0 + 1 = 1)$ IR of the $O(3)$ group. All atomic s orbitals ($1s$, $2s$, $3s$, etc.) are transformed according to this IR. The irreducible representation $D^{(1)}$ is three-dimensional $(2l + 1 = 2 \cdot 1 + 1 = 3)$. Three p AOs (both complex and real) are transformed according to it, while five d orbitals are transformed according to the $D^{(2)}$ IR, etc.

Unsöld's theorem. What is the actual spatial distribution of electron density obtained in terms of the one-electron approximation? The answer was provided by Unsöld* (1927) who demonstrated that since the population density of all AOs with the given n and l (but different m) is equally probable statistically, the probability density averaged over different

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* Albrecht Otto Johannes Unsöld, born 1905, German physicist and astrophysicist. Worked at Munich, Hamburg and Kiel (GFR). Known for his research in astrophysics, especially stellar atmospheres.

m possesses the spherical symmetry (Fig. 16*a*):

$$\sum_{m=-l}^{m=+l} |\Phi_{nlm}(r, \theta, \varphi)|^2 = \frac{2l+1}{4\pi} R_{nl}^2(r)$$

whereas the symmetry of an individual AO may differ (for example, may be depicted in the form of a "dumbbell"). Thus Unsöld demarcated the notions of the AO symmetry and the symmetry of an atom or, more exactly, the symmetry of the electron density distribution in an atom. J.H. Van Vleck called Unsöld's result "one of the first triumphs of quantum mechanics in chemistry".

Chapter Three

SYMMETRY AND STEREOCHEMISTRY

> The meticulous observation of reality indicates that its spatial relationships—manifestations of symmetry—lend the basis for all physical and chemical phenomena that we study.
>
> V.I. Vernadsky

Stereochemistry (from "στερεο", Greek for "solid") is the science about the spatial disposition of atoms in a molecule. From this definition it follows that stereochemistry relates directly to symmetry of a system. This is not, however, the mutual one-to-one relation since the stereochemical characteristics may be different for different molecules even if they possess the same symmetry. For example, such different geometric configurations as the square pyramid (the IF_5 molecule—Fig. 17*a*) and the bipyramid (the SF_5Cl molecule—Fig. 17*b*) possess the same C_{4v} symmetry.

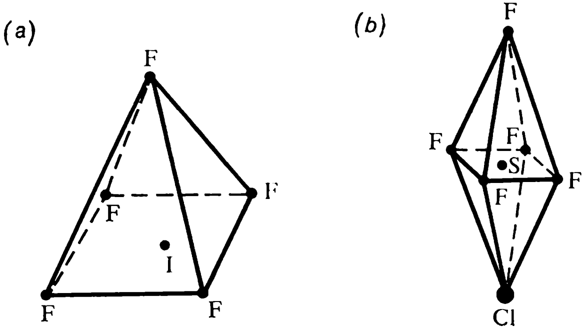

FIG. 17

The principal problem of stereochemistry is the relationship between the composition (stoichiometry) of molecules and the spatial configuration of their nuclei. That is why we shall first consider the simple theoretical models that permit correlating these two aspects.

First Variation on the Theme of Coulomb Law

Bakerian lecture of 1940. The British Royal Society maintains the tradition of holding annually the so-called Bakerian lecture dedicated to the urgent scientific problems. That was the last will made by the famous British naturalist Henry Baker (1698-1774). Two British scientists, N.V. Sidgwick* and H.M. Powell**, were invited to deliver the Bakerian lecture of 1940. Their lecture was dedicated to problems of inorganic stereochemistry. The authors had analysed an enormous amount of data. Suffice it to say that the lecture submitted for publication covered 17 pages in a journal and quoted 357 references to experimental investigations of molecular geometry. The authors proposed a simple model making it possible to corre-

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* Nevil Vincent Sidgwick (1873-1952), prominent British chemist, chairman of the Faraday Society of long standing, a specialist in electronic theory of valency and chemical bond (the coordination bond in particular). Investigated nitrogen-containing organic compounds.

** Herbert Marcus Powell, born 1906, British chemist and crystallographer, professor of Cambridge University; X-ray studies of crystal structure of various compounds, primarily complexes of transition metals. Originated a new class of molecular compounds (clathrates) in which one atom or molecule is enclosed in a cavity ("cage") formed by a crystal structure of some substance.

late the composition of a molecule and its geometry, i.e. stoichiometry and stereochemistry. True, the model could not solve all stereochemical problems and was confined to the less pretentious task of determining the type of a nuclear polyhedron, i.e. the skeleton of a molecule.

LEP model. In accordance with the model of localized electron pairs (LEP, in abbreviated form) the arrangement of chemical bonds around an atom depends on the number of its valence electron pairs. Due to the mutual repulsion of electrons the most advantageous arrangement of electron pairs corresponding to the minimum repulsion will be their maximum separation.

Now let us recall how the force F acting between two point charges depends on the distance r between them. According to the Coulomb law it is inversely proportional to the square of the distance:

$$F \propto 1/r^2$$

However, the valence electrons of an atom sometimes disobey this law. R.G. Gillespie* suggested that the interaction force changes in inverse proportion to the interelectronic distance with an exponent differing, in general, from 2:

$$F \propto 1/r^n$$

Assuming the spherical symmetry of the atomic kernel we have to expound the following problem.

Given: the number of electron pairs is equal to q.

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* Ronald James Gillespie (born 1924), Canadian chemist, was born and educated in London, where he worked as a lecturer for some time. In 1960 left for Canada. Now professor of chemistry at the McMaster University, Hamilton, Ontario.

Required: to distribute them over the sphere surface so that the distance between them is the greatest (and the repulsion, correspondingly, the least).

The solution of this problem proved that both laws, e.g. $1/r^2$ (exact Coulomb) and $1/r^n$ ($n > 2$), led to the same results with the exception of the case when the number of electron pairs is seven (and, probably, 10)*.

This simple model may be supplemented with three amendments.

Gillespie and Nyholm amendments. Until now we have been discussing electron pairs without specifying what pairs in particular we imply: whether those participating in the chemical bond formation or lone electron pairs.

Gillespie and Nyholm** showed in 1957 that the LEP model gets essentially improved if the following amendments are made:

1. The effective dimensions of the space volume occupied by a pair of shared electrons are less than those of the space volume in which lone electron pairs move.

2. If the central atom is surrounded with the ligands*** capable of drawing off electron density to

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* For $q = 7$ a pentagonal bipyramid is obtained for $n = 2$ (IF_7, UF_7^{3-}, $UO_2F_5^{3-}$), a trigonal prism with the seventh electron pair located opposite one of the rectangular faces for $2 < n < 6$ (TaF_7^{2-}, NbF_7^{2-}) and an irregular octahedron with the seventh electron pair located opposite the centre of one of the octahedron faces for $n \geqslant 6$ (the oxides of La, Ce, Pr, Nd).

** Ronald Sidney Nyholm (1917-1971), professor of London University. His basic works are dedicated to synthesis of complex compounds of transition metals as well as stereochemistry and spectral and magnetic properties.

*** Ligands are atoms or groups of atoms located around the central atom.

themselves, the shared electrons spend most of the time near the ligands and therefore the effective space volume occupied by these electrons in the vicinity of the central atom is diminished.

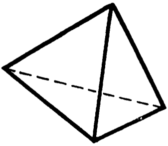
3. Two electron pairs responsible for the double bond (or three pairs of the triple bond) occupy more space around the central atom than one pair of the ordinary bond.

Model in action. Merits ... And now let us see how the LEP model works. Table 5 shows the anticipated

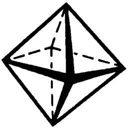
TABLE 5

Number of LEP	Configuration
2	Linear
3	Equilateral triangle
4	Tetrahedron
5	Trigonal bipyramid
6	Octahedron
7	Octahedron with an additional apex or pentagonal bipyramid ($n = 2$)
8	Square antiprism
9	Trigonal prism with three additional apices
10	Square antiprism with two additional apices
11	Icosahedron without one apex
12	Icosahedron

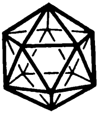
Note. For better understanding of the terms of Table 5 some geometric figures are pictured below (see also Fig. 19).



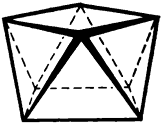
Tetrahedron



Octahedron



Icosahedron



Square antiprism

relationship between the total number of electron pairs and the geometry of a molecule.

We shall first examine molecules with all valence electron pairs shared, i.e. involved in the chemical bond formation.

Well, and what if there are some lone electron pairs as in the water molecule in which two out of the four pairs are lone? In this case the water molecule configuration may be conceived as the tetrahedron with two "empty" apices (Fig. 18), i.e. the water molecule is imagined as the "fragment" of the tetrahedron.

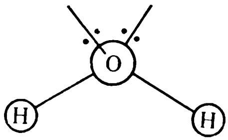


FIG. 18

Fig. 19 illustrates space configurations of the AX_nE_m molecules (where A stands for the central atom, X for the univalent ligand, one shared electron pair, E for the lone electron pair) and some of them are reviewed in Table 6.

The LEP model enables the conclusions about the arrangement of nuclei in a molecule and consequently its symmetry to be made on the basis of simple considerations. It becomes clear why the molecules of similar composition such as BF_3 and NF_3 belong to different point groups (D_{3h} and C_{3v} respectively). This is due to the fact that in the first case the molecule belongs to the AX_3 type while in the second it is a "fragment" of the tetrahedron AX_3E. What is more, the first amendment by Gillespie and Nyholm predicts a decrease of the valence angle in the series CH_4, NH_3, H_2O where the number of lone electron pairs grows from left to right:

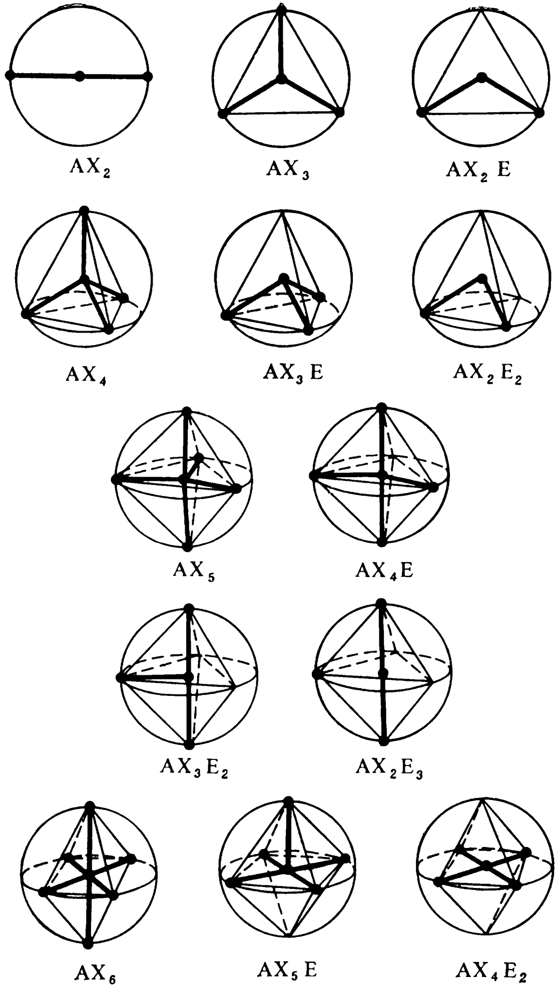
CH_4	$:NH_3$	$H_2\ddot{O}:$
no lone electron pairs	one lone electron pair	two lone electron pairs

TABLE 6

Type of molecule	Configuration	Examples
AX_3	Regular triangle	BX_3 (X = F, Cl, Br, CH_3), $AlCl_3$, SO_3, $Sb(CH_3)_3^{2+}$
AX_2E	V-shaped	O_3, PbX_2, SnX_2 (X = Cl, Br, I)
AX_4	Tetrahedron	CH_4, NH_4^+, BH_4^-, $SiCl_4$, GaH_4^-, AlH_4^-, $InCl_4^-$, XeO_4
AX_3E	Triangular pyramid	NH_3, H_3O^+, $SnCl_3^-$, $SnCl_2 \cdot H_2O$, PX_3 (X = H, F, Cl, Br, I)
AX_2E_2	V-shaped	H_2O, NH_2^-, F_2O, H_2S, ICl_2^+, BrF_2^+, Cl_3^+
AX_5	Trigonal bipyramid	PCl_5, SiF_5^-, $SnCl_5^-$, SOF_4, IO_2F_3 (?)
AX_4E	Bisphenoid	SF_4, $(CH_3)_2TeCl_2$, $IO_2F_2^-$, IF_4^+, XeO_2F_2
AX_3E_2	T-shaped	ClF_3, BrF_3, $C_6H_5ICl_2$
AX_2E_3	Linear	I_3^-, ICl_2^-, $IBrCl^-$, IBr_2^-
AX_6	Octahedron	SF_6, XeO_6^{4-}, IO_6^{5-}, IOF_5, IF_6^+, $Te(OH)_6$, PF_6^-, SbF_6^-, $Al(H_2O)_6^+$
AX_5E	Square pyramid	$SbCl_5^{2-}$, $BiCl_5^{2-}$, TeF_5^-, IF_5, BrF_5, XeF_5^+
AX_4E_2	Square	ICl_4^-, I_2Cl_6, XeF_4, $Te[SC(NH_2)_2]_2\,Cl_2$

Each new electron pair that does not participate directly in the chemical bond formation forces the shared electron pairs to make room which results in a decrease of the valence angle:

$$\begin{array}{ccc} CH_4 & NH_3 & H_2O \\ \angle HCH \approx 109^\circ & \angle HNH \approx 107^\circ & \angle HOH \approx 105^\circ \end{array}$$



AX_2 AX_3 AX_2E

AX_4 AX_3E AX_2E_2

AX_5 AX_4E

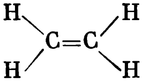
AX_3E_2 AX_2E_3

AX_6 AX_5E AX_4E_2

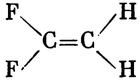
FIG. 19

The second amendment subscribes, for example, to the conclusion that the angle HCH in the ethylene molecule must be greater than the angle FCF in the 1,1-difluorethylene molecule

117° approx.



110° approx.



And finally, the third amendment indicates that the configuration of molecules with double and triple bonds between central atoms and ligands can be predicted from the assumption that two or three electron pairs of the multiple bond together occupy the space destined for one electron pair of a univalent ligand.

... and drawbacks. One may quote many drawbacks and inadequacies of the LEP model but we shall point out only two of them. First, the LEP model does not allow for the peculiarities of ligands and the interaction between them. As the ligand size grows the predicting capabilities of the model decline dramatically. Second, it does not take into account what particular atomic and molecular orbitals (AO and MO) are occupied by electrons. Consequently, the model cannot explain why the BeF_2 molecule ($q = 2$) is linear while the MgF_2 molecule ($q = 2$) is not.

Electrostatic models rendered assistance to chemists more than once—recall, for example, the ionic model. But one should not expect too much from electrostatics. Chemistry cannot be squeezed into the narrow frame of the Coulomb law.

Second Variation on the Theme of Coulomb Law

Idea of Emanuele Paterno. By the seventies of the last century the idea of the carbon tetrahedron was already "floating in the air". By that time chemists had elaborated the concept of equivalence of four valence units in the carbon atom. The historians of science are inclined to connect the emergence of the tetrahedral model for the carbon atom having four *identical* bonds, directed toward the corners of a tetrahedron, in the centre of which the carbon atom is located, with the names of Van't Hoff* and Le Bel** and date it back to 1874. For the sake of justice, though, it should be pointed out that the hydrocarbon tetrahedron model was proposed five years earlier by the Italian chemist Paterno***. Since that time the tetrahedron model for the methane molecule in which all four C—H bonds are equivalent and the angle between them is equal to 109°28′ became classical.

Linus Pauling's idea. One should note that more than once the methane molecule supplied the theoreticians with the motive for meditation. The relative lull in the "hydrocarbon" section of theoretical organic che-

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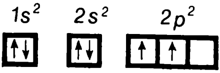
* Jacobus Hendricus Van't Hoff (1852-1911), Dutch chemist, one of the founders of modern physical chemistry and stereochemistry. Worked in a number of European universities and laboratories. The first Nobel prize winner in chemistry.

** Joseph Achille Le Bel (1847-1930), French chemist, student of Ch. Wurtz, one of the founders of stereochemistry. Independently of J.H. Van't Hoff advanced the theory of optical activity having related it to molecular asymmetry.

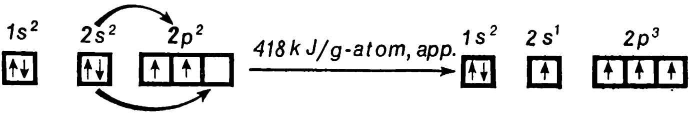
*** Emanuele Paterno (1847-1936), Italian chemist, professor of universities in Palermo and Rome; known for his works in physical, inorganic and organic chemistry.

mistry lasted till the mid-twenties of this century. The trouble began as soon as the electronic structure of the carbon atom was elucidated.

The carbon atom is known to have the following configuration in the ground state:



Thus the carbon atom has only two unshared electrons ($2p^2$) in the ground state and in order to form four bonds the atom needs to be excited:



But it was still inexplicable why all four bonds in the methane molecule are equivalent and form the space tetrahedron. After all, the 2*s* and 2*p* electrons differ quite essentially (recall, for instance, the difference in the shapes of electron clouds), besides, the 2*p* electron "dumb-bells" are located at an angle of 90° to each other while the HCH angle is equal to 109°28′. To overcome the difficulty L. Pauling*, J. Slater**

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* Linus Carl Pauling, born 1901, famous American physicist and chemist. Such achievements of quantum chemistry as the hybridization theory, concept of resonance, electronegativity, etc. are related to Pauling's name. Made enormous contribution to molecular biology (research in structure of protein, etc.). Nobel prize in chemistry (1954) and Nobel Peace prize (1962).

