REVIEWS OF
MODERN PHYSICS

VOLUME 8 OCTOBER, 1936 NUMBER 4

Group Theory and the Vibrations of Polyatomic Molecules

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INTRODUCTION

THE analysis of the vibrational spectrum of a polyatomic molecule consists in correlating the observed infrared and Raman frequencies with the normal modes of vibration of the molecule.[1] By analogy with the diatomic case we consider the nuclei of the N atoms to be vibrating around an equilibrium configuration with amplitudes small compared with the internuclear distances. This assumption is actually justified by experimental data. We know from classical mechanics that under these conditions there are certain definite combinations of the displacements of each particle which give rise to definite mechanical frequencies. These *fundamental* frequencies and the *normal* coordinates corresponding to them obviously depend on the potential and kinetic energies of the particles. It may be shown that the *fundamental* frequencies found in this fashion are identical with those obtained by quantum-mechanical calculations. We may hence restrict ourselves to classical mechanics.

Consider a system of N nuclei forming a stable configuration. The first step in any dynamical problem is to set up the Hamiltonian with the potential energy V as some unknown function of the mutual displacements of the particles. If we call q_{ij} the distance between the ith and jth nucleus, and let δ refer to the change in any quantity, we may expand the potential energy as a Taylor's series in terms of the δq's. No terms linear in them appear since the undisturbed configuration is an equilibrium one. Also, as a first approximation, we may neglect terms of higher order than the second which amounts to postulating harmonic forces between the nuclei.[2] Then the potential energy is written as:

$$V=\tfrac{1}{2}\sum k_{iji'j'}\delta q_{ij}\delta q_{i'j'}. \qquad (1)$$

In some cases there may be definite physical or chemical reasons for assuming certain specific values for the various k's, but as a rule we have to consider them at first as unknown constants with the hope of being able to determine them later from experimental data.

The usual way of expressing the kinetic energy T is in terms of the displacements of the various particles from their equilibrium positions. If we assume a cartesian coordinate system xyz, then:

$$T=\tfrac{1}{2}\sum_{i=1}^{N} m_i(\delta\dot{x}_i^2+\delta\dot{y}_i^2+\delta\dot{z}_i^2), \qquad (2)$$

where m_i is the mass of the ith particle.

To have a Hamiltonian suitable for further calculations, we must express both the kinetic and potential energies in terms of the same variables. Obviously there are functional relations between the δq's and the δx's, δy's, and δz's and in the case of small vibrations (i.e., if the various δq's etc., are small quantities of the first order) the relations are linear. However, both

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[1] For a treatment of the vibrations of polyatomic molecules without the use of group theory, cf. D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931). The specific points mentioned in this introduction are discussed there in detail.

[2] For a detailed discussion see Whittaker, *Analytical Dynamics*, 2nd edition (Cambridge, 1927), p. 178.

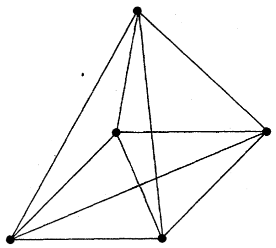

FIG. 1. The number of lines connecting the various nuclei in a tetrahedral pentatomic molecule.

sets of variables turn out to be extremely cumbersome for any actual calculations. Another difficulty has to be taken into account. The system has $3N-6$ degrees of internal freedom, since rotation and translation claim three each, but the number of lines connecting the various nuclei may be larger than this (as, for example, in the case of a pentatomic tetrahedral molecule; see Fig. 1). Then all the δq_{ij}'s are not linearly independent and one or more of them have to be eliminated by means of relations giving the linear dependence. Also in Eq. (2), T is a function of $3N$ variables, i.e., the kinetic energies due to rotation and translation have not been subtracted. The most satisfactory way of treating the problem is to select $3N-6$ independent variables $s_1, s_2, \cdots s_{3N-6}$ (which may be expressed linearly in terms of the original variables) and transform both the kinetic and potential energy to them. The conditions of conservation of linear and angular momenta have to be taken into account when performing the transformation on T (i.e., the translational and rotational energy have to be subtracted). We obtain then:

$$T=\tfrac{1}{2}\sum_1^{3N-6}\mu_{ij}\dot{s}_i\dot{s}_j \quad (\mu_{ij}=\mu_{ji}), \tag{3}$$

$$V=\tfrac{1}{2}\sum_1^{3N-6}K_{ij}s_is_j \quad (K_{ij}=K_{ji}), \tag{4}$$

where the μ_{ij} are functions of the masses, but the K_{ij} are not. We know from the theory of small vibrations[2] that the Hamiltonian may be transformed to the form:

$$T=\tfrac{1}{2}\sum\dot{Q}_i^2, \quad V=\tfrac{1}{2}\sum\lambda_iQ_i^2, \tag{5}$$

where $\lambda_i=\omega_i^2$ and the ω_i's are the fundamental frequencies (expressed in suitable units). We know, furthermore, that the λ_i's are the roots of the determinantal equation[3]

$$|\lambda T-V|=0. \tag{6}$$

The resultant equation in λ would be one of degree $3N-6$. It happens, however, that for a large number of so-called "*symmetrical*" molecules, the equation in λ factors out into a number of component equations of lesser degree. This implies that it should be possible by a proper choice of the variables to resolve the original determinant immediately into a product of determinants of less orders (cf. Fig. 16).

This question of the proper choice of variables is intimately connected with a study of the symmetry properties of molecules. For some simpler cases, geometrical intuition may lead to satisfactory results, but in general more powerful mathematical methods are needed.

A suitable formalism for the treatment of the problem has been developed in group theory. The purpose of this report is to present elements of the theory of groups and their representations and to use these methods in the solution of the problem of molecular vibrations. The knowledge of group theory actually necessary for this is very small and in what follows no attempt will be made to furnish proofs of the various statements made. Their validity can be easily demonstrated by means of the specific groups used as illustrations, but for a general proof the reader must go to texts on group theory.[4]

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[3] Eq. (6) means:

$$\begin{vmatrix} \lambda\mu_{11}-K_{11} & \lambda\mu_{12}-K_{12}\cdots & \lambda\mu_{1,\,3N-6}-K_{1,\,3N-6} \\ \lambda\mu_{12}-K_{12} & \lambda\mu_{22}-K_{22}\cdot & \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \\ \cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \\ \cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \end{vmatrix}=0.$$

[4] We have found the following, especially the first three, to be useful references for the general theory of groups: Wigner, *Gruppentheorie* (Braunschweig, 1931). (This book is always meant, whenever we refer to Wigner, loc. cit.); Schoenflies, *Theorie der Kristallstruktur* (Berlin, 1932); Speiser, *Theorie der Gruppen von endlicher Ordnung* (Berlin, 1927); Bauer, *Introduction à la théorie des groupes* (Paris, 1933); van der Waerden, *Gruppentheoretische Methode in der Quantenmechanik* (Berlin, 1932); Mathewson, *Elementary Finite Groups* (Boston, 1930); Eckart, "Group Theory," Rev. Mod. Phys. **2**, 305 (1930); Weyl, *Theory of Groups and Quantum Mechanics* (London, 1931); Burnside, *The Theory of Groups* (Cambridge, 1927). The theory of groups as applied to molecular vibrations has been developed by Wigner, *Göttinger Nachrichten* (1930), p. 133.

GENERAL CONCEPTS

1. Definition of a group

An ensemble of elements, E, A, B, G, $\cdots$ is said to form a *group* if the following four postulates are obeyed:

I. There is a rule of combination such that the combination of any two elements A and B of the group will give a third element of the group, C, called the product of A and B and written $C=AB$.