** John Clarke Slater, born 1900, prominent American physicist and chemist, one of the founders of quantum chemistry, distinguished for his work in solid state physics and electronics.

and, independently, R. Mulliken and F. Hund* advanced in 1931 the conception of electron cloud hybridization. In accordance with their model the four electrons of the carbon atom find themselves not in the different ($2s$ and $2p$) states but in the identical states which kind of sum up from the $2s$ and $2p$ states. As a result, four equivalent tetrahedrally directed hybridized electron clouds are formed (Fig. 20).

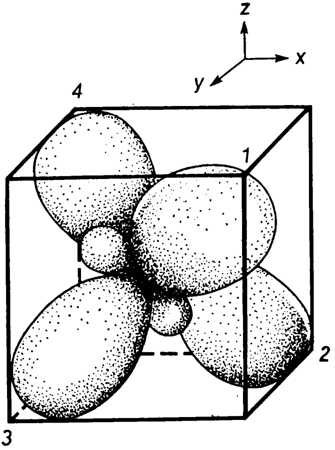

FIG. 20

The elongated shape of the hybridized electron clouds ensures their adequate overlapping, i.e. fosters "condensation" of the negative charge which attracts the nuclei and makes the chemical bonding stronger.

Every hybridized electron cloud is described by the wave function which is the linear combination of the $2s$ and $2p$ functions:

$$\Psi_{hybr} = C_{2s}\Psi_{2s} + C_{2p_x}\Psi_{2p_x} + C_{2p_y}\Psi_{2p_y} + C_{2p_z}\Psi_{2p_z}$$

The coefficients C_{2s}, C_{2p_x}, C_{2p_y}, C_{2p_z} define the contribution that one or another atomic orbital submits to the hybrid formed. The hybridization conception has been widely adopted in chemistry and especially in organic chemistry. However, in spite of all

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* Friedrich Hund, born 1896, German physicist, one of the founders of the method of molecular orbitals. Basic research in quantum theory of atoms and molecules, Mendeleev's Periodic Table of elements and spectroscopy.

the merits of the model one should not forget that from the very beginning it ran into...

... some difficulties. Unfortunately the choice of hybridization type is not unique for molecules of the same symmetry. So besides the sp^3 hybridization (when one s and three p functions participate in the linear combination) the sd^3 hybridization (one s AO and three d AOs) is also possible for methane, both describing the same T_d symmetry. In order to choose some definite type of hybridization one has to calculate the coefficients. In the carbon atom, for instance, the $3d$ electron energy is much higher than that of $2s$ and $2p$ electrons and the coefficients corresponding to the d AO are expected to be very small. This is the evidence that the formation of chemical bonding in the methane molecule does not involve any $3d$ electrons. It is due to this fact that the CH_4 molecule is described by means of the sp^3 hybridization.

Pauling's criterion. Pauling suggested the following hybridization criterion: the chemical bond energy is proportional to the degree of overlapping of atomic wave functions (electron clouds) which may be either hybridized or ordinary AOs.

A bit of history. In Copenhagen at the N. Bohr Archives a notebook is kept in which L. Pauling was making his draft records in 1927-28. Having analysed that document we realized that the impetus that led Pauling to the creation of the hybridization concept was given by his acquaintance with E. Schrödinger's paper devoted to the Stark effect in a hydrogen atom. The Stark effect is the alteration of energy levels in atoms, molecules and solids in the presence of electric field. This alteration is detected as shifting and splitting of spectral lines. The wave functions $\widetilde{\Psi}$ describing the state of a hydrogen atom in the axial electric field are the linear combinations of the wave functions of an isolated atom, for example:

$$\widetilde{\Psi}_1 = (\Psi_{200} + \Psi_{210})/\sqrt{2}$$
$$\widetilde{\Psi}_2 = (\Psi_{200} - \Psi_{210})/\sqrt{2}, \text{ etc.}$$

(The subscripts correspond to the values of the quantum numbers n, l and m respectively.) The functions $\widetilde{\Psi}_1$ and $\widetilde{\Psi}_2$ represent the hybrid orbitals (sp_0 hybridization) while $\Psi_{21,\pm 1}$ AOs stay nonhybridized in the case considered. Note that in a free hydrogen atom the electron energy depends only on n. For other atoms energy levels depend on both n and l. But even in this case one may expect the AOs from the same shell (i.e. having the same n but different l) to get mixed, provided the energy difference between the levels E_{nl} and $E_{nl'}$ is small compared to the energy of the external field. From Pauling's viewpoint such a situation has to develop in molecules in which atoms are located in the electric field of nuclei and electrons. Due to the anisotropy of this field the electron angular momentum is not maintained and the quantum number l loses its meaning. Consequently, it turns out to be possible for the AOs possessing both equal and different l's to get mixed. This gives rise to hybrid AOs (HAOs). Frequently HAOs are called equivalent because under transformations of the molecular symmetry point group they are converted into one another, i.e. are transformed according to the reducible representation of the molecular symmetry group. In the case of methane, for example, such representation is four-dimensional.

Such is the chemical aspect of the problem. But there is also the physical approach to it.

Symmetry without hybridization. As we have already seen the hybridization type is closely related to the symmetry point group to which the molecule belongs. Let us consider this fact at greater length. In contrast to the foregoing summary we shall proceed from the method of molecular orbitals introducing them as the LCAO. However, we must include in the linear combination only those AOs which are transformed according to the irreducible representations of the symmetry group of the molecule. The T_d group to which the methane molecule belongs has five IRs: A_1, A_2, E, T_1, T_2. The detailed analysis reveals that the $2s$ AO of the carbon atom and the sum of the $1s$ AOs of the hydrogen atom are transformed according to the A_1 IR. Table 7 also shows the linear combinations of the hydrogen AOs which are transformed according to the T_2 IR. The other IRs have no corresponding combinations of the hydrogen AOs or the carbon AOs involved in the chemical bonding.*

TABLE 7

IR	Carbon AO	LCAO of hydrogen
A_1	$2s$	$\sigma_1+\sigma_2+\sigma_3+\sigma_4$
	$2p_x$	$\sigma_1+\sigma_2-\sigma_3-\sigma_4$
T_2	$2p_y$	$\sigma_1-\sigma_2+\sigma_3-\sigma_4$
	$2p_z$	$\sigma_1-\sigma_2-\sigma_3+\sigma_4$

Note. The hydrogen $1s$ AOs are denoted by σ_i. The numeration of hydrogen atoms is shown in Fig. 20.

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* The carbon $1s$ AOs are transformed according to the A_1 IR and $3d$ AOs according to the E and T_2 IRs, but neither the former nor the latter participate effectively in the bond formation.

According to the data of Table 7 the MOs must have the following form:

$$\Psi_1^{(A_1)} = a\Psi_{2s} + b(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

$$\Psi_2^{(T_2)} = c\Psi_{2p_x} + d(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$$

$$\Psi_3^{(T_2)} = c\Psi_{2p_y} + d(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

$$\Psi_4^{(T_2)} = c\Psi_{2p_z} + d(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4)$$

where a, b, c and d are the numerical coefficients. So the carbon AOs in CH_4 turn out to be nonhybridized in this case.

Meditation over results. First of all it should be emphasized that the MOs obtained are not localized between the atoms but "surround" the whole molecule. Besides, the calculations show that the energy corresponding to the $\Psi_1^{(A_1)}$ MO differs from that of the triply degenerate level described by the $\Psi_2^{(T_2)}$, $\Psi_3^{(T_2)}$ and $\Psi_4^{(T_2)}$ orbitals. This implies that we are bound to get two different values for the ionization potential. Indeed, the experiment yields two values of energy for the process $CH_4 \rightarrow CH_4^+ + e^-$: 13.2 and 22.1 eV.

This result is worth thinking over. It cannot be predicted if the electron structure of the CH_4 molecule is treated as eight equivalent electrons stationed in four absolutely identical localized orbitals.

At first sight it seems that when we use the MO method according to which electrons in their motion surround the whole molecule, and then the method of valence bonds or the version of the MO method according to which the MOs are localized between two atoms (the method of localized orbitals, LMO, in short), differing results are gained; in the latter case all the bonds in the methane molecule turn out to be equivalent and all eight electrons have the same energy. But this contradiction is only seeming.

Theory allows us to use both the localized MOs corresponding to the motion of electrons in some limited molecular space (between two nuclei, for example) and the delocalized orbitals corresponding to electrons that in their motion envelop all nuclei of the molecule. But in terms of physics these methods differ from each other by their "informative" abilities. One cannot attribute the definite energy to each LMO but only some "average value", so that "on the average" all methane LMOs are indeed the same. We have just seen that when the delocalized MOs are used each orbital has a definite energy value but the obvious picture of the "equalizing" distribution of electron density over the molecular bonds vanishes.

Besides, it should be noted that delocalized MOs are transformed according to the IRs of the molecular symmetry group while the LMOs turn one into another under the symmetry transformations, i.e. are transformed according to the reducible representations of high dimension.

Thus we have discussed two comparatively simple models making it possible to correlate the chemical formula of the compound with the spatial configuration of its nuclei and consequently with the symmetry of the nuclear polyhedron. Now we shall turn to another aspect, the correlation between the spatial configuration of a molecule and its electron structure. We shall consider the area in which the ideas of symmetry theory are most widely used, that is the investigation of molecular structure of complex compounds of transitional metals. And we start with the simplest, and historically first, theory of crystalline field.

Theory of Crystalline Field (TCF)

TCF idea. In 1929 the German physicist H. Bethe published a paper in which the basic aspects of the quantum mechanical theory of the structure of complex compounds were presented. Bethe's idea consisted in the following. Five *d* orbitals of an isolated atom are known to have the same energy, i.e. the order of degeneracy is five. But it is one thing when an atom is isolated and quite different when it gets surrounded by a few ligands. The symmetry of surrounding ligands gets lower than the spherical one and is determined by the way the ligands are arranged around the central atom. For example, in the complex compounds $[Ti(H_2O)_6]^{3+}$, $[MnF_6]^{4-}$, $[Fe(CN)_6]^{4-}$ the ligands are located in the apices of the octahedron while such compounds as $TiCl_4$, $[FeO_4]^{2-}$, $[VCl_4]^-$, $[MnO_4]^-$ have the tetrahedral configuration.

But when the symmetry of the surrounding ligands gets lower the degenerate energy levels split. This is the general law of quantum mechanics. However, one should not presume that the lowering of symmetry necessarily splits *all* degenerate levels. Some levels may stay degenerate.

Let us consider a comparatively simple example of the hexaquacomplex Ti(III)—$[Ti(H_2O)_6]^{3+}$. The Ti^{3+} ion possesses one *d* electron extra compared with the argon shell $[Ar]3d^1$. The ground state of the complex is ^2D $(L = 2,\ S = 1/2)$. This complex has the octahedral shape and the titanium d_{xy}, d_{xz} and d_{yz} orbitals with the lobes located between the coordinate axes (Fig. 21) are absolutely symmetrical relative to all six ligands. Having the same energy the orbitals give origin to the triply degenerate energy level.

In the states $d_{x^2-y^2}$ and d_{z^2}, however, the electron experiences stronger repulsion from the ligands as their electron clouds are extended along the coordinate axes x, y and z, i.e. directed toward the ligands. Occupying these states the electron has higher energy compared with the case when it occupies the d_{xy}, d_{xz} and d_{yz} orbitals which avoid the "frontal" interaction with the water molecule due to the symmetry of the complex compound.

Thus, the five d states of the atom (ion) which were degenerate initially separate into two groups when located in the octahedral field of ligands. The orbitals of one group (d_{z^2} and $d_{x^2-y^2}$) possess higher energy than the initial atom (ion) had and are twice degenerate while the orbitals of the other group (d_{xy}, d_{xz} and d_{yz}) possess lower energy and are characterized by the triple degeneracy. The former are denoted by the symbol E_g and the latter by T_{2g}. Such a notation indicates the symmetry of orbitals, i.e. the irreducible representation of the O_h group according to which the respective wave functions (orbitals) are transformed. In Fig. 22 the $^2D(5)$ term is identified with the free atom (ion) and $^2D'(5)$ with the free atom or positive ion in the field of ligands (due to repulsion of outer

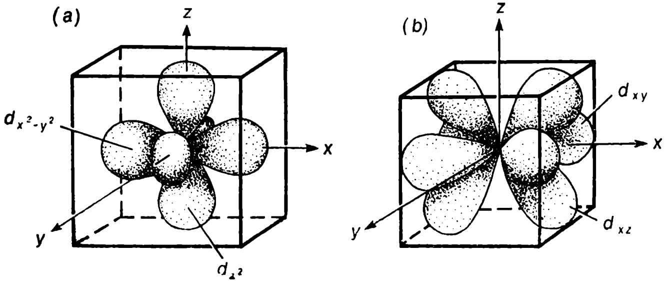

FIG. 21

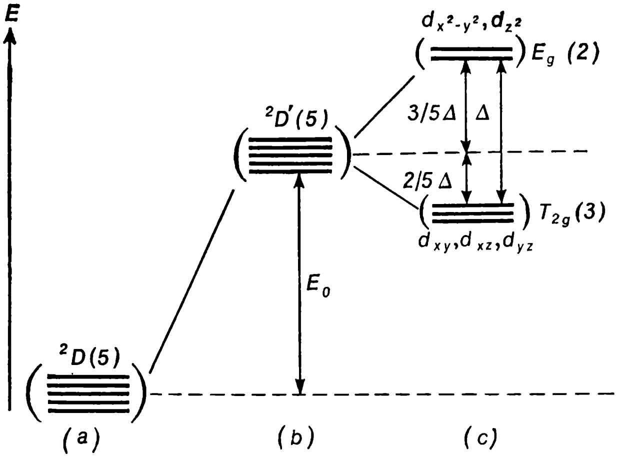

FIG. 22

electrons the energy of all states of the term increases by the value E_0). E_g (2) and T_{2g} (3) are the terms which emerged after the splitting of the $^2D'$ (5) term of the free ion in the ligand octahedral field: $^2D'(5) \rightarrow \rightarrow T_{2g}(3) + E_g(2)$. The numbers in brackets indicate the order of degeneracy.

Other symmetries. Depending on the symmetry of the ligand arrangement around the central ion the splitting pattern will be different. Fig. 23 shows the splitting of the *d* orbitals of the central ion in the fields of different symmetry.

It is seen from the diagram that for the tetrahedral surrounding, as well as for the cubic one, the splitting of the *d* orbitals occurs in the fashion which is reverse to that characteristic for the octahedron. Besides, the order of degeneracy of energy levels diminishes as the

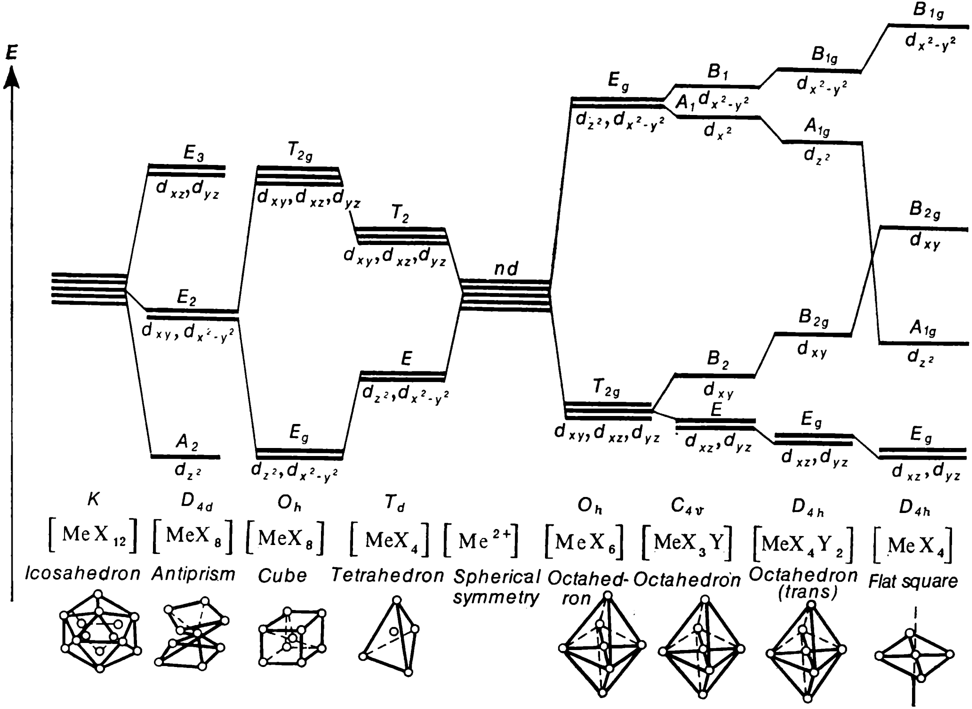
E
E3
dxz,dyz
E2
dxy, dx2-y2
A2
dz2
T2g
dxy,dxz,dyz
Eg
dz2,dx2-y2
T2
dxy,dxz,dyz
E
dz2,dx2-y2
nd
Eg
dz2,dx2-y2
T2g
dxy,dxz,dyz
B1
A1 dx2-y2
dx2
B2
dxy
E
dxz,dyz
B1g
dx2-y2
A1g
dz2
B2g
dxy
Eg
dxz,dyz
B1g
dx2-y2
B2g
dxy
A1g
dz2
Eg
dxz,dyz
K
[MeX12]
Icosahedron
D4d
[MeX8]
Antiprism
Oh
[MeX8]
Cube
Td
[MeX4]
Tetrahedron
[Me2+]
Spherical symmetry
Oh
[MeX6]
Octahed-ron
C4v
[MeX3Y]
Octahedron
D4h
[MeX4Y2]
Octahedron (trans)
D4h
[MeX4]
Flat square

FIG. 23

symmetry of the complex gets lower. So passing from the O_h symmetry to the C_{4v} symmetry we observe the splitting of the levels E_g and T_{2g} which were initially degenerate. The higher is the symmetry, the greater is the number of degenerate levels.