II. The associative law holds: $(AB)C=A(BC)$.

III. Every group contains a unit element, E, for which $AE=EA=A$.

IV. Every element of the group has an inverse, $X=A^{-1}$ such that $XA=A^{-1}A=E$. An element and its inverse may be identical and obviously, $E^{-1}=E$.

The members of a group may be considered as abstract elements to which a meaning is to be assigned later. They may be identified with real or complex numbers, matrices or the motions of a geometrical figure in space.

In what follows, the rule of combination is multiplication and if necessary matrix multiplication. In the case of ordinary multiplication, the four numbers ± 1, $\pm i$ form a group and it is easily verified that the four group postulates as given above are fulfilled.

If the group contains a finite number of elements, it is called a *finite group* and the number of its elements, h is called the *order* of the group. Infinite groups are of considerable interest in quantum mechanics but here we are mainly concerned with finite groups. If the commutative law holds, $AB=BA$, and the group is said to be *Abelian* but in general $AB \neq BA$.

A simple group has been given above. An example of a slightly more complex group of order 6 will now be given and some additional group properties presented. A group is completely defined if all of its products are known. Let the elements of the group, E, A, B, C, D, F be arranged in rows and columns in such a way that the products stand at the intersections. For example, the product AB will stand at the intersection of the row headed by A and the column by B. Let the multiplication table for this group be:

$$\begin{array}{c|cccccc} & E & A & B & C & D & F \\ \hline E & E & A & B & C & D & F \\ A & A & B & E & D & F & C \\ B & B & E & A & F & C & D \\ C & C & F & D & E & B & A \\ D & D & C & F & A & E & B \\ F & F & D & C & B & A & E \end{array} \tag{7}$$

It is easy to see that the six elements form a group and that the group postulates are obeyed. Every product is contained in the group and every element has an inverse. This group is not Abelian for $AC=CB\neq CA$.

2. Sub-groups

Consider some one element of the group, say X and form successive powers of this element. Since the element chosen and all of its powers are members of the group and since the group is finite, this series will eventually repeat itself. Let $X^n=E$, then

$$X,\ X^2,\ X^3,\ \cdots X^{n-1},\ X^n=E$$

is called the *period of* X and is indicated by the symbol $\{X\}$. If n is the smallest number for which $X^n=E$, n is called the order of X. The period of A in the group above is:

$$A,\ A^2=B,\ A^3=E, \text{ its order is } 3.$$

The period of B is B, $B^2=A$, $B^3=E$ and its order is also 3. The order of C is 2, however, since $C^2=E$. The period of X forms a group itself since all the group postulates are fulfilled and it is said to be a sub-group of the original group, $\mathfrak{G}$. In the above group, the sub-groups are:

$$\begin{aligned} \{A\}=\{B\}&=E,\ A,\ B,\\ \{C\}&=E,\ C,\\ \{D\}&=E,\ D,\\ \{F\}&=E,\ F. \end{aligned}$$

The order of a sub-group may be shown to be a divisor of the order of the whole group. Since the only divisors of 6 are 2 and 3 (besides 1 and 6) these are the only possible sub-groups.

3. Conjugate elements

If A, B, and X are elements of a group and

$$B=XAX^{-1}, \tag{8}$$

A and B are said to be conjugate to one another. The following laws about conjugate elements are almost self-evident and are readily verified using the group multiplication table given above:

I. Every element is conjugate with itself.
II. If A is conjugate with B, then B is conjugate with A.
III. If A is conjugate with B and also with C, then B and C are conjugate.

The elements conjugate with each other are called a *class*. The whole group then splits into a number of classes none of which contains elements in common. For the group (7), the class of A is A and B. For,

$EAE^{-1}=A$, $AAA^{-1}=A$, $BAB^{-1}=A$, $CAC^{-1}=B$, $DAD^{-1}=B$, $FAF^{-1}=B$.

Similarly, it can be shown that the class of C (also D and F) is C, D, F.