Splitting parameter. Until now we were discussing the splitting in the ligand field qualitatively. Now we shall dwell on the quantitative aspects of the phenomenon. Let us turn again to the octahedral complex $[Ti(H_2O)_6]^{3+}$ as an example. The energy difference between the levels E_g and T_{2g} is usually denoted either by the symbol Δ or by 10 Dq (see Fig. 22). The Δ quantity is called the splitting parameter; it depends both on the nature of the central atom (ion) and on the nature of the ligand. Besides, Δ changes with the symmetry of the complex. For example, the level splitting in tetrahedral complexes is less than that in octahedral ones so that in most cases the following relation holds:

$$|\Delta_{oct}| \approx \frac{9}{4} |\Delta_{tetr}|$$

Note that for complexes of the O_h symmetry the energy of each of the two E_g orbitals is greater than the energy E_0 by $\frac{6}{10}\Delta$ ($6Dq$), i.e. the total energy increment is equal to $2\frac{6}{10}\Delta = \frac{12}{10}\Delta$ ($12Dq$). The energy of each of the three T_{2g} orbitals lies below the initial level by $\frac{4}{10}\Delta$ ($4Dq$) and the total lowering is also equal to $3\frac{4}{10}\Delta = \frac{12}{10}\Delta$ ($12Dq$).

The Δ parameter is the basic quantitative characteristic of splitting in the case of cubic symmetry complexes (cube, octahedron, tetrahedron).

Symmetry and colour. We shall get back to our hexaquacomplex of Ti(III): $[Ti(H_2O)_6]^{3+}$ possessing only one *d* electron at the T_{2g} level in the principal state. The interaction of this complex with an energy quantum $E = h\nu = \Delta$ (ν is the quantum frequency) results in the absorption of the quantum by the molecule and the promotion of the electron from the T_{2g} level to the E_g level. Commonly when the transition is being characterized the symmetry of the initial and the final orbital is specified in addition to the transition energy. For instance, $T_{2g} \rightarrow E_g$. Generally speaking, the total spin S of the system may change in electronic transitions and consequently the spin multiplicity of the electronic term, i.e. the $2S + 1$ quantity, may also change. Accordingly, the value of $2S + 1$ is written as an upper index to the left of the symmetry symbol. True, in the previous example the $T_{2g} \rightarrow E_g$ transition is not accompanied with a change of the $2S + 1$ value as there is only one electron in the T_{2g} orbital. Thus the total spin in this case is equal to 1/2 and $2S + 1 = 2 \cdot 1/2 + 1 = 2$. Therefore we may designate the electronic transition by the symbol ${}^2T_{2g} \rightarrow {}^2E_g$.

The experimental data show that this transition in the $[Ti(H_2O)_6]^{3+}$ ion is characterized by the wavelength of approximately 50 000 nm that corresponds to the absorption of the green component of the visible light. But the colouring of a compound is known to be complementary to the absorbed colour. Since the mixing of the red, green and blue produces the white, the red and blue are the colours which are complementary to the green and this particular solution has the violet colouring.

Orgel's* diagrams. It has already been established (see p. 75) that the value Δ may change from one ligand to another. Fig. 24 shows the relationship between the octahedral and tetrahedral splittings for the case of one *d* electron. The diagrams of the type shown in Fig. 24 are referred to as *Orgel's diagrams*.

The right part of Orgel's diagram shows the splitting of the initial atomic term vs the Δ value for the O_h symmetry complexes with the d^1 and d^6 electron configurations of the central atom (ion) as well as for the tetrahedral (T_d) coordination with the d^4 and d^9 configurations. The left part of the diagram refers to the octahedron with the d^4 and d^9 and the tetrahedron with the d^1 and d^6 electron configurations of the central atom (ion).

In other cases Orgel's diagrams are more complicated and we shall not consider them here.

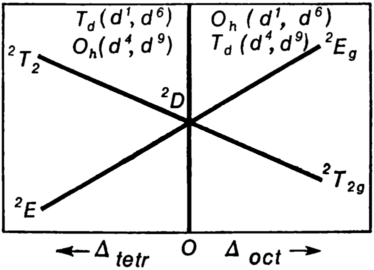

FIG. 24

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* Leslie Orgel, born 1927, worked in Oxford and Cambridge Universities, professor of University of California since 1964. Studied the stucture of complex compounds of transition elements; known for his research devoted to the origin of life and molecular evolution.

Laporte's* rule. In a free atom or ion not all electronic transitions are permitted. There are special rules, called *selection rules*, which forbid certain transitions.

In the complex compounds formed by transitional elements the electronic transition induced by the visible or ultraviolet light quantum will be observed between two *d* orbitals of different energies as it follows from the model of a complex adopted in the theory of crystalline field. But still there are some transitions in a free atom (ion) that are forbidden. Such are the transitions for which:

(a) the number of unpaired electrons changes (these transitions are said to be forbidden in terms of spin);

(b) the parity does not change.

In other words, permitted are only the transitions between the states of different parity: $g \leftrightarrow u$ (the Laporte rule)**.

Since the atomic states with the same quantum number l have the same parity (see p. 49) the electronic transitions between them are forbidden according to the Laporte rule; in particular, *d-d* transitions are forbidden.

But when an atom or ion is involved in a complex compound as a central atom both kinds of forbiddenness may be revoked. Whether the forbiddenness is really revoked depends on many factors including symmetries of complexes.

Theory predicts that in octahedral complexes possessing the centre of inversion all *d-d* transitions have to be weak and some of those which are forbidden in terms of spin must be still weaker than the rest; in

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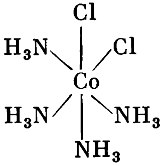
* Otto Laporte (1902-1971), German, and since 1924 American, physicist. His basic studies are devoted to atomic and molecular spectra.

** Note that the Laporte rule is also valid for the molecular systems possessing the centre of inversion.

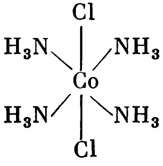
tetrahedral complexes which do not possess symmetry centres *d-d* transition intensities must be much greater.

The Co(II) compound may be taken as an example. The $[Co(H_2O)_6]^{2+}$ ion weakly absorbs light in the violet part of the spectrum and so it has the pale pink colouring. As to the tetrahedral $[CoCl_4]^{2-}$ complex it absorbs light in the visible region in a greater degree. Inasmuch as the absorption occurs in the red region the compound is coloured dark blue. The same can be said about many other tetrahedral Co(II) complexes.

The other examples are the Co(III) compounds such as the *cis*- and *trans*-isomers of $[Co(NH_3)_4Cl_2]^+$:



cis-isomer
C_{2v} symmetry
violet colouring



trans-isomer
D_{4h} symmetry
green colouring

The *cis*-isomer in contrast to the *trans*-isomer has no symmetry centre so that the greater absorption is to be expected of *cis*-$[Co(NH_3)_4Cl_2]^+$.

It is seen from the examples quoted that the selection rules may be violated. So, for instance, according to the Laporte rule the $[Ti(H_2O)_6]^{3+}$ ion must be colourless while in fact it is coloured. This is because a complex ion does not always possess the ideal O_h symmetry; it may be so distorted (for example, due to atomic vibrations) that the symmetry centre vanishes.

A few words about selection rules. Selection rules are always closely associated with the symmetry of a system. However, they are not absolute and the term "forbiddenness" should not be understood literally.

Usually the transitions forbidden by theory are observed in reality, though their intensity is several orders of magnitude less than that of allowed transitions. Selection rules play an important role in theoretical and experimental chemistry. Using them one can determine, for example, what kind of a spectrum a molecule has. Thus selection rules forbid the chlorine molecule to have the vibration spectrum in the infrared region.

In order to determine the selection rules theoretically it is necessary to consider the integral containing-two wave functions Ψ_1 and Ψ_2 describing the states between which the transition occurs. The precise wave functions, i.e. the precise solutions of the Schrödinger equation for molecular systems, are not known. And that is where the symmetry theory holds out a helping hand. It enables us to determine whether the integral in question is equal to zero or not without knowing the analytical or tabulated form of the functions Ψ_1 and Ψ_2. It is sufficient to know only to what IR of the symmetry group of the system these functions (and other quantities involved in the integral considered) belong. Inasmuch as the corresponding transition probability depends on this integral we can determine the selection rules having defined the conditions under which the above-mentioned integral turns to zero.

In quantum mechanics there is a very general theorem specifying the necessary conditions under which the integral mentioned is not equal to zero. With the aid of this theorem one can obtain the selection rules for each specific case.

Let well alone. We have already noted that the theory of crystalline field does not take into account the electron structure of ligands and consequently all properties conditioned by the nature of the chemical bonding between a central atom and a ligand. Qualitative conclusions drawn in the framework of the theory of crystalline field are based on the general symmetry properties of a complex and, accordingly, are more reliable than quantitative evaluations. The more complete theory is related to the application of the method of molecular orbitals.

Method of Molecular Orbitals and Structure of Complex Compounds

Complex as a single whole. The method of molecular orbitals makes use of the most valuable part of the theory of crystalline field. It takes symmetry into account and gives a more general picture of the electron structure of complex compounds.

According to TCF individual atoms and atomic groups of a complex or, more precisely, atomic orbitals retain their specificity undergoing only slight alterations due to the interaction with ligands. In the MO method a complex is considered as a single whole and specific features of atoms and atomic groups dissolve in the sea of electron-nuclear, interelectronic and other interactions. For example, the $[Ti(H_2O)_6]^{3+}$ complex is treated in the MO method as the carcass consisting of 6 oxygen nuclei, 12 hydrogen nuclei and one titanium nucleus together with 79 electrons moving in the field of nuclei.

In order to compute the requisite properties of a complex in quantum mechanical terms one has to find the molecular orbitals which are in their turn represented ordinarily as a linear combination of atomic orbitals, i.e. in the MO LCAO approximation (see p. 44).

The symmetry theory makes it possible to simplify radically the procedure of MO determination and these simplifications compare favourably with other methods of making the problem easier.

Michelangelo used to say that a piece of sculpture is already contained in a stone block and the task of a master is only to chisel off what is redundant. The symmetry theory has an analogous objective, it chisels off what is redundant without debasing the description. In this particular case it "chisels off" those linear combinations of atomic orbitals that do not correspond to any IR of the symmetry point group of the complex.

Let us examine this in more detail. We shall not, however, enter into particulars of the mathematical procedure of MO determination, we shall confine ourselves to its general features and results obtained.

The symmetry theory permits one to determine the IRs of the symmetry point group of the complex according to which the atomic orbitals of the central atom are transformed.

The classification of AOs in terms of symmetry for octahedral, tetrahedral and square complexes is presented in Table 8.

Ligand orbitals. In a similar manner we should also classify ligand orbitals now. Let us assume for the beginning that only σ bonds are formed between the central atom and the ligands. Having necessary linear combinations of ligand AOs worked out and classified according to the IRs of the symmetry group of the complex, we may get busy with the π bonding as well.

Let us consider an octahedral complex in which the central atom is surrounded with six univalent ligands. These six ligands form six chemical bonds of the σ type: σ_1, σ_2, σ_3, σ_4, σ_5 and σ_6. In other words, each ligand is represented by its own orbital which we shall denote by the letter σ with a subscript indicating the number of the ligand. It can be demonstrated that the sum of ligand orbitals $(\sigma_1 + \sigma_2 + \sigma_3 + + \sigma_4 + \sigma_5 + \sigma_6)$ is transformed under symmetry

TABLE 8

AO of central atom	Symmetry groups		
	O_h	T_d	D_{4h}
s	A_{1g}	A_1	A_{1g}
p_x	T_{1u}	T_2	E_u
p_y			E_u
p_z			A_{2u}
d_{z^2}	E_g	E	A_{1g}
$d_{x^2-y^2}$			B_{1g}
d_{xy}	T_{2g}	T_2	B_{2g}
d_{yz}			E_g
d_{xz}			E_g

operations of the O_h group according to the IR A_{1g} of this group, i.e. according to the same IR as the s-AO of the central atom is transformed.

One may work out other linear combinations of σ functions transformable according to other IRs of the O_h group. The group theory allows one not only to find out the IR according to which every linear combination is transformed but, what is more important, to obtain the combinations themselves.

The linear combinations of ligand orbitals, which are transformed according to the O_h group IRs, are listed in Table 9 (such combinations are called *ligand group orbitals*). Fig. 25 shows how the ligands are enumerated (the letters c.a. stand for "central atom").

If besides σ bonds there are π bonds between the central atom and ligands, the symmetry theory admits of working out such linear combinations of π type orbitals that are transformed according to one of the group IRs under symmetry operations.

TABLE 9

O_h group IRs	σ type group orbitals
A_{1g}	$1/\sqrt{6}(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$
T_{1u}	$1/\sqrt{2}(\sigma_2-\sigma_5)$
	$1/\sqrt{2}(\sigma_3-\sigma_6)$
	$1/\sqrt{2}(\sigma_1-\sigma_4)$
E_g	$1/\sqrt{2}(\sigma_2+\sigma_5-\sigma_3-\sigma_6)$
	$1/\sqrt{12}(2\sigma_1+2\sigma_4-\sigma_2-\sigma_5-\sigma_3-\sigma_6)$

Table 10 rounds up ligand group orbitals for the case of the octahedral complex and Fig. 26 shows six σ orbitals of a metal ion with ligand orbitals of corresponding symmetry. It can be seen from the table that in the case of the octahedral complex *s*-AOs of a metal are involved only in the formation of σ bonds, while *p*-AOs of a metal are involved in both σ and π bonds (MOs possess the T_{1u} symmetry) and their corresponding energy level is triply degenerate, i.e. *p*-AOs can form complicated MOs of the "combined"

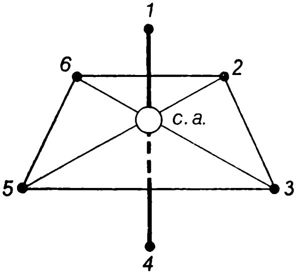


FIG. 25

TABLE 10

O_h group IRs	Central atom AO	σ type	π type
A_{1g}	s	$1/\sqrt{6}(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$	
T_{1u}	p_x p_y p_z	$1/\sqrt{2}(\sigma_2-\sigma_5)$ $1/\sqrt{2}(\sigma_3-\sigma_6)$ $1/\sqrt{2}(\sigma_1-\sigma_4)$	$1/2(\pi_1-\pi_4+\pi_3-\pi_6)$ $1/2(\pi_1-\pi_4+\pi_2-\pi_5)$ $1/2(\pi_2-\pi_5+\pi_3-\pi_6)$
E_g	$d_{x^2-y^2}$ d_{z^2}	$1/2(\sigma_2+\sigma_5-\sigma_3-\sigma_6)$ $1/\sqrt{12}(2\sigma_1+2\sigma_4-\sigma_2-\sigma_5-\sigma_6-\sigma_3)$	— —
T_{2g}	d_{xy} d_{xz} d_{yz}	— — —	$1/2(\pi_2+\pi_5+\pi_3+\pi_6)$ $1/2(\pi_1+\pi_4+\pi_2+\pi_5)$ $1/2(\pi_1+\pi_4+\pi_3+\pi_6)$
T_{1g}	— — —	— — —	$1/2(\pi_1+\pi_4-\pi_3-\pi_6)$ $1/2(\pi_2+\pi_5-\pi_1-\pi_4)$ $1/2(\pi_3+\pi_6-\pi_2-\pi_5)$
T_{2u}	— — —	— — —	$1/2(\pi_1-\pi_4-\pi_2+\pi_5)$ $1/2(\pi_3-\pi_6-\pi_1+\pi_4)$ $1/2(\pi_2-\pi_5-\pi_3+\pi_6)$

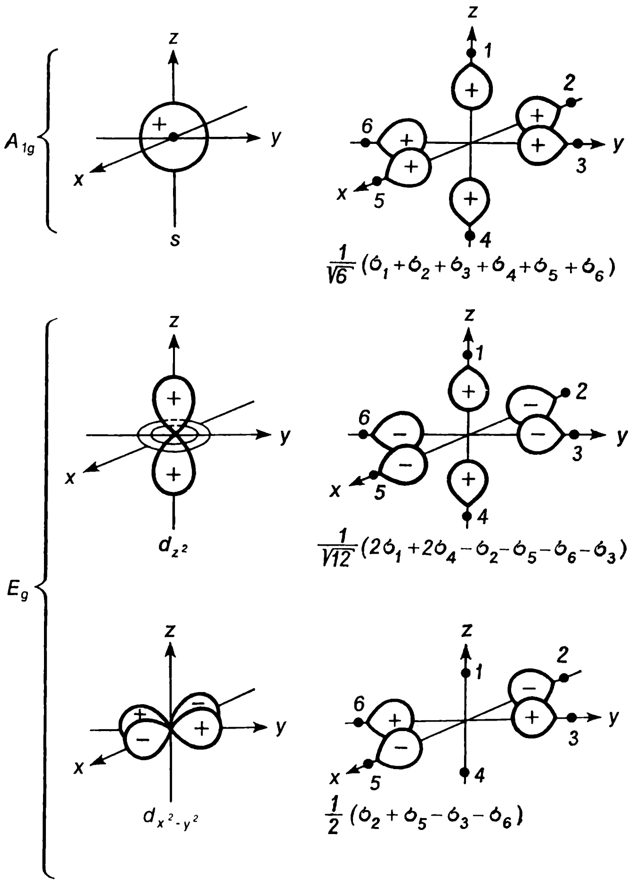
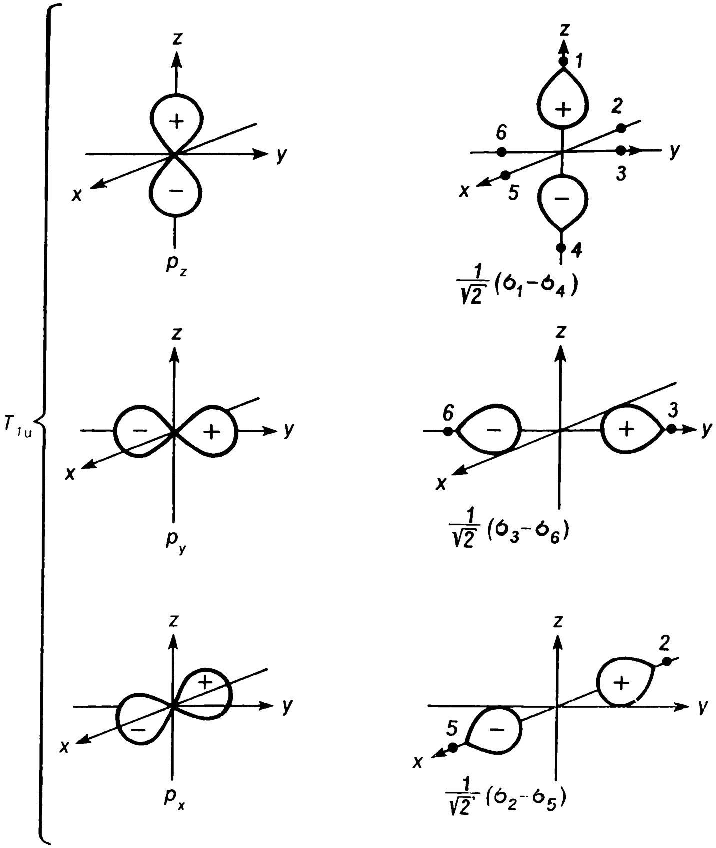
A_{1g}
z
y
x
+
s
z
1
2
3
4
5
6
y
x
$\frac{1}{\sqrt{6}}(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$
E_g
z
y
x
d_{z^2}
$\frac{1}{\sqrt{12}}(2\sigma_1+2\sigma_4-\sigma_2-\sigma_5-\sigma_6-\sigma_3)$
z
y
x
$d_{x^2-y^2}$
$\frac{1}{2}(\sigma_2+\sigma_5-\sigma_3-\sigma_6)$

FIG. 26


T_{1u}
z
y
x
+
−
p_z
z
y
x
1
2
3
4
5
6
+
−
$\frac{1}{\sqrt{2}}(\sigma_1-\sigma_4)$
z
y
x
−
+
p_y
z
y
x
6
3
−
+
$\frac{1}{\sqrt{2}}(\sigma_3-\sigma_6)$
z
y
x
+
−
p_x
z
y
x
2
5
+
−
$\frac{1}{\sqrt{2}}(\sigma_2-\sigma_5)$

σ-π type. This fact indicates the conditionality of the adopted subdivision of chemical bonds into σ and π types*. As to d-AOs, some of those are involved in the σ-MOs (E_g) of double degeneracy.

If a complex has no π bonds, d_{xy}, d_{xz} and d_{yz} AOs of a metal are not involved in bonding at all since such a complex has no partners that would be suitable for them in terms of symmetry and consequently the T_{2g} level remains atomic.

The combinations of the ligand π orbitals of the T_{1g} and T_{2u} symmetries are not involved in the bonding with the central atom providing its f-AOs do not participate in bond formation.

What symmetry cannot do. Considering a complex compound we come to the following conclusions:

A complex possesses a certain symmetry, that is, belongs to a certain symmetry point group (in our example, O_h).

This symmetry group possesses a definite number of IRs of different dimensions (in our example, A_{1g}, A_{2g}, A_{1u}, A_{2u}, E_g, E_u, T_{1g}, T_{2g}, T_{1u}, T_{2u}).

Each molecular orbital of the complex (Ψ_{MO}) is put down as a linear combination of atomic orbitals

---

* The concepts of σ-, π- and δ-orbitals as well as of σ-, π- and δ-bonds are associated with the $D_{\infty h}$ and $C_{\infty v}$ point groups. These concepts possess the clear physical sense for linear molecules of the $D_{\infty h}$ and $C_{\infty v}$ symmetries and for separate linear fragments: they pertain to the orbitals transforming according to the IRs of the Σ, Π and Δ types of the above-mentioned groups (the corresponding orbitals are denoted by small Greek letters). For other symmetries the orbitals with such transformation properties can be selected only in a few exceptional cases (e.g. for the C_{5v} and D_{5d} symmetries). However, it is often agreed to regard the p-orbital oriented along the line connecting a ligand and a central atom as the σ orbital, while other orbitals which are perpendicular to that line are referred to as the π orbitals.

of a central atom (Ψ_{ca}) and a molecular orbital of a ligand system (Φ_{lig}), for both σ type and π type:

$$\Psi_{\mathrm{MO}} = a_{ca}\Psi_{ca} + b_{lig}\Phi_{lig}$$

where a_{ca} and b_{lig} are some numbers.

A molecular orbital Φ_{lig} describing ligands may also be identified as an IR of a symmetry group of a complex.

Only those Ψ_{ca} and Φ_{lig} orbitals may be combined in the sum as shown above that have the same symmetry, i.e. are transformed according to one and the same IR.

Thus, the symmetry theory copes with MO sorting very well, forbidding those of them which do not meet the symmetry requirements. However, chemists take an interest not only in MOs themselves and their degeneracy degree but also in the energies corresponding to them. And here is where the weak point of the symmetry theory comes through: it cannot predict even the relative positions of MOs on the energy scale. One has to make use of the computer technique to calculate those. Fig. 27 shows the most probable MO arrangements for the O_h and T_d symmetry complexes.

Chemical bonding in inert gas compounds. In combination with the MO theory the symmetry theory helps to decipher the electronic structure of inert gas compounds. We shall look at the XeF_2 molecule as an example. It can be shown that in inert gas fluorides and related fluorohalides the central atom-ligand interaction is of the pure p-type nature: each partner submits a single p_σ orbital. In XeF_2, for example, the bonding is realized due to $5p_z$ AO of Xe and $2p_z$ AO of two fluorine atoms. With the molecular symmetry being $D_{\infty h}$ $5p_z$ AO of Xe is transformed according to the Σ_u^+ IR and two linear combinations (two group

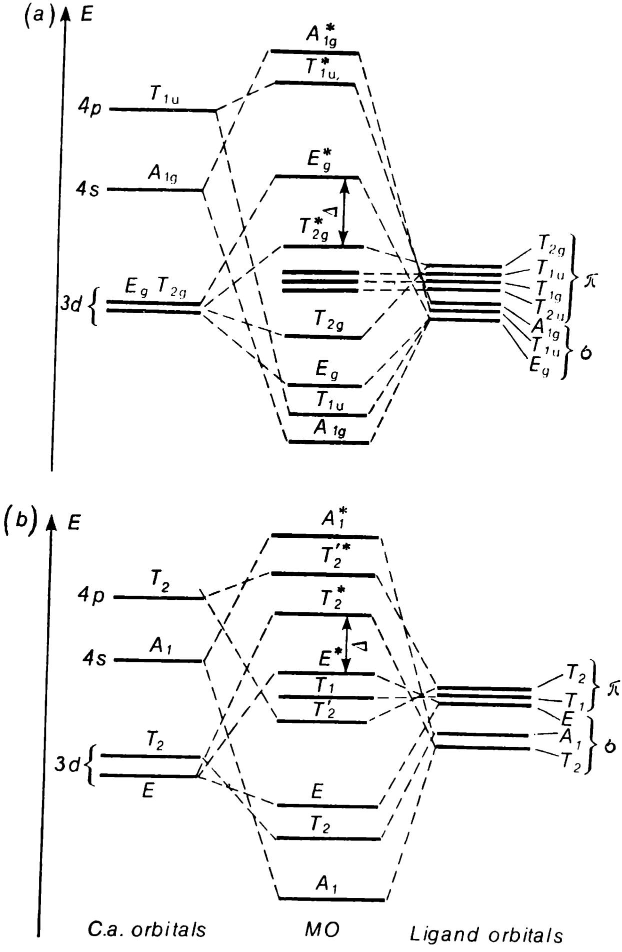

(a)
E
A^*_{1g}
T^*_{1u}
T_{1u}
4p
A_{1g}
4s
E^*_g
Δ
T^*_{2g}
3d
E_g T_{2g}
T_{2g}
E_g
T_{1u}
A_{1g}
T_{2g}
T_{1u}
T_{1g}
T_{2u}
π
A_{1g}
T_{1u}
E_g
σ
(b)
E
A^*_1
T'^*_2
T_2
4p
T^*_2
A_1
4s
Δ
E^*
T_1
T'_2
T_2
3d
E
E
T_2
A_1
T_2
T_1
E
π
A_1
T_2
σ
C.a. orbitals
MO
Ligand orbitals

FIG. 27

orbitals) are formed from the $2p_z$ AO of two fluorine atoms:

$$\Sigma_g^+: [\Psi_{2p_z}(F_1) + \Psi_{2p_z}(F_2)]/\sqrt{2}$$

$$\Sigma_u^+: [\Psi_{2p_z}(F_1) - \Psi_{2p_z}(F_2)]/\sqrt{2}$$

Thus three MOs may be worked out:
bonding $1\sigma_u^+$: $\sim\Psi_{5p_z}(Xe) + \Psi_{2p_z}(F_1) - \Psi_{2p_z}(F_2)$;
nonbonding σ_g^+: $\sim\Psi_{2p_z}(F_1) + \Psi_{2p_z}(F_2)$;
antibonding $2\sigma_u^+$: $\sim\Psi_{5p_z}(Xe) - (\Psi_{2p_z}(F_1) - \Psi_{2p_z}(F_2))$.

The arrangement of these MOs is shown in Fig. 28. We have obtained three three-centre MOs from which only $1\sigma_u^+$ and σ_g^+ are electron-populated. The electron pair which was originally localized at the Xe atom, in the XeF_2 molecule is delocalized over all three atoms, i.e. the filling up of the $1\sigma_u^+$ and σ_g^+ orbitals is accompanied with the transfer of electronic density

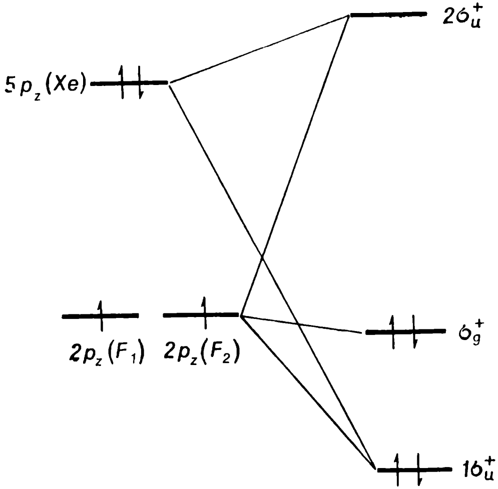


FIG. 28

from the Xe atom (donor) to electronegative ligands (acceptors).

In inert gas fluorides of the AF_{2k} type ($k = 1, 2, 3$) all A—F bonds arise as a result of the four-electron three-centre interactions in the linear F—A—F fragments described above.

Jahn-Teller Effect

“Skewed” complexes. Very often the geometric configuration of a complex differs from that of a regular polyhedron.

Let us examine, for instance, the complex compounds in which the central ion is Cu^{2+} with the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$. When this ion is surrounded with octahedral ligands, nine $3d$ electrons will occupy the T_{2g} and E_g levels with the E_g level having one free site, a “hole”. Its position can be different. When it is based at the d_{z^2} orbital the attraction between the L_1 and L_2 ligands lying along the z-axis (Fig. 29) and the Cu^{2+} ion would be greater compared to that between the central ion and other ligands. This is due to the fact that the L_3, L_4, L_5 and L_6 ligands are screened from the Cu^{2+} ion to a greater degree compared to the L_1 and L_2 ligands since the $d_{x^2-y^2}$ orbital involves more electrons than the d_{z^2} one. This being the case, the L_1 and L_2 ligands will come nearer to the central ion than the others; consequently, the complex will be distorted due to the compression along the z-axis.

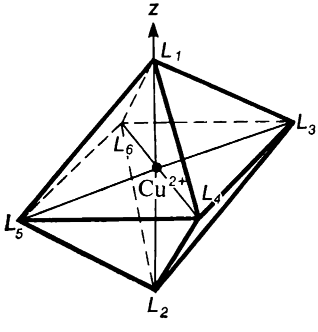


FIG. 29

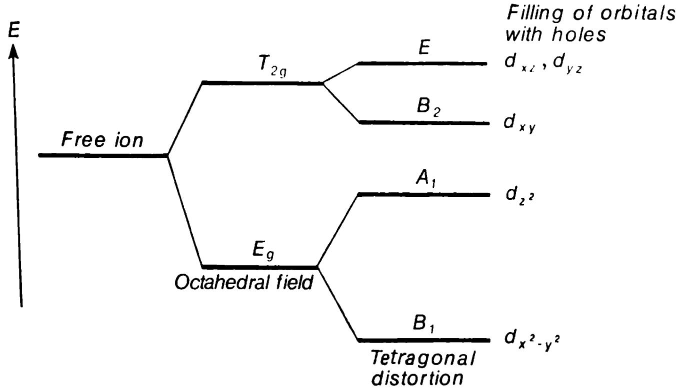


FIG. 30

In another case, when the hole occupies the d_{x^2-y} orbital, the "equatorial" ligands (L_3, L_4, L_5 and L_6 get nearer to the centre and the complex stretches out, as it were, along the z-axis.

Both types of distortion cause the symmetry reduction of the complex—from O_h to D_{4h}—and the removal of degeneracy (Fig. 30). This type of the octahedral distortion (compression or stretching along the four-fold axis) is called tetragonal.

Jahn-Teller theorem. The tetragonal distortion of the octahedral copper complexes is a particular case of the Jahn*-Teller** theorem (sometimes it is referred

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* Herman Arthur Jahn, born 1907, British physicist and mathematician. His basic work is dedicated to application of group theory to quantum mechanics and nuclear physics, as well as to various problems of applied mathematics.

** Edward Teller, born 1908, well-known German physicist; after the nazist take-over emigrated to the USA. Basic contributions in quantum mechanics, quantum chemistry and theory of thermonuclear reactions. One of creators of the hydrogen bomb.

to as the Jahn-Teller effect), which was named after the scientists who formulated it in 1937. The essence of the theorem is as follows: if for the given symmetry the ground state of a nonlinear molecule must be degenerate for certain reasons, the disposition of the nuclei changes in such a way that the symmetry of a particle gets reduced whereupon the degeneracy of the principal term is removed. The additional splitting arising therefrom leads to new spectral transitions and may considerably affect the magnetic properties.

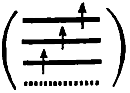
Examples again. In the $CuCl_2$ crystal each copper atom is surrounded with six chlorine atoms positioned at the apices of the irregular octahedron: the length of the bond between the copper atom and the chlorine atom located at the z-axis is equal to 29.5 nm whereas the equatorial chlorine atoms are located 23 nm away from the centre. A similar arrangement is also observed in $CuBr_2$, CuF_2, etc.

The Jahn-Teller distortions are also evident in Mn(III) compounds. Indeed, the Mn^{3+} ion in MnF_3 is surrounded with the "octahedron" of F^- anions, the two Mn—F bond lengths being 17.9 nm, two others 19.1 nm and the rest 20.9 nm. It is not accidental that we put the quotation marks over the word "octahedron" since the existence of three different bond lengths points to the substantial distortion of the regular octahedral symmetry of the complex and the significant splitting of the energy levels.

Perfidious theorem. However attractive the Jahn-Teller theorem is, one must be very careful in using it. First of all, the theorem has nothing to say about the type and degree of distortion. Indeed, the octahedron can be distorted differently, it can stretch or contract along the z-axis (tetragonal deformation), the square formed by four octahedral apices can be transformed into a rhombus (rhombic deformation), etc.

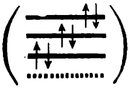
The manifestation of the Jahn-Teller effect is known to be largely determined by the *highest occupied MO (HOMO)*, to wit, its electron population density and symmetry.

First, we shall deal with the population density. If the number of electrons at the highest occupied level is equal to the degeneracy multiplicity or the double value of that (there cannot be more, in accordance with the Pauli principle), i.e. when the electrons are arranged either this way:



(the number of electrons is equal to the degeneracy multiplicity)

or this way:



(the number of electrons is equal to the doubled degeneracy multiplicity)

the Jahn-Teller effect does not manifest itself and no conclusions as to the symmetry of such molecules can be drawn on the basis of the Jahn-Teller theorem.

As regards the symmetry of the highest occupied orbital, in octahedral complexes, for example, the Jahn-Teller effect manifests itself better when the HOMO possesses the E_g symmetry and to a lesser degree in case of the T_{2g} symmetry.

Besides, the splitting can largely depend on the spin-orbit coupling. Owing to this many modern textbooks on inorganic chemistry state that a particular fact "can be due to the Jahn-Teller effect, but another explanation is also possible ...".

The interpretation of the Jahn-Teller theorem by itself causes a considerable difficulty. Usually it reduces to the simple statement that a nonlinear polyatomic molecule with electronic degeneracy possesses an unstable nuclear configuration. However, as I.B. Bersuker pointed out, such a treatment of the theorem should be reviewed. The fact of the existence of the electronic degeneracy in a molecule alone does not entail the spontaneous change of its geometry. Later on it will be seen that in the theoretical investigation of a molecule use is made of the quantum-mechanical equations describing the motion of electrons, rather than that of nuclei. That is why in order to answer the question of whether the *nuclear* configuration will be spontaneously distorted in case of degeneracy, one has to solve the equations describing the motion of nuclei in a molecule.

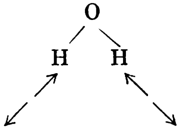
Pearson's Rule

In recent years the quantum chemistry experts have paid attention to the symmetry rule formulated by Ralph Pearson which allows the shape of a molecule in some cases to be determined. But first we should become familiar with certain important notions which at first glance are not related.