The unit element always forms a class by itself. There are then 3 classes in $\mathfrak{G}$: E; A, B; C, D, F. Elements of the same class have the same order, in the above example, 1, 3 and 2, respectively. The number of elements in any class is always a factor of the order of the whole group.

A *complex* is a set of elements from a group and is designated by German script letters. The complex of elements forming a class is always indicated by $\mathfrak{C}$. If the complex $\mathfrak{A}$ contains A, B, C, the product $C\mathfrak{A}$ will contain CA, CB, C^2. By the product of two complexes $\mathfrak{A}\mathfrak{B}$ is meant the product of every element of $\mathfrak{A}$ with every element of $\mathfrak{B}$ but products occurring more than once are only taken once. If the complex $\mathfrak{H}$ is a sub-group

$$\mathfrak{H}\mathfrak{H}=\mathfrak{H}^2=\mathfrak{H}$$

$\mathfrak{H}$ and $X\mathfrak{H}X^{-1}$ are called *conjugate sub-groups.*

4. Isomorphism

Two groups are said to be isomorphous if elements A, B and C of $\mathfrak{G}$ are associated with elements A', B' and C' of $\mathfrak{G}'$ in such a way that if $AB=C$, also $A'B'=C'$. If the multiplication tables of the two groups are known, there will be a one-to-one correspondence with the elements of the isomorphous groups throughout the tables, although the meaning of the elements will be different in each case. Instead of a simple isomorphism as illustrated here, it is possible to extend this concept to the case of general or multiple isomorphism where instead of having a one-to-one correspondence of elements in two groups, there may be several elements of one group isomorphous to a single element of another group.

GEOMETRICAL BASIS

5. Elementary properties of motions

While group theoretical methods are extremely elegant from a purely mathematical point of view, they have the disadvantage of not being easily visualized unless studied on a more geometrical basis. We shall proceed therefore with a consideration of some simple geometrical properties. We are interested only in the possible motions[5] of a figure when one of its points remains fixed in space.[6] Since the position of any rigid figure is determined by the positions of any three of its points which are not collinear, the only two possible types of motion are rotations through some angle φ around an axis passing through the fixed point and reflections in a plane containing that point; all other types of motion may be reduced to a combination of these two fundamental ones. Hence two different positions of the same figure (or any two identical figures that have a point in common) may be brought into superposition by means of a rotation; both the direction of the axis and the angle of rotation are determined by the initial positions of the two figures. Also any two mirror images may be brought into superposition by a reflection plus a rotation around an axis perpendicular to the plane of reflection.

6. Combined motions

A product of two motions may be defined as their combination. Obviously the product of two rotations is another rotation; the axis and angle of this resultant motion are determined by the axes and angles of the components. The product of two reflections must be a rotation, since by reflecting the mirror image of a figure F once

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[5] Motion is meant here in the strictly geometrical sense.

[6] While the motions discussed here are not to be correlated with the actual movements of a molecule, we can take advantage of the fact that in the problem of determining the energy levels the center of gravity of the system may be considered to be stationary.

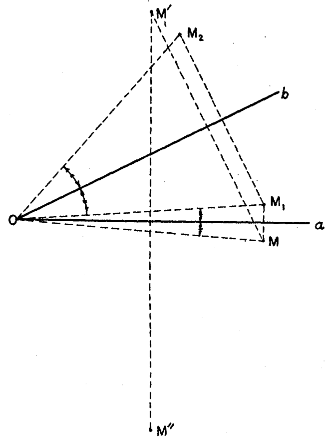

FIG. 2. Reflections from two intersecting mirrors.

more, we get F again. This last case may serve as an illustration and will therefore be discussed in a little more detail.

Consider two intersecting mirrors a and b and a point M. In Fig. 2, a and b are taken to be perpendicular to the plane of the paper with M in the plane. The reflection in a will bring M to the position M_1; the reflection in b will further shift it to M_2. It is evident from the figure that[7] $(OM, OM_2)=2(a, b)$. Also $OM=OM_1=OM_2$ and OM and OM_2 are both perpendicular to the line of intersection.

Hence the product of two reflections is a rotation by an angle $2(a, b)$ around the line of intersection of the mirrors a and b.

Corollary.—The product of a rotation and a reflection in a plane containing the axis of rotation is equivalent to a reflection in another plane passing through this axis. The angle between the two planes is equal to half the angle of rotation.

Assume now that the order of the two reflections has been interchanged. The effect of b would be to bring M to M' and then a would reflect it to M''. Now: $(OM, OM'')=2(b, a)=-2(a, b)$. The result is a rotation by the same angle as before but in the opposite direction—the order of two reflections may not be interchanged.

Another important result is the following: The product of two rotations by π around intersecting axes u and v is equal to a rotation around an axis perpendicular to u and v, by an angle equal to $2(u, v)$.

The correctness of this statement can be shown as follows: The product has to be a rotation. Now take any point M on a line perpendicular to u and v and passing through their intersection O (Fig. 3). The first rotation by π brings M to another position M' *on the same line*, such that $MO=OM'$; the second rotation brings it back to M. Hence this perpendicular line remains unchanged and is actually the axis of the resultant rotation. To determine the angle, consider the axis u itself. The rotation around u obviously leaves it unchanged; the rotation around v brings it to a position u' such that $(u, v)=(v, u')$. Hence $(u, u')=2(u, v)$ as was stated above. In an exactly similar way, we may show that the product of the two rotations taken in reverse order is a rotation around the same axis and by the same angle only in the opposite direction.

The product of two operations depends in general on the order in which they are taken. However, the following special operations are interchangeable (as shown in the less obvious cases in the corresponding figures):

I. Two rotations around the same axis;

II. Two reflections from perpendicular planes —they are equivalent to a rotation by π;

III. Two rotations by an angle π around perpendicular axes;

IV. A rotation and a reflection in a plane perpendicular to the axis of rotation (Fig. 4).

The product of a rotation and a reflection in a perpendicular plane which is thus defined unambiguously is called an *improper rotation* or a *rotary reflection*. We may treat an improper rotation as being the fundamental operation involving a reflection. An ordinary reflection is an improper rotation by the angle zero. There is another important special case of it if the rotation is by an angle π. As may be seen from Fig. 5,

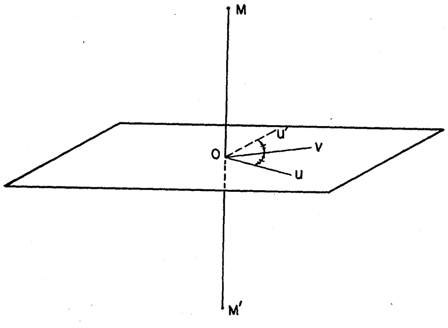

FIG. 3. Rotations by an angle π around two intersecting axes.

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[7] (a, b) will always denote the angle between two lines a and b, the positive direction being from a to b.

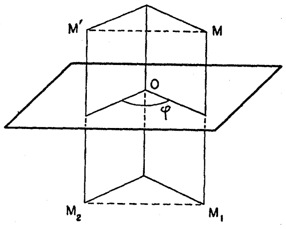

FIG. 4. Rotation and reflection in a plane perpendicular to the axis of rotation.

every point M is transferred by this operation to a position M_1 such that the three points M, O, and M_1 are collinear and $MO=OM_1$ (O is the point of intersection of the axis with the plane). The result is thus independent of the direction of the axis and depends uniquely upon the position of the point O_1 (i.e., of the fixed point); the operation is called an *inversion* and O is the *center of inversion.* We may add to our list of interchangeable operations:

V. An inversion and any other operation (this is a consequence of I and IV).

7. Symbolic notation

Following Schoenflies we denote symbolically any rotation by an angle φ around an axis c by $C(\varphi)$, similarly a reflection in a plane s is called σ_s. If there is no ambiguity, we may omit writing s. In a case where there are several axes, a rotation around an axis a may be represented by $A(\varphi)$. An improper rotation is represented by $S(\varphi)$ and an inversion by I. The identity operation, one which leaves all points unchanged, is symbolized by E. Since $C(2\varphi)$ is equivalent to two successive rotations by φ, i.e., to the *product* of two such rotations, we define:

$$C^2(\varphi)=C(2\varphi);$$

or more generally:

$$C(\varphi)C(\varphi')=C(\varphi+\varphi') \quad \text{and} \quad C^k(\varphi)=C(k\varphi); \tag{9}$$

k being any number whatsoever. Thus if $k=-1$, $C^{-1}(\varphi)=C(-\varphi)$. If $\varphi=2\pi/n$, where n is an integer, C_n may be used instead of $C(\varphi)$. With this notation we have the following set of relations, which are an analytical statement of the various geometrical properties discussed above:

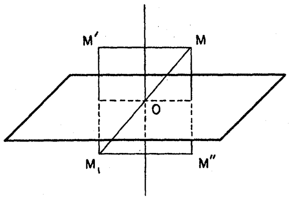

FIG. 5. Inversion.

$$\begin{gathered}
C_n{}^{-1}C_n=C_nC_n{}^{-1}=E, \quad C_n{}^n=E, \quad C_n{}^p=C_{n/p},\\
C_1=E, \quad \sigma^2=E; \quad \sigma^{-1}=\sigma.
\end{gathered}$$

$$\begin{gathered}
C_n\sigma_h=\sigma_hC_n=S_n; \quad S_{2n}{}^{2n}=E; \quad S_{2n+1}{}^{2n+1}=\sigma_h \qquad (10)\\
\sigma_v\sigma_h=U_2;\\
C_2\sigma_h=I; \quad I^2=E; \quad I=I^{-1};\\
I\sigma_h=C_2; \quad IC_n=C_nI.
\end{gathered}$$

h and v are two mutually perpendicular planes intersecting in u and c is a line perpendicular to h.

8. Symmetry properties and elements

Among all the possible rotations and reflections, we may select certain ones which have the special property of bringing the figure into superposition with itself. These motions are called *covering operations.* If the only motion which will accomplish this result is a rotation by 2π (or zero), the system is said to have no proper symmetry; however, the only cases of interest are those which do have some kind of proper symmetry. Take for example an equilateral triangle (Fig. 6). The three positions obtained by rotations of $2\pi/3$ and $4\pi/3$ around an axis through the center of the triangle and perpendicular to its plane are undistinguishable. We may thus have axes, planes and centers of symmetry depending on whether the covering operation is a rotation, a reflection or an inversion. If the covering operation is a rotation by $2\pi/n$, the symmetry axis is said to be *n-fold.* The symmetry element corresponding to an improper rotation is called an *axis of the second kind* or an *improper axis.* The following relations hold between various symmetry elements:[8]

I. The intersection of two symmetry planes is a symmetry axis. If the planes form an angle of

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[8] The statement in parentheses indicates the general nature of the proof.

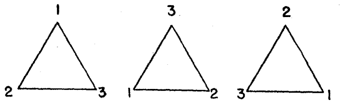

FIG. 6. Proper symmetry of equilateral triangle.

π/n, the axis is n-fold. (Cf. the discussion about the product of two reflections.)

II. If a symmetry plane contains an n-fold symmetry axis, there are $n-1$ additional symmetry planes going through that axis, the angle between two successive planes being π/n. (This follows from the repeated application of the corollary in §6.)

IIa. An important special case of II is $n=2$. A twofold axis and two perpendicular symmetry planes passing through it are always present together; if a figure has two of these elements, it must necessarily have the third.