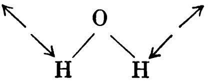
Choice of MO. Peripheral or valence electrons are known to play an important part in atoms. Their coupling with a nucleus is less rigid and they pass readily from one atom to another during chemical reactions. A similar conclusion can be drawn concerning molecular orbitals. In many cases one may consider only the "frontier" orbitals, i.e. the highest (in terms of energy) MO still containing electrons, and the next one which is the lowest MO containing no electrons. They are customarily abbreviated as HOMO (highest occupied MO) and LUMO (lowest unoccupied MO).

Symmetry of normal vibrations. Atoms in molecules are not at rest in the fixed points, they oscillate about the equilibrium positions. There are various kinds of vibrational motion. In a diatomic molecule the vibrational motion takes place only along the bond. In more complicated molecules the number of possible vibrations increases.

The vibrations are referred to as the valence vibrations if the bond lengths vary as a result of them while the bond angles remain constant:



On the other hand, the vibrations associated with the change of the bond angles and with practically constant bond lengths are called the deformation vibrations:



In most cases the complex molecular vibration can be expanded into a comparatively small number of the so-called *normal* vibrations, each of which has its own frequency. To some extent this technique is similar to the vector expansion into components. It is known that a vector can be expanded in many different ways. Each concrete task specifies the most convenient and natural expansion. For example, the particle velocity vector is conveniently expanded into the "vertical" and "horizontal" components—just remember the school problem on the motion of a stone cast at an angle to the horizontal! The complex vibration can also be represented in various ways. The expansion into normal vibrations is very convenient because in this case the expression for the energy of the complex vibration acquires an especially simple form.

The vibration energy E_{vib} of a molecule is given in this case by the following expression:

$$E_{vib}=\frac{1}{2}\sum_{i}\sum_{\alpha}\dot{Q}^2_{\alpha i}+\frac{1}{2}\sum_{\alpha}w^2_{\alpha}\sum_{i}Q^2_{\alpha_i}$$

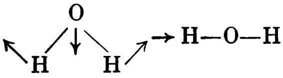
Here $Q_{\alpha i}$ are normal coordinates which are selected in a special manner and determine particle displacements from an equilibrium position; indices i enumerate coordinates corresponding to one and the same frequency; α is an index defining the frequency number; w_α are normal vibration frequencies; the point over $Q_{\alpha i}$ denotes the time derivative.

Sometimes several normal vibrations have one and the same frequency. This frequency is then called *multiple* or *degenerate*.

Generally speaking, the number of independent normal vibrations is determined by the number of atoms in a molecule and its symmetry. The normal vibration energies (and the corresponding frequencies) can be classified according to the IRs of the molecular symmetry point group. In this case the frequency multiplicity defines the IR dimension. For example, a molecule which has the shape of a regular octahedron and consists of 7 atoms (a central atom and six ligands) may have $3 \cdot 7 - 6 = 15$ normal vibrations*. In accordance with the symmetry theory they can be combined into groups corresponding to the definite symmetry types, i.e. the definite IRs.

Hence we obtain the following result: the molecule has one normal vibration of the A_{1g} type, two of the E_g type, and three of each of the following types: T_{2g}, T'_{1u}, T_{2u}, T''_{1u}.

The normal vibrations from the same group, i.e. corresponding to the same IR, have the same frequencies and, consequently, energies. Thus, the vibration of the octahedral molecule can be represented as the combination of 15 normal vibrations generating six different frequencies which can be experimentally observed. It is often possible to select two (at least two!) geometric configurations of a molecule, such that one can be converted into another through the simple continuation of some type of normal vibrations. For example, the angular structure of the water molecule can be converted into the linear one through the simple continuation of one of the deformation vibrations:



A few words about Pearson's rule. The Pearson** symmetry rule relates possible types of normal vibrations to the symmetry of the electronic transition between

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* The number of normal vibrations and corresponding frequencies is equal to $3N - 6$, where N is the number of atoms in a molecule. In case of a linear molecule the number of normal vibrations increases up to $3N - 5$.

** Ralph Gottfrid Pearson, born 1919, American chemist, investigated structure of complex compounds and mechanisms of inorganic reactions. Developed theory of strong and weak acids and bases.

the HOMO and LUMO. The stability of one or another geometric configuration of a molecule depends first of all on the energy of the electronic transition between the occupied and unoccupied levels and their symmetries. Many theorists claim that if the energy difference of the HOMO and LUMO (ΔE) exceeds 4 eV, the given nuclear configuration is stable. Well, and what if $\Delta E \leqslant 4$ eV? In that case one has to clarify whether one or another nuclear configuration is stable, and if not, how it should be altered to become such. This is just where the Pearson symmetry rule helps, which specifies a definite procedure of checking the configurational stability:

1st step—the symmetry (the irreducible representation) of the HOMO and LUMO is determined;

2nd step—the symmetries of normal vibrations varying the molecular symmetry point group (for example, converting a square molecule into a tetrahedral one) are determined;

3rd step—providing the characteristics indicated conform one can claim the given nuclear configuration unstable.

In other words, with the given symmetry of a molecule and the given energy and population density of its MO, there may exist such vibrations that are capable of either distorting or breaking up the molecule. In the presence of such vibrations it is easy to ascertain the possible type of the molecular deformation or its break-up pattern. This is a very important circumstance since we can assess not only the stability of the particular nuclear polyhedron but also the way it will change when unstable.

A few examples. At first glance the practical application of the Pearson symmetry rule meets no difficulties. But in reality this is not the case since the first step of the procedure for checking the molecular configurational stability, described above, does not reduce only to the determination of the HOMO and LUMO symmetry but in the more precise formulation also requires some mathematical operations. Therefore the statement of Pearson's rule needs refinement.

We shall comment briefly on this point. Let us suppose that one molecular orbital (Ψ_i) is transformed according to some IR of the molecular symmetry group whereas another MO (Ψ_k) corresponding to another energy level is transformed according to some other IR. Theorists have often to decide according to what IR (or IRs) will the conventional product $\Psi_i\Psi_k$ be transformed. This problem is studied quite comprehensively in quantum mechanics, but its presentation goes beyond the scope of this booklet. We shall look at some specific examples and comment on the results.

Suppose we are interested in a $D_{\infty h}$ molecule. Recall that to the $D_{\infty h}$ type belong the molecules with the symmetry plane which is perpendicular to the principal axis (N_2, CO_2, etc.). Suppose also that one MO is transformed according to a single-dimensional IR of the A_{1u} type and another MO according to a two-dimensional IR of the E_u type (as we shall see later on, this is a quite practicable case). Well, now Pearson's rule prescribes first of all to find the IR according to which the MO product $\Psi_i^{A(1u)} \cdot \Psi_k^{(E_u)}$ is transformed. In order to find this IR one has to multiply the original IRs, i.e. to multiply A_{1u} by E_u. We shall put aside the question of how it is done*.

---

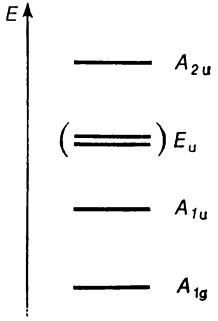
* The detailed information (of mathematical nature, basically) can be found in the book *Symmetry in Chemistry* by H.H. Jaffé & M. Orchin, John Wiley & Sons, Inc., 1965.

For our purpose it is sufficient to just remember the result of the symbol multiplication. For the irreducible representations mentioned above we have

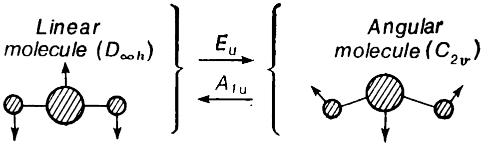
$$(A_{1u})\,(E_u) = E_g$$

Thus, we have defined more accurately the first step in the determination of the molecular configurational stability. It reduces to the definition of the symmetry (i.e. the IR type) of the HOMO and LUMO and the multiplication of these IRs.

Now we can get back to our example. According to the calculations the MO arrangement on the energy scale for the dihydrides of the second period elements (BeH_2, BH_2^+, NH_2, CH_2, H_2O and others) possessing the $D_{\infty h}$ symmetry is as follows (only those MOs are shown that contain outer valence electrons of molecule's atoms):

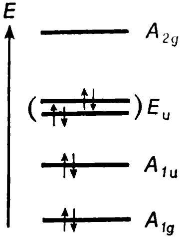


The symmetry of normal vibrations converting a linear molecule into an angular one is E_u:



Now let us consider the beryllium dihydride molecule (BeH_2). Its four valence electrons (two from the Be atom and one from each of the hydrogen atoms) occupy the MOs of the A_{1g} and A_{1u} symmetries. Thus, the HOMO possesses the A_{1u} symmetry and the LUMO the E_u symmetry. In accordance with Pearson's rule we can define the $(A_{1u})(E_u)$ product. As we know it is equal to E_g which differs from the E_u symmetry of normal vibrations bending the molecule. Consequently the BeH_2 molecule must keep the $D_{\infty h}$ symmetry in the ground state.

Let us examine a water molecule as another example. If it were linear its eight valence electrons would be arranged at the energy levels as follows:



The highest occupied MO turns out to possess the E_u symmetry whereas the lowest unoccupied MO has the A_{2g} symmetry. In this case $(E_u)(A_{2g}) = E_u$ which corresponds to the symmetry of the normal vibration transferring a water molecule from the $D_{\infty h}$ into C_{2v} group.

Thus Pearson's rule elucidates why a water molecule has an angular shape.

Many other examples could be quoted but one fact should be noted here: in order to employ the symmetry rule one has to know the energies of molecular orbitals.

Unfortunately, the theoretical calculations are not always reliable enough so that the chances of a successful application of Pearson's rule are small in such cases.

The symmetry theory not only enables one to cut down the computations but leads to significant qualitative conclusions possessing a high degree of generality and beauty which are distinctive for the most fundamental laws of nature.

Symmetry Appears and Disappears

Adiabatic potential. We have already mentioned that the quantum-mechanical treatment of multi-electronic systems comes across some serious mathematical difficulties making researchers resort to approximation methods. Apart from the electron abundance additional difficulties emerge in case of a molecule due to the presence of two kinds of particles, that is, electrons and nuclei. The method to overcome these difficulties was proposed by Max Born* and Robert Oppenheimer** (1927) who elaborated the so-called *adiabatic approximation* (called sometimes the Born-Oppenheimer approximation). What assumptions does it involve?

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* Max Born (1882-1970), outstanding German physicist, one of creators of quantum mechanics. Worked in German. British and American universities. Nobel prize winner of 1954. Born's research influenced considerably the development of chemical bond theory and crystal lattice theory (Haber-Born cycle). Active proponent of the world's peace.

** Robert Oppenheimer (1904-1967), American physicist; basic research in quantum mechanics and theory of atomic nucleus. During World War II he was one of the leaders of the project directed to creation of the atomic bomb. In 1953 Oppenheimer was removed from all posts and charged with "disloyalty" for his statements against production of hydrogen bombs and for his demands to use atomic energy only for peaceful purposes.

It is known from spectroscopy that the intrinsic frequencies of the electron motion in molecules (visible and UV regions) are about 100 times higher than those of nuclear vibrations (infrared region). Therefore one may assume that electrons manage to follow the comparatively slow displacements of nuclei. Hence the energy of electrons depends on the spatial arrangement of nuclei, i.e. on the molecular symmetry point group. The potential energy of nuclei is usually denoted by $V(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M)$ where $\vec{R}_1, \vec{R}_2, \ldots$ are coordinates of nuclei. What is the physical meaning of the quantity just introduced? The $V(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M)$ function describes both the potential energy of interaction between nuclei and the average energy of electrons with the fixed nuclear positions. This function is customarily referred to as the adiabatic potential.

But however good is the Born-Oppenheimer approximation it is still an approximation. This fact should be borne in mind, especially when the nuclear vibration energy (the vibration quantum energy $h\nu_{vib}$) is comparable with the energy difference $E_k - E_i$ between the electron levels of a molecule. In this case the nuclei cannot be regarded as moving many times slower than the electrons and the adiabatic approximation is not valid. Thus we can put down its validity condition as

$$h\nu_{vib} \ll E_k - E_i$$

The less is the difference of energy levels E_k and E_i, the less satisfying becomes the adiabatic approximation. And if a molecule has degenerate energy levels ($E_k = E_i$) the Born-Oppenheimer approximation may prove to be inapplicable. In this case the adiabatic potential turns into a formal quantity. It does not imply the potential energy of nuclei in the field of electrons and movements of nuclei and electrons cannot be regarded independent.

"Mysticism" of experiment. If a molecule has no degenerate energy levels and the validity condition of the adiabatic approximation is met, the adiabatic potential has as a rule a single minimum which corresponds to a definite stable spatial configuration of nuclei. Indeed, a molecule in this case can be represented as a geometric figure possessing a definite symmetry. Everything is right in this case.

And what if there is an electronic degeneracy? It is not even necessary for the actual degeneracy to occur. A molecule may have two very close energy levels, a pseudodegeneracy. What then?

In that case the adiabatic potential can have several equivalent minima, each corresponding to a definite distortion of the nuclear configuration. Therefore we cannot characterize the molecule with some permanent spatial arrangement of nuclei. The molecule seems to get alive. The regular stationary geometric shape of the nuclear polyhedron is not characteristic for this molecule any more. The intricate dynamics of the nuclear motion and the low potential barriers between the minima of the adiabatic potential make the coordinates of nuclei uncertain. Now the nuclei cannot be described as making small oscillations around definite equilibrium positions. Such notions as the "equilibrium structure" and the "point symmetry of the nuclear polyhedron" lose their meaning.

Suppose that in order to pass from one distorted configuration to another a molecule has to overcome a high energy barrier. Therefore it may be assumed that a molecule resides in each configuration for the time interval τ before passing into a new one. If during this time we manage to define experimentally the molecular symmetry, a distorted configuration is obtained. If the interval τ is small and the molecule passes several times from one distorted configuration into another during the time of experiment, we shall obtain some time-mean picture. The molecule might seem fairly symmetric because one distortion cancels out another, as it were. A similar picture is obtained if the energy barrier between the minima of the adiabatic potential is low and the system "slips" through all possible configurational distortions.

Therefore, the symmetry of a molecule is a fairly complex concept. The answer to the question concerning the symmetry of a molecule depends on the method and conditions in which the experiment is carried out. Note that a situation of this kind is typical of quantum-mechanical problems in general. Being a quantum-mechanical system, a molecule "cannot stand impartially" any experiment performed on it including the one determining its symmetry. This should always be remembered whenever the geometric notions of the structure theory are discussed.

Chapter Four

SYMMETRY AND CHEMICAL REACTION

All generalizations are hazardous including even this one.
A. Dumas fils

Until now we talked only of the molecules themselves putting aside the question concerning the role of the symmetry theory in the studies of chemical reactions. This is only natural because one has to begin with the object of research and then proceed to the study of processes in which this object is involved. Indeed, the group theory methods began infiltrating into molecular quantum chemistry from its very origin in the late twenties, whereas their wide application in chemical kinetics started only 10 to 15 years ago. In this chapter we shall briefly discuss some interesting results obtained in this area. But first...

A Few Words about Chemical Process

Reaction energy profile. The chemical reaction between molecules may occur only if they come in contact, i.e. collide. However, if every collision had resulted in a chemical transformation the process rates would have been incredibly high and all reactions would have come about practically instantaneously. This would have altered our world as well as ourselves beyond any recognition. What then protects molecules from infinitely fast transformations? There are many reasons. The most important factor is the activation energy. The collision is successful, i.e. the molecules are forced to react, if they possess the energy sufficient to break up certain chemical bonds. In other words, the colliding molecules must possess the energy surplus as compared to their mean energy. This implies that a certain energy barrier needs to be overcome in order to bring about a reaction (Fig. 31). The E_a energy equal to the barrier height, i.e. the energy surplus mentioned, is called the *activation energy*.

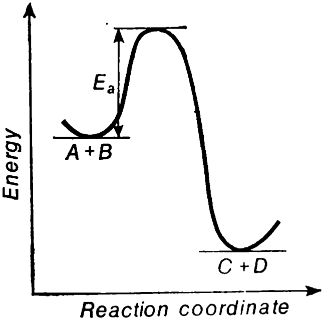

FIG. 31

The abscissa axis which is indicated in Fig. 31 as the "reaction coordinate" shows how reacting particles are located relative to one another, i.e. characterizes the change of internuclear distances in a reaction process.

The activation energy concept was introduced in chemistry in 1889 by S. Arrhenius*. In accordance with his theory E_a is the difference between the energies of active and inactive molecules. Following the advent of quantum mechanics the German scientist Fritz London** disclosed the nature and the origin of the activation energy. The details of chemical pro-

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* Svante August Arrhenius (1859-1927), outstanding Swedish physicist and chemist, creator of the theory of electrolytic dissociation. Research in chemical kinetics, astronomy, astrophysics, biochemistry. Nobel prize winner of 1903.

** Fritz London (1900-1954), German physicist, one of creators of contemporary theory of chemical bond, author of spin-valency concept. Fundamental research on theory of molecular interaction and superconductivity. Worked in universities and research institutes of Germany, France, USSR and USA.

cesses were elucidated due to the quantum-mechanical "interference" into chemical kinetics, which was initiated by F. London and continued by other investigators.

Barrier is cleared. In classical chemistry the following mechanism of the molecular reaction is adopted: first, the initial molecules disintegrate completely into the constituent atoms (or ions) due to the break-up of all chemical bonds, whereupon from the particles formed the new molecules are created. For instance:

$$AB + CD \rightarrow A\cdot + B\cdot + C\cdot + D\cdot \rightarrow AC + BD$$

One of the most important contributions of quantum-mechanical kinetics is the introduction of the transition state concept (or, as they sometimes say, the activated complex). This concept describes the state of reacting molecules at the top of the energy barrier when the transition state possesses the maximum energy. The activation energy as such is needed for weakening the AB and CD bonds (AB → A . . . B; CD → C . . . . . . D) as much as it is necessary for the formation of at least the very weak AC and BD bonds. Hence the transition state resembles to a certain extent a molecule in which all initial atoms (A, B, C and D) are chemically bonded; but inasmuch as this system corresponds to the barrier top and not to the bottom of the energy well, it turns out to be an unstable transient formation with a lifetime varying from 10^{-13} to 10^{-1} of a second. The energy barrier is thus cleared not by separate molecules but by a single system of interacting atoms. Later, on the very top of a barrier, the final redistribution of chemical bonds occurs.

Below we shall discuss several specific examples paying attention primarily to the employment of symmetry considerations in studies of chemical reactions.

Permitting Symmetry and Forbidding Symmetry

General considerations. Thus, chemical reactions are accompanied with the break-up of old chemical bonds and the formation of new ones, i.e. the electrons pass from one kind of atoms or molecules to another, from some atomic or molecular orbitals to others. The most significant part here is played by the energies of the highest occupied MOs (HOMOs) of a molecule which gives electrons away (a donor molecule) and the lower unoccupied MOs (LUMOs) of a molecule receiving electrons (an acceptor molecule). The donor HOMO energy must exceed that of the acceptor LUMO. Consequently, first of all we have to determine wherefrom and whereto electrons will pass.

But the energy is not the only factor. Symmetry also plays a considerable part. For instance, when diatomic molecules interact the transition state may have different geometries. The reaction may proceed either through the formation of a linear structure (AB . . . . . . CD) or through the parallel attachment of molecules*:

$$\left(\begin{array}{ccc} A & \ldots & B \\ \vdots & & \vdots \\ C & \ldots & D \end{array}\right)$$

Of course, the MO overlapping in these two cases occurs differently. Table 11 lists the possible cases of the MO overlapping both for the parallel and linear molecular orientations. The "+" sign shows that the MO overlapping and the corresponding chemical reaction are permitted in terms of symmetry. The large

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* For the sake of simplicity we have mentioned only two extreme cases of the mutual orientation of molecules in the transition state.

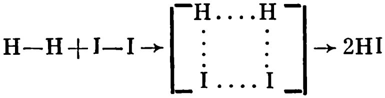
TABLE 11

MO	Parallel orientation				Linear orientation			
	σ_g	σ_u	π_u	π_g	σ_g	σ_u	π_u	π_g
σ_g	+	−	+	−	+	+	−	−
σ_u	−	+	−	+	+	+	−	−
π_u	+	−	+	−	−	−	+	+
π_g	−	+	−	+	−	−	+	+

"+" signs are used to draw the reader's attention to the absence of any forbiddenness (in terms of symmetry) whenever the MOs of the same symmetry are overlapped.

Now we shall illustrate these general considerations with concrete examples.

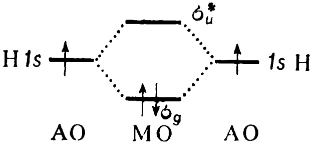
$H_2 + I_2 \rightarrow (?) \rightarrow 2HI$. For a long time the reaction between the I_2 and H_2 molecules was believed to proceed through the formation of the square activated complex:



$$H{-}H + I{-}I \rightarrow \left[\begin{matrix} H \cdots\cdots H \\ \vdots \qquad \vdots \\ I \cdots\cdots I \end{matrix}\right] \rightarrow 2HI$$

Is it really the case? In order to make out the mechanism of this reaction one has to identify first what molecule is a donor and what an acceptor. Since the electron affinity of an iodine molecule is greater than that of a hydrogen molecule ($A_{I_2} = 2.4$ eV; $A_{H_2} = -0.72$ eV), the electrons will pass from the hydrogen molecule to the iodine molecule during the reaction. Thus, the former molecule is the donor and the latter is the acceptor of electrons.

The HOMO of the H_2 molecule possesses the σ_g symmetry:



The LUMO of an iodine molecule, as of all halogen molecules, possesses the σ_u^* symmetry.

Let us have a look at Table 11 and see whether the overlapping of the σ_g and σ_u orbitals is possible. In case of a parallel arrangement of molecules (a square complex) the reaction turns out to be forbidden in terms of symmetry while in case of a linear arrangement (H—H . . . I—I) the reaction is feasible. This does not mean though that the reaction will necessarily proceed through the formation of such a transition state. The experimental studies have shown that the reaction involves either the H_2 molecule and the I atom (at elevated temperatures) or the H_2 molecule and the two I atoms (at room temperatures) with the formation of the linear activated complex H ... H ... I. For example, the flowsheet may look like this:

$$I_2 \rightarrow 2I$$

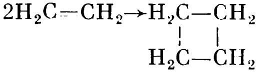
$$I + H_2 \rightarrow HI + H$$

$$H + I \rightarrow HI$$

As a detailed analysis shows the reaction $I + H_2 \rightarrow HI + H$ proves to be allowed in terms of symmetry.

Orbital Symmetry Conservation in Some Organic Reactions

The American chemists R. Woodward* and R. Hoffman** proposed in 1965 the symmetry rules which make it possible to analyse various reactions in more detail. The application of the Woodward-Hoffman rule will be illustrated by the analysis of the reaction which is familiar to everybody who studied organic chemistry:



$$2H_2C{=}CH_2 \rightarrow \begin{array}{c} H_2C{-}CH_2 \\ | \quad\;\; | \\ H_2C{-}CH_2 \end{array}$$

Ethylene molecular orbitals. The electronic structure of ethylene can be represented by four σ C—H bonds, one σ- and one π C—C bonds (Fig. 32).

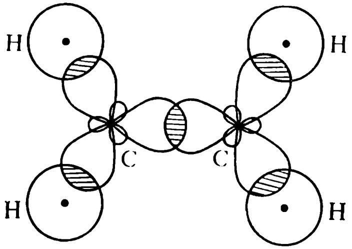


FIG. 32

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* Robert Burns Woodward, born 1917, outstanding American chemist, Nobel prize winner of 1965. For the first time synthesized a number of important compounds: quinine, chlorophyll, tetracyclin, etc. In Woodward's laboratory at Harvard University the structure of ferrocene, penicillin, strichnin, etc. was determined.

** Roald Hoffman, born 1937, American chemist, professor of Cornell University; worked in the field of quantum chemistry. Developed the method of calculation of electronic structure of molecules, named after him.

A peculiar feature of the σ-bonding is its cylindrical symmetry relative to the line which connects the nuclei. Each σ-bond has the corresponding energy levels σ and σ*, that is, one bonding and one antibonding MO of the σ-type. The electrons are located only at the bonding σ-MO. Inasmuch as each σ-bond involves two electrons, the total number of the electron pairs located at the σ-MOs is equal to 5. The π-bonding in the ethylene molecule is formed due to the overlapping of two $2p_z$ clouds (Fig. 33), i.e. the *p*-AOs combine and form the MOs of π-type.

The bonding π-MO differs from the antibonding one by the way in which electron clouds overlap. If the overlapping occurs "in phase", i.e. the overlapped segments of the "dumb-bells" have the same sign of the wave function (as in Fig. 33), the bonding π-MO is formed. If the clouds are overlapped "in antiphase" the antibonding π*-MO is formed. In the former case the electronic cloud density between the carbon atoms increases whereas in the latter case the electron waves as if cancel out each other so that a plane with the zero electron density in all its points (the nodal plane) can be drawn between the nuclei.

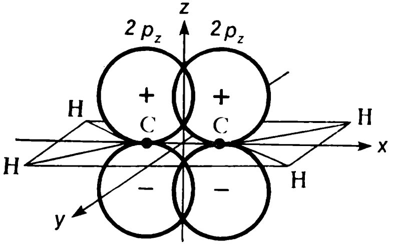

FIG. 33

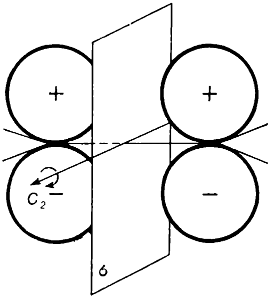

FIG. 34

The ethylene molecule possesses two symmetry elements of this type which help us to classify the orbitals: the symmetry plane σ and the C_2-axis (Fig. 34). It is easy to note that the π-MO is symmetric relative to the reflection in the symmetry plane σ (the *S* operation) and changes sign with the rotation about the C_2-axis or, as it is customary to say, it is antisymmetric relative to the rotation about the C_2-axis (the *A* operation). Since the overlapping of the two 2*p*-orbitals is substantially less than that associated with the σ-bond formation, the π-bond is weaker than the σ-bond. The energy levels corresponding to the π- and π^*-MO are located between the levels of the σ- and σ^*-MOs.

TABLE 12

MO type	Symmetry relative to operations	
	σ	C_2
π^*	*A*	*S*
π	*S*	*A*

Table 12 shows the symmetry classification of π and π^* orbitals in ethylene.

Cycle formation. Let us consider now the cycle addition reaction:

$$H_2C{=}CH_2 + H_2C{=}CH_2 \rightarrow \begin{array}{c} H_2C{-}CH_2 \\ |\quad\;\; | \\ H_2C{-}CH_2 \end{array}$$

cyclobutane

During this reaction the π-orbitals of ethylene (there are four of them, two from each molecule) are transformed into the σ-orbitals of cyclobutane. We do not examine σ-bonds of ethylene since their symmetry does not change in this reaction. As to the σ-MOs of

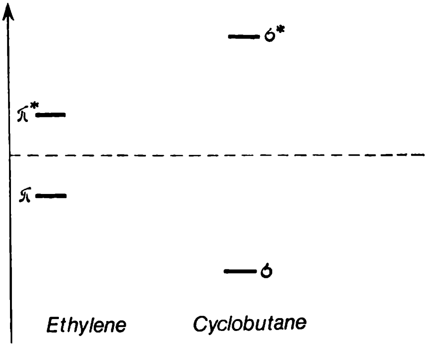

FIG. 35

cyclobutane, they are separated by the greater distances (in terms of energy) compared to the π-MOs of ethylene (Fig. 35).

Considering the reaction of cyclobutane formation we assume that the ethylene molecules are getting arranged in parallel as they draw together. The convergence of molecules may be accomplished by several methods.

Suppose that the ethylene molecules draw together in the way it is shown in Fig. 36*a*. Such a combination of π-orbitals is symmetric relative to the reflection both in the S_1 and S_2 planes. This is denoted by the *SS* symbol.

The case illustrated in Fig. 36*b* is opposite to the previous one. It should be denoted, as one can easily guess, as *SA* (the symmetry relative to the reflection in the S_1 plane and the antisymmetry relative to the reflection in the S_2 plane).

When the distance between the ethylene molecules is great the *SS* and *SA* cases are not distinguished in terms of energy, but as the molecules draw together the more symmetric overlapping (*SS*) becomes slightly more profitable, i.e. the *SS* symmetry MO lies below that of the *SA* symmetry on the energy scale*.

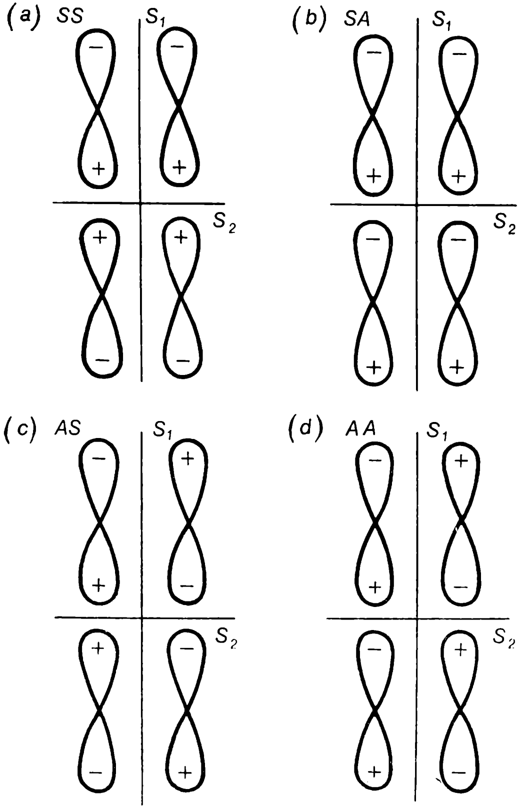

FIG. 36

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* Note that in this case we classify the MO not according to the molecular symmetry group IR. Here the orbital classification criterion is the behaviour in case of the reflection in certain symmetry planes of a molecule or a transition state.

The cases discussed above pertain to the overlapping of the bonding π-MOs of two molecules $H_2C{=}CH_2$. In much the same way one can examine various possibilities emerging as a result of the overlapping of antibonding orbitals. They are illustrated in Fig. 36*c* and *d* and apparently do not require any special explanation.

Now let us direct our attention back to the cyclobutane molecule. The bonding between the carbon atoms is brought about by the overlapping of the hybrid

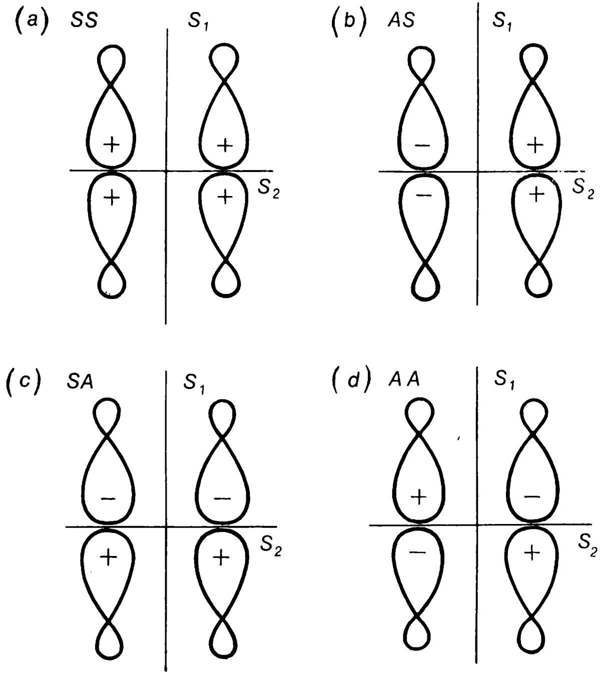


FIG. 37

orbitals. These orbitals have the shape of the asymmetric figure "eight" with the opposite signs of the wave function (indicated in the loops). The overlapping of these clouds can be accomplished through the overlapping of either the bonding orbitals (Fig. 37*a* and *b*) or the antibonding orbitals (Fig. 37*c* and *d*).

Let us compare now the energies of all MOs. The *SS* level corresponding to the system of two ethylene molecules located at a close range is the lowest compared to the *SA*, *AS* and *AA* levels (see the right part of Fig. 38). In the cyclobutane molecule the lowest level is also the one corresponding to the *SS* symmetry (the left part of Fig. 38).

It is also seen from Fig. 38 that as the ethylene molecules draw closer together, the *SA* level rises higher and higher up the energy scale transforming gradually into the antibonding level whereas the *AS* level on the contrary falls down and turns into the bonding level.

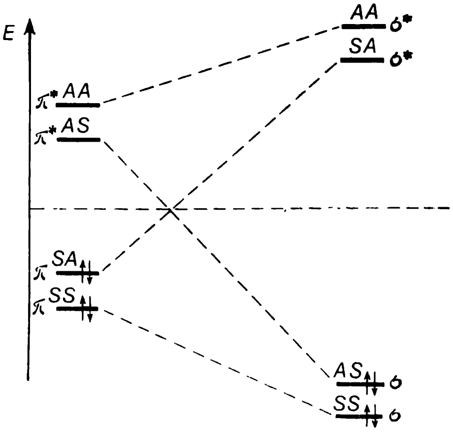
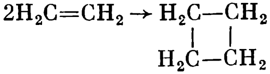


FIG. 38

Fig. 38 depicts the so-called *correlation* chart. The method proposed by Woodward and Hoffman is based on the correlation charts of energy levels for reaction products and original reagents and their analysis in terms of symmetry. If the highest occupied orbitals of reaction products in the ground state possess the symmetry correlating with that of original compounds in the ground state too, such a reaction is thermally permitted, i.e. it can proceed in the conventional conditions (a thermal reaction). If the ground state of reaction products correlates with the excited state of original compounds, the reaction is thermally forbidden, but can be accomplished photochemically, i.e. when reagents are irradiated by light.

Now we come back to our example. The correlation chart depicted in Fig. 38 shows that the highest occupied orbital of the cyclobutane molecule possessing the AS symmetry correlates with the antibonding π^*AS-orbital of the system ethylene + ethylene. To keep the orbital symmetry constant the π^*AS-orbital ought to be populated with electrons. This can be done by exciting the ethylene molecules activating the electronic transition $\pi SA + 483\ \text{kJ/mol} \rightarrow \pi^*AS$. During this reaction electrons will pass between the orbitals of the same symmetry (AS).

Thus, we come to the following conclusion: according to the orbital symmetry conservation law the reaction



$$2H_2C{=}CH_2 \rightarrow \begin{array}{c} H_2C{-}CH_2 \\ |\quad\ \ | \\ H_2C{-}CH_2 \end{array}$$

can be realized only as a photochemical one.

The general rule can be formulated as follows:

(a) a reaction is thermally permitted if $m + n = 4q + 2$, where m and n are the numbers of π-electrons in reagents, $q = 1, 2, \ldots$;

(b) a reaction is thermally forbidden if $m + n = 4q$;

(c) a reaction is photochemically permitted if $m + n = 4q$;

(d) a reaction is photochemically forbidden if $m + n = 4q + 2$.

In the example that we studied above $m = n = 2$, $m + n = 4$, so that according to the items (b) and (c) the reaction is forbidden thermally and permitted photochemically.

Catalysis comes to assistance. Many reactions which are forbidden in terms of symmetry are easily realized in the presence of catalyzers, for example complex compounds of transition metals. What is their action based upon? Recently a proposal has been made that the catalyzer changes the HOMO symmetry of reacting molecules.