III. An even-fold axis, a plane perpendicular to it, and a center of inversion are also interdependent; any two of these elements require the presence of the third. (See the definition of rotary reflection and inversion in §6.)

IV. Two twofold axes forming an angle of π/n require a perpendicular n-fold axis. (See discussion in §6 of result of two rotations by π.)

V. A twofold axis and an n-fold axis perpendicular to it postulate $n-1$ additional twofold axes, the angle between two adjoining ones being π/n. (This follows from the repeated application of result mentioned under IV.)

9. Geometrical definition of a group

From the very definition of covering operations, it is evident that they obey the postulates stated in §1; hence, the total set of covering operations of a symmetrical figure constitute a group. Any operation of the group will transform the system of symmetry elements into itself, since the figure to which the system belongs is by definition brought into superposition with itself. Symmetry elements which may thus be transformed into one another are called equivalent.

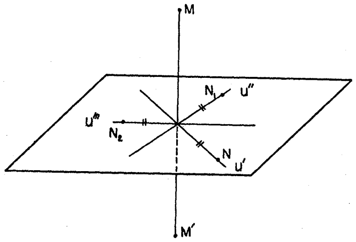

FIG. 7. One-and two-sided axes of rotation.

In this connection, consider the following case: a system consists of a threefold axis c and 3 twofold axes, u', u'' and u''', perpendicular to it. (Fig. 7.) Take any point M on c above the plane of the u axes; a rotation by π will bring it to the position M' below the plane. The two halves of the axis c may be transformed into one another, the axis is said to be *two-sided*. Take now any point N on say u'. Rotations around either c or u'' and u''' can bring it only to the positions N_1 on u'' and N_2 on u''', there is no operation which can bring one part of the u' axis in superposition with the other. The axes u are *one-sided*. If the axis c were $2n$-fold, the twofold axes would be two-sided for there would be an operation $C_{2n}{}^n=C_2$, and a rotation by π can bring one-half of any line perpendicular to the axis into superposition with the other half.

10. Transformed operations

Consider an operation A with the element a and an operation G which transforms a into b; then the operation B which is connected to b in the same way as A is connected to a is its conjugate[9] $B=GAG^{-1}$. While this result is perfectly general, the proof will be restricted to the case where A is a rotation, $A=A_n$. GAG^{-1} is obviously a rotation. Consider the effect of it on b; if G transforms a into b, then G^{-1} transforms b into a. A acting upon the result will leave it unchanged and finally G will transform it back to b. Since the resultant rotation GA_nG^{-1} leaves b unchanged, b is its axis. To show that the angle of rotation around B is also $2\pi/n$ we must show[10] that

$$B^n=E \qquad \text{and} \qquad B^p\neq E \qquad \text{if} \qquad p\neq n.$$

$$B^p\equiv(GA_nG^{-1})^p=\underbrace{GA_nG^{-1}GA_nG^{-1}\cdots GA_nG^{-1}}_{p\text{ factors}}$$

$$=GA_n{}^pG^{-1}\begin{cases}=E \text{ if } p=n\\ \neq E \text{ if } p\neq n\end{cases}. \qquad (11)$$

A purely visual, very elementary proof may be given in the special case of an equilateral triangle (Fig. 8) where a and b are twofold axes and A is a rotation by π. We let G be a rotation (in the trigonometric sense) by $2\pi/3$ around the threefold axis passing through O and perpendicular to

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[9] We make the convention that in a product of operations like LMN, N is performed first, then M, then L. This is in accord with the usual rules of matrix multiplication but disagrees with Schoenflies.

[10] Cf. §3.

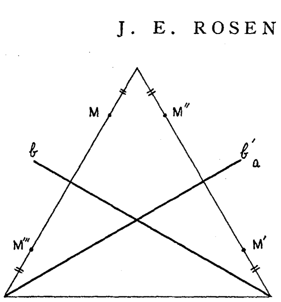

FIG. 8. Transformed operations illustrated