We shall illustrate this with the example of the formation of a cyclobutane molecule from two ethylene molecules. To make the reaction thermally permitted in terms of symmetry it is necessary to populate somehow the antibonding π^*AS-orbital of the ethylene system with electrons. We have already mentioned one method—the irradiation of reagents by light. But there is another way to populate the π^*AS-orbitals which is associated with the application of transition metal complexes as catalyzers. The function of the metal consists in the removal of

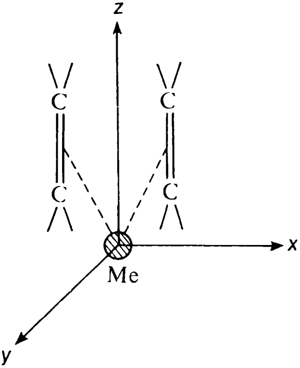


FIG. 39

electrons from the πSA-orbital in order to populate the $\pi^* AS$-orbital. In this case, during the reaction process, the transition complex “metal-two ethylene molecules” is formed in which the electron pair can pass from the HOMO of ethylene, that is from the πSA-orbital, to the d-AO of the metal of the corresponding symmetry. In the coordinate system chosen (Fig. 39) there is the following symmetry correspondence between the orbitals:

Symmetry of MO of two ethylene molecules	Symmetry of d-AO of metal
SS	d_{z^2}, $d_{x^2-y^2}$
SA	d_{xy}
AS	d_{yz}
AA	d_{xz}

Hence, the electrons from the πSA-orbital will pass to the d_{xy}-AO of the metal.

Moreover, besides the unoccupied d_{xy}-AO the metal must also have the occupied d_{yz}-AO. Then due to the

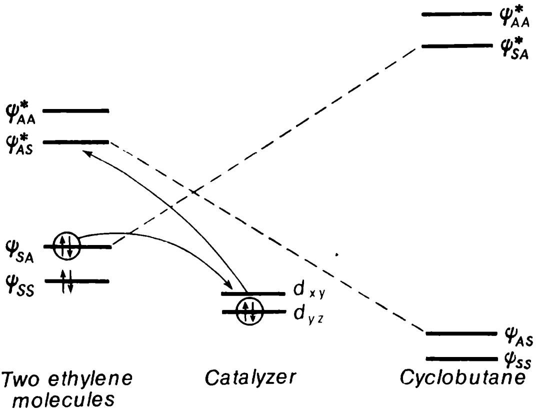


FIG. 40

interaction of the π^*AS and d_{yz} orbitals, the electrons of the metal (from its d_{yz}-AO) will get "pumped over" to the π^*AS-MO of the ethylene system (Fig. 40).

Needless to say that the examples discussed above do not exhaust all multiform applications of the symmetry theory in chemical kinetics. The controversy over the Woodward-Hoffman rules has not come to an end yet. The employment of the symmetry theory in chemical kinetics makes it possible to obtain new information about the chemical reaction mechanisms and also permits of looking at the well-known phenomena and processes from the more fundamental viewpoint.

Chapter Five

FORWARD INTO HISTORY!

Symmetry, as wide or as narrow as you may define its meaning, is one idea by which man through the ages has tried to comprehend and create order, beauty and perfection.

H. Weyl

Σιμμετρια— Apocryphal Times

The famous Soviet scientist Academician V.I. Vernadsky wrote that the concept of symmetry arose from the studies of living organisms and living matter. Long time ago the great Greek sculptors and architects were associating the very term "symmetry" with the idea of beauty and harmony. One can find numerous examples and references to symmetry in antique art, philosophy and science. By the time of Pythagoras (born about 530 B.C.) this concept had become habitual. The Greeks recognized symmetry not only as a geometric property but also as something proportional, commensurate and harmonic in an object, as a method of coordination of components and a law of their integration into a single whole. For example, the Pythagoreans distinguished ten pairs of counterparts: even-odd, straight-curved, true-false, etc. Among them there were distinctions between "right" and "left", between an object and its mirror image. The investigation of the latter distinction repeatedly attracted the attention of scientists. Even now this is one of the central problems in modern physics of elementary particles.

Another philosopher of the ancient Greece, Plato (born about 430 B.C.), believed that the surrounding world consists of four elements: the earth, the water, the fire and the air. These elements, having combined in definite proportions, form the whole surrounding world. Plato assumed each of the four initial elements to possess a definite geometric shape: the earth is a cube, the fire, a tetrahedron, the water, an icosahedron and the air, an octahedron. The expression "Plato's bodies" originated owing to this assumption.

The atomists of the ancient Greece Leucippos (5th century B.C.) and Democritus (born about 470 B.C.) attributed to atoms not only size, weight and other properties, but also a geometric form. But in contrast to Plato, they believed that their "bricks of the universe" possess the innumerable shapes of various symmetries—spherical, pyramidal, etc.—or may have an irregular shape.

The ancient mathematicians (especially those from Greece) were successful in studies of various polygons and polyhedrons and, in particular, five regular Plato's bodies.

Thus since the ancient times the teaching of symmetry was developing in three areas of knowledge: philosophy, natural science and mathematics. We shall discuss only two latter areas.

Testament of Evariste Galois

The chosen one. For over 100 years the idea of a group was forcing its way in the mathematical communications, from J.L. Lagrange who used it spontaneously to solve algebraic equations (1771), through the works of P. Ruffini (1799) and N.H. Abel (1824), to the investigations of the great French mathematician Evariste Galois (1830) who used the idea of a group deliberately enough and was the first to introduce the term in practice.

Full of hardships and deprivations the life of Evariste Galois (1811-1832) came tragically to an end in a duel when he was only 21 years old. On the eve of the duel Galois wrote about his discoveries to one of his friends. The final words of the letter were: "You should publicly ask Jacobi or Gauss to draw the inference not about the validity but about the significance of these theorems. Afterwards, I hope, some people would regard it necessary to decipher all this rigmarole."

That "rigmarole" contained the groundwork of modern algebra. But Galois' letter had apparently reached neither Gauss nor Jacobi. Many years later the French mathematician C. Jordan identified Galois' letter while sorting out the archives of another outstanding mathematician of the last century O. Cauchy. Jordan at once recognized the significance of the document which he had found.

Another contribution to the group theory was made by Arthur Cayley (1821-1895) who defined the general abstract group (1854) as we now know it and who at the same time developed the matrix theory. The theory of representations, which from the viewpoint of chemists is the most important domain of the group theory, was developed almost single-handedly at the turn of the century by the German algebraist G.F. Frobenius (1849-1917).

Erlangen programme. A few words are due here about the state of mathematics in the seventies of the last century. Although by 1870 mathematics had grown into a huge edifice, its various parts were still isolated, they were not linked up by any common ideas, so that only few mathematicians could work simultaneously in several areas of their science. As you see the problem of a narrow specialization is not only the 20th century phenomenon. But any science, especially a theoretical one, cannot be in such a "disintegrated" state for a long time. The separateness breeds the tendency to find certain principles and theories capable of combining various scientific divisions into a single whole. The group theory proved to be one of such "uniting" theories. Its development during the last three decades of the 19th century was primarily due to the efforts of the prominent German mathematician F. Klein and the Norwegian mathematician M.S. Lie. In 1870 they both met Jordan who called their attention to the Galois research. Since that time the group theory had become the main subject of their work: Klein concentrated his efforts on discrete groups while Lie on continuous ones.

In 1872 Klein became university professor in the small German town Erlangen. In his introductory lecture he explained why the concept of a group is so important for mathematics and, in particular, geometry.

Usually the symmetry group of a geometric figure was interpreted as the set of all its self-matchings. Klein used the symmetry considerations not for the sorting of geometric objects but as the criterion for classification of "geometries" themselves which in the last century came to replace the single (and, it seemed, unique) antique Euclidean geometry. That lecture delivered by Klein and known in the history of science as the "Erlangen programme" influenced to a very high degree the development of both mathematics and theoretical physics for the decades to come.

Here we shall break the chronological order of our narration in order to come back to problems which are somewhat closer to chemistry.

Non-Euclidean Geometries and Chemistry

Extraordinary symmetry of hydrogen atom. The outstanding Soviet physicist Academician A.A. Migdal once expressed the remarkable thought that "the beauty of science consists not only, and not so much, in the logical harmony but also in the wealth of relationships". The symmetry theory is the spectacular confirmation of this statement. At first glance such different things as non-Euclidean geometry and chemistry have nothing in common. However, on more careful scrutiny the section heading does not seem surprising.

In this booklet (as in the overwhelming majority of comprehensive monographs dealing with the group theory application in quantum chemistry) a symmetry transformation is considered as one of the specific cases of geometric transformations in the ordinary three-dimensional space. However, there are such systems whose properties cannot be explained only in terms of geometric transformations (rotations, reflections, etc.). A hydrogen atom may serve as an example. It is well known that the state of an electron in the hydrogen atom is defined by four quantum numbers: the principal one n, the orbital l, the magnetic m and the spin number m_s. But the energy of an electron depends only on one of those, on n:

$$E_n = -13 \cdot 6/n^2 \text{ eV}$$

Hence we have the degeneracy with respect to the rest of quantum numbers. What is it associated with? We mentioned in Chapter 2 that the degeneracy multiplicity of energy levels depends on the symmetry of a system. The hydrogen atom belongs to the continuous symmetry group $O(3)$, i.e. the Schrödinger equation and the structure of energy levels defined by it remain invariable—or, as we sometimes say, invariant—relative to any rotations in the ordinary three-dimensional space. In other words, the symmetry group of the hydrogen atom coincides with that of a sphere—whatever its orientation the sphere is always matched with itself. It is just due to this sphericity of the hydrogen atom that the energy does not depend on the magnetic quantum number m. This fact was established soon after the inception of quantum mechanics (1925-26).

The fact that energy is independent of l remained inexplicable till 1935 nevertheless. From the general symmetry considerations one could assume that the electron energy does not depend on l due to the presence of a certain symmetry transformation group. But what group in particular? That was the question. The answer was found by the Soviet Academician V.A. Fok who showed that the complete symmetry group of the hydrogen atom which describes all of its properties, including the l-degeneracy, coincides with the rotation group for the four-dimensional sphere, i.e. together with ordinary geometric transformations it contains the symmetry transformations of the more general and more abstract (and consequently less obvious) type. The symmetry group for the four-dimensional sphere is customarily denoted by the symbol $O(4)$.

Fok space. In order to link the hydrogen atom theory with the symmetry of the four-dimensional sphere Fok wrote down the Schrödinger equation not in the routine space coordinates x, y, z, but in the special coordinates depending on the electron momentum components p_x, p_y and p_z. Fok entitled his paper "The Hydrogen Atom and the Non-Euclidean Geometry". When the electron is bound to the nucleus and its energy may assume only discrete values, i.e. is quantized, the abstract "momentum space" proposed by Fok turns out to obey the Riemann geometry, whereas when the electron is detached from the nucleus so that its energy may assume any value, the momentum space obeys the laws of the Lobachevsky geometry. Both geometries differ from the common Euclidean one.

Symmetry of the periodic system. It is clear from what was said above that the hydrogen atom possesses the "hidden" symmetry of the four-dimensional sphere. Consequently, the wave functions describing the state of an electron in the hydrogen atom have to be transformed according to the irreducible representations of the $O(4)$ group.

In recent years the group theory methods have been used by some scientists, including the Soviet ones, for the study of the Mendeleev periodic table of elements.

The groups which help to reveal the "hidden" symmetry of the system have a very complicated mathematical character. The elements of such groups are not the conventional symmetry operations described in Chapters 1 and 2, but the linear transformations ("rotations") in the abstract n-dimensional space. We shall not go into mathematical details but shall only mention a few results.

The atoms of chemical elements can be considered as different "states" of a certain imaginary atomic system just as statistics considers not an individual man but "a head of the population", "a man in general".

The group theory admits of combining chemical elements in definite sets (multiplets). The elements which have got into one and the same multiplet possess some similar properties. Each multiplet corresponds to a definite IR. This resembles the familiar classification of energy levels in accordance with the IR of the molecular symmetry point group: the set of elements with similar fs is analogous to the f-fold degenerate energy level. Here the elements can be subdivided into the customary "Mendeleev" groups and periods. On the other hand, the elements can be divided into those having the even sum $(n + l)$ and those for which this sum is odd (n and l are the principal and the orbital quantum numbers of valence electrons).

It is interesting to note that the continuous groups which M.S. Lie studied in his time are widely used in modern physics and in particular for the classification of elementary particles. The elementary particle taxonomy is one of the most complicated problems, and the success achieved in this area is associated primarily with the employment of the continuous Lie groups. According to the present-day consensus both the classification of elementary particles and the periodic system of elements rest on one and the same mathematical basis. In fact, any scientific classification is based eventually on the establishment of symmetry properties of the objects classified. Even when a researcher does not use (as, for example, Mendeleev did not) conscientiously and explicitly the group theory methods, the group basis of a classification will be eventually revealed because a classification assumes the grouping of objects according to the generality of their properties and structure, as well as the invariance of this generality during various changes—either geometric transformations or transitions from one chemical element to another, for example, from Li to Na and then to K, Rb, Cs and Fr.

Look into the future. To conclude our discussion of "hidden" symmetries and their detection we have to note that in 1966 the Soviet physicists S.P. Alliluev and A.V. Matveenko demonstrated that the molecular hydrogen ion H_2^+ also possesses the higher symmetry than the geometric $D_{\infty h}$.

We have seen that the molecular structure theory was the area in which the group theory methods were extensively used (energy level classification and splitting, selection rules, etc.). However, in most cases only comparatively simple point groups were employed forasmuch as they were determined by the shape of a nuclear polyhedron. Who knows, maybe in the near future the employment of higher symmetries will yield new information about the structure and properties of molecules.

Symmetry Concept in Natural Sciences

Apparently the first symmetric objects of nature which attracted the attention of researchers were crystals which, as the great Russian crystallographer E.S. Fyodorov said, "glitter with their symmetry". It was the investigation of crystals that evolved the concepts of symmetry axes and planes and led to the understanding of what symmetries are at all possible in the surrounding inorganic nature. Although the description of crystal bodies lies outside the scope of this booklet, we shall comment—very briefly—on the main events and dates in the history of crystallography.

Christmas gift from Johann Kepler. In 1611 in Germany the famous German astronomer Johann Kepler published a book entitled *The Christmas Gift, or on the Hexagonal Snow*. That was perhaps the first treatise on crystallography. Written in a peculiar semi-jocular style (Kepler tells about his meditations on the way to a king's counselor whom he was about to present with a Christmas gift), the book contains a lot of brilliant conjectures on the structure of crystals. First of all Kepler wanted to know why pentagonal and heptagonal snow flakes would never fall out and only hexagonal ones would. Translated into the modern scientific language, Kepler's question sounds as follows: why are there no five-fold or seven-fold symmetry axes in inorganic nature? The problem was solved in a general form only over 200 years later by the outstanding French crystallographer A. Bravais.

Furthermore, in a short treatise Kepler expressed his ideas about various modes of the dense packing of particles constituting a crystal. The scientist also noted the constancy of the angle of 60° between the adjacent rays of snowflakes.

Crystallography becomes science. Later in 1669 the Danish scientist N. Steensen (he is often called in the Latin manner Steno or Stenon) established the law of constancy of facet angles in crystals. True, the validity of his discovery Steensen demonstrated by the only example of a rock crystal. Besides, the law was formulated not in the main text of the paper but in the form of the figure captions included in the appendix. Because of that the contemporaries did not pay due attention to the Steensen law and other researchers discovered it later over and over again. The final precise and clear statement of the law of the facet angle constancy was given in 1783 by the French crystallographer Jean Baptiste Rome Delisle (1736-1790).

The next remarkable regularity is associated with another French scientist, R.J. Haüy (1743-1822) who discovered the law of whole numbers. According to this law the spatial position of any crystal facet can be expressed by means of three whole numbers.

Obviously the discovery of that law greatly influenced the work of the famous British scientist, the founder of atomic theory John Dalton (1788-1844) who discovered in 1802-08 the law of multiple proportions in chemistry. Dalton had been to Paris and attended Haüy's lectures.

Dalton believed that atoms in a chemical compound had to be arranged in a symmetric pattern. It should be pointed out that as the atomistic concepts penetrated chemistry many scientists felt that identical (in their properties) parts of chemical molecules had the identical symmetric arrangement. That idea was later reflected even in the notation of chemical compounds, organic ones in particular. For instance, in the formula of acetic acid CH_3COOH the difference between the two carbon atoms is emphasized by the symbol C written twice. The same may be said about the oxygen atom. As to the four hydrogen atoms, they are sorted out otherwise: the three atoms which are similar in their functions are shown by one symbol while the hydrogen atom responsible for the acidic properties of a molecule is written separately.

For a long time there was an opinion, or at least an intuitive hypothesis, among chemists, and not only chemists, that a law of maximum symmetry existed in nature. Frequently that claim led to the correct guess about the geometric shape of molecules although there is no such law in nature.

The beauty and power of the symmetry theory is not in the existence of a certain law of maximum symmetry but in the fact that there are laws relating the symmetry of a compound with its electronic structure and properties, as well as in the fact that the characterization of each phenomenon involves symmetry elements. But of course, at the beginning of the last century this could not be understood yet. Even the conventional geometric symmetry was associated only with symmetry planes. Symmetry axes were suggested in 1809 by the German scientist H.S. Weiss (1780-1856).

Weiss appreciated from the very beginning of his scientific activity the advantage of the precise mathematical approach to crystallography proposed by Haüy over the verbal description of crystals practised by other researchers. The cornerstone of Weiss' theory was the concept of a symmetry axis. However, speaking strictly, the axes about which Weiss wrote were not the symmetry axes in the modern sense and even the idea of different symmetry classes was only originating at the time.

In 1815 Weiss introduced the concept of crystal syngonies. That was the first step on the way to the classification of crystal bodies in terms of symmetry.

Magic number of crystallography. In 1820 a German *Physical Handbook* published an article by Hessel (1796-1872) under the brief (suitable for a handbook) title *Crystal*. That was a remarkably profound study in which for the first time the classification of geometric figures was made in accordance with their affiliation with one or another symmetry point group. Hessel classified not only crystals, he was interested in polyhedrons in general, so that his work is also important for general geometry. He showed that 32 symmetry classes are possible for crystalline polyhedrons, that is all the wealth of the kingdom of crystals can be distributed over 32 symmetry point groups. Unfortunately Hessel was unlucky: his work was not recognized and appreciated by his contemporaries. He was recalled only many years after his death.

In 1869 the 32 symmetry classes were established anew by the Russian scientist A.V. Gadolin who was honoured for this achievement with the Lomonosov prize of the Academy of Sciences.

The genuine triumph of geometric crystallography was the discovery in 1890-91 of 230 spatial symmetry groups. This was done almost simultaneously and independently by the Russian crystallographer E.S. Fyodorov (by geometric approach) and the German mathematician A. Schönfliess (by group theory methods).

Thus, the teaching of symmetry was firmly incorporated in the science of crystals in the second half of the last century. As Academician V.I. Vernadsky noted, the last century witnessed the development of "only those symmetry phenomena that pertained to crystallography and that later spread over to stereochemistry". In other words, having covered the world of crystals the symmetry theory started infiltrating into the world of molecules. The first to become aware of the need of using symmetry to explain molecular properties was the great French scientist Louis Pasteur (1822-1895).

Cream of tartar puzzle. The first paper by Pasteur dedicated to optical properties of organic substances appeared in 1848. The optical activity phenomenon was discovered much earlier, in 1815-17, by the French scientist Biot. The essence of the discovered phenomenon consisted in the fact that light passing through some substances may, speaking in modern language, change the polarization direction, i.e. the direction of the electric field vector in the light wave. For example, according to the data of the German chemist E. Mitscherlich, sodium-ammonium bitartrates rotate the polarization plane of light wave clockwise whereas the analogous salts of racemic acid do not. Checking Mitscherlich's results Pasteur discovered that racemate crystals exist in two mirror configurations. The solution of one salt rotates the polarization plane clockwise (like a tartaric acid) while that of another salt counterclockwise. Mitscherlich dealt with the mixture of clockwise and counterclockwise configurations and therefore regarded racemates optically inactive.

Like any other scientific discovery Pasteur's work raised more questions than furnished answers. The principal question was: why are some molecules optically active while others are not?

Asymmetry produces a phenomenon. Pasteur spent about 10 years to find an answer. He came to the conclusion that the optical activity of a substance is associated with the asymmetrical molecular structure: a molecule is optically active only when its structure cannot be matched with its mirror image. The asymmetry can arise either when a molecule has a spiral structure (according to Pasteur atoms can be grouped "following the turns of the right ear concha") or when atoms are positioned in the apices of an irregular tetrahedron.

This Pasteur alternative gave rise to two trends in the theory of optical activity. The former possibility formed the basis of the physical theory developed by the German physicist P. Drude. The latter one promoted the creation of stereochemistry which originated owing to the investigations of the French chemist J.A. Le Bel and the Dutch scientist J.H. Van't Hoff. Pasteur wrote the following: "The Universe is an asymmetric ensemble. I believe that life in the form that is known to us has to be the function of the world's asymmetry or of its consequencies".

Asymmetric atoms. The principal aspects of the stereochemical theory of Van't Hoff and Le Bel are as follows:

(1) the carbon atom is tetravalent and its four valencies are directed toward the apices of the tetrahedron containing the carbon atom in its centre;

(2) when all four valencies of the carbon atom are saturated by four different univalent groups ($CR_1R_2R_3R_4$), one can obtain either of two different tetrahedrons which are the mirror images of each other and cannot be matched;

(3) any organic compound whose solution deflects the polarization plane, possesses the asymmetric carbon atom*;

(4) the derivatives of optically active compounds lose their rotative power as soon as the asymmetry of all carbon atoms disappears.

It is evident that Van't Hoff and Le Bel related all assumptions of the stereochemical theory only to carbon compounds. But already in 1875, i.e. one year after the origination of stereochemistry, one of the physics professors of the Uhtrecht University addressed Van't Hoff with the "Open letter" in which he suggested that the theory should necessarily be extended to the compounds of other elements and primarily to the nitrogen compounds. Similar ideas were also expressed by other scientists.

The first stereochemical models of nitrogen compounds, in particular NH_4Cl, were proposed by Van't Hoff himself. Nevertheless they did not pay for themselves in the future.

In 1890 A.R.Hantzsch** and A. Werner*** published the results of the investigation of the spatial arrangement of atoms in nitrogen-containing molecules. According to the principal assumption of their investigation three valencies of the nitrogen atom are directed in some compounds toward the corners of the tetrahedron (in the general case, an irregular one), the fourth corner being occupied by the nitrogen atom itself.

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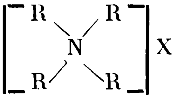
* Van't Hoff called the carbon atom "asymmetric" if it was bonded to four different substituents.

** Arthur Rudolf Hantzsch (1857-1935), German chemist known for his studies in chemistry of nitrogen-containing compounds.

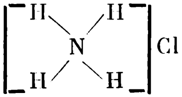
*** Alfred Werner (1866-1919), prominent Swiss chemist, founder of coordination theory and stereochemistry of nitrogen compounds. Nobel prize winner in chemistry of 1913.

As to the optical activity, the conclusion about its presence is not difficult to draw now: the $NR_1R_2R_3$ compounds, that is the compounds with the asymmetric nitrogen atom, have to be optically active.

According to Werner, ammonium salts have the following structure:



This signifies that the NH_4Cl molecule can be depicted as follows:



It is implied that the radical also has a tetrahedral configuration.

Stereochemistry, together with the theory of optical activity, was applied in studies of sulphur, selenium, tin, silicon and phosphorus compounds already at the end of the last century and the beginning of the present century. Werner wrote in 1893: "Now stereochemistry of cobalt and platinum compounds goes next to stereochemistry of carbon and nitrogen compounds." That was the origination of the coordination theory and A. Werner was its founder. He applied the stereochemical concepts to explain the properties of complex compounds. In the process the number of symmetry types to be studied was increased to include the octahedral, for example $[Co(NH_3)_6]Cl_3$, and the square, Pt(II), complexes. The most important result of the Werner theory was the correct forecast of the optical isomerism of complex compounds.

Refinements of Woldemar Voigt. In 1905 the German physicist Woldemar Voigt substantially extended and refined the theory of optical activity. He formulated three conditions for the optical activity: a molecule should not possess (a) a symmetry centre, (b) a symmetry plane, and (c) a rotation-reflection axis.

In Chapter 1 we mentioned that the presence of the two-fold rotation-reflection axis in a molecule is equivalent to the presence of the inversion centre:

$$i \equiv S_2$$

It may be added that S_1 is equivalent to the presence of a symmetry plane, i.e. $S_1 = \sigma$.

Indeed, $S_n = C_n\sigma_h$. i.e. if $n = 1$, $S_1 = C_1\sigma_h$. But $C_1 = E$, so that $S_1 = E\sigma_h = \sigma_h$.

That is why all the three conditions cited above can be replaced, from the mathematical viewpoint, by only one condition, the third one.

Sometimes chemists, especially those majoring in organic chemistry, use the simpler Van't Hoff criterion: if a molecule has an asymmetric atom it can exist in the form of mirror or, as it is more often said, optical isomers. But speaking strictly this condition is neither necessary nor sufficient. For example, it is possible to obtain seven different spatial models of hexachloran ($C_6H_6Cl_6$) among which there will be some optical isomers, despite the fact that the molecule has no asymmetric carbon atoms.

Nature takes its choice. Nature is abundant in optical isomers. Some of them exist as "left" forms while others as "right" ones. For instance, two forms of asparagine are known: the levorotatory form (it is tasteless) and the dextrorotatory one (sweet taste); there are two nicotines (one of them is more poisonous), two adrenalines (differing in the intensity of their influence on the nervous system), etc. Everybody knows very well of the colossal biochemical role of amino acids serving as the structural material in the protein synthesis. The majority of natural amino acids turn out to be "levorotatory".

The reasons of such a "one-sided" choice of nature are not yet known. The mirror asymmetry in organic nature is assumed to be caused by historic reasons (for example, due to the Earth's rotation or to the accidental accumulation of the "left structural material" in the part of the planet where life initially originated, etc.), but the detailed and well-founded answer is yet to be given.

Group Theory in Quantum Chemistry

"Group plague". The group theory began to be employed actively in quantum mechanics (and later on in quantum chemistry) in the late twenties. Among the first who started working in this area were such prominent scientists as the physicist E. Wigner, the mathematicians H. Weyl* and B.L. Van der Waerden**. Wigner, who was awarded in 1963 the Nobel prize for the studies of the group theory application in

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* Hermann Weyl (1885-1955), most distinguished mathematician of our century; his research is dedicated to theory of numbers, algebra, geometry, foundations of mathematics. His scientific activity is distinctive with profound interest in problems of theoretical physics and chemistry. Some of his publications are devoted to development of chemical bond theory in terms of group theory.

** Bartel Leendert Van der Waerden, born 1903, Dutch mathematician and historian of science; worked at the universities of Leipzig, Amsterdam and Zürich; principal research in algebra, algebraic geometry and group theory. His investigations accomplished the development stage of modern algebra.

quantum mechanics, developed back in 1927-30 certain classification rules for atomic energy levels. However, initially Wigner did not take into account the electron spin. A few years later together with the outstanding mathematician von Neuman* he managed to work out the complete classification of the whole system of atomic terms (with the spin taken into account).

The group theory was also used by many scientists for the development of the two fundamental methods of quantum chemistry, e.g. the valence bond method and the molecular orbital method. The employment of symmetry concepts in theoretical chemistry is due to the German physicists H.Bethe, F.Hund, W.Heitler**, the Soviet physicist Yu.B. Rumer and the American scientists P. Mulliken and J. Van Vleck. However, the need to study the group theory did not particularly appeal to many researchers. The scientific literature of the thirties even coined the term "group plague". It should be noted that the negative attitude to the group theory is associated with the fact that many results could be obtained by conventional computing methods.

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* John von Neuman (1903-1957), distinguished mathematician, was born and studied in Hungary, lectured in Berlin, since 1930 worked in the USA. One of the creators of function analysis and some branches of modern mathematics (computer theory, game theory and theory of automats), participated in creation of first computers, contributed to mathematical foundations of quantum mechanics.

** Walter Heitler, born in 1904, German physicist, one of the founders of modern chemical bond theory. Was among the first to apply group theory in quantum chemistry; formulated basic principles of theory of electronic structure of molecules. Some publications are dedicated to quantum theory of radiation and cosmic rays. Worked in universities of Germany and Great Britain.

Left in shadow. Possibly due to this prejudiced attitude to the group theory most scientists did not pay attention to the paper of the German theorist H. Bethe (1929) in which the theory of crystalline field (TCF) was developed.

The general idea of TCF according to which the metal ion in a complex is subjected to the ligand electric field and as a result has its energy levels split, belongs to the French chemist and spectroscopist Jean Becquerel, the son of the discoverer of radioactivity H. Becquerel. However, J. Becquerel only voiced the idea whereas Bethe developed the rigid theory based on the mathematical group theory. And here is what one of the founders of modern quantum chemistry John Van Vleck recollects: "I remember especially my stroll with H. Cramers* along sand-dunes in Holland. He told me about the remarkable group theory paper by Bethe.... I felt that I had learned more during the single stroll than during the rest of my staying in Europe."

Using TCF Van Vleck elucidated most of the magnetic properties of complex compounds in 1932. In the same year the American physicist C. Horter discovered that the electrostatic field generated by the ligands which are arranged tetrahedrally around the central ion, gives rise to the same energy levels as the octahedral symmetry field does, but with the inverse order of levels.

In the works of Van Vleck and Mulliken the LCAO MO method was used for the first time for the investigation of transition metal complexes and other compounds. The symmetry theory was employed there for the classification of molecular orbitals.

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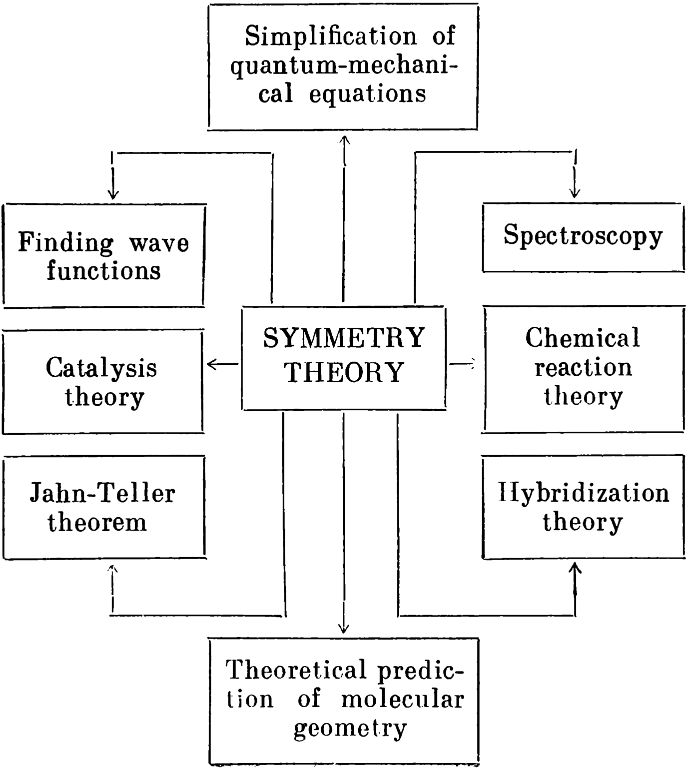
* Hendrick Cramers (1894-1952), Dutch physicist, known for his works in the field of quantum mechanics and theory of atomic spectra.

In modern quantum chemistry the symmetry theory provides a reliable basis for the description, classification and interpretation of the large amount of experimental data. The language and methods of the symmetry theory gain still more and more recognition among the contemporary chemists.

Conclusion

And now our story has come to an end. We have seen that the study of the molecular electronic structure is based to a considerable degree on the investigation of symmetry properties of molecules. On p. 146 we present a diagram showing (incompletely, of course) the major divisions of theoretical chemistry in which the symmetry theory is used, and which in some measure sums up our brief trip into the world of molecules.


Simplification of quantum-mechanical equations
Finding wave functions
Spectroscopy
SYMMETRY THEORY
Catalysis theory
Chemical reaction theory
Jahn-Teller theorem
Hybridization theory
Theoretical prediction of molecular geometry

INDEX
VOCABULARY

A **group** is a set of elements which satisfy the following conditions: (1) every ordered pair of elements *a* and *b* of this set is associated with a certain element *c* from the same set (group multiplication rule), (2) the group multiplication is associative, (3) there is an identity element, and (4) every element of the group has the corresponding reciprocal element (p. 15).

Group orbitals are such orbitals that are transformed according to one of the irreducible representations of the symmetry group (p. 83).

A **matrix** is the collection of numbers (real or complex) written down in the form of a table (p. 32).

An **irreducible representation** is such a representation of a group for which there is no algebraic transformation capable of converting it into a new group representation with matrices of smaller dimensions (p. 40).

A **symmetry operation** is an operation which, when applied to an object, carries it into a new spatial orientation indistinguishable from the initial one and coinciding with it (pp. 10-11).

A **representation of a group** is any collection of square matrices brought into correspondence with group elements and obeying the group multiplication table (p. 38).

A reducible representation is such a representation of a group from which new representations with matrices of smaller dimensions can be obtained as a result of an algebraic transformation (p. 41).

A symmetry point group is a set of all symmetry operations carrying a figure into a new position indistinguishable from the initial one, with at least one point of the figure remaining stationary in space (p. 19).

TO THE READER

Mir Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make.

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OTHER MIR TITLES

Golovin, I.

ACADEMICIAN IGOR KURCHATOV

This is a short biography and survey of the scientific work of the outstanding physicist Igor Kurchatov who was head of the atomic energy programme of the USSR. The book covers briefly his work on the uranium chain reaction, the building of an atomic industry in the Soviet Union, the construction of the world's first nuclear power station, and the problem of thermonuclear energy. The author of the book, Igor Golovin, D. Sc. (Phys. and Math.), was one of Kurchatov's close associates. He gives an exciting picture of the intensive, self-sacrificing work of Soviet physicists to harness the energy of the atomic nucleus, tells about the team of scientists who worked together with Kurchatov and the great difficulties they had to overcome when the USSR, just through the trying times of World War II, undertook the building of an atomic industry. I. Golovin's book is well documentated with photographs, and will be of interest both to nuclear physicists and the general reader.

Kondratov, 1.

SOUNDS AND SIGNS

From time immemorial man has been concerned with the nature of his speech, the diversity of languages, the differences between the sound signals of beasts and human speech. *Sounds and Signs* describes the methods of investigating languages: mathematical statistics and information theory, the theory of probability and mathematical logic, cybernetics, and the theory of signs. It also considers machine languages, various projects for "universal" languages to facilitate communication between nations, and, finally, the development of "Lincos" a language designed for communicating with the inhabitants of other worlds.

Soviet linguist and popular-science writer Alexander Kondratov has produced an exciting book of appeal to all who are interested in language.

Anfilov, G.

PHYSICS AND MUSIC

What is it that gives the violin its enchanting voice? Is it the wood or its noble, exquisite shape? Can a square violin be made? Yes, it can. In fact, it was made at one time, and its sound was as beautiful. Yet, violinists rejected it.

The story of the square violin is but one of the many intriguing stories told by Gleb Anfilov in his *Physics and Music.* The key-note of the book is man's desire to penetrate the world of the beautiful with the exact sciences—physics, mathematics, and electronics—so as to place it within the reach of the man in the street. The reader will find many an interesting page about the history of music, about the development of notation in music, he will learn the secret of famous voices, get acquainted with electronic music and the "painted sound", music accompanied by a play of colours, and many other things. The advantage of the book is that it will be interesting not only for musicians, but for every inquisitive man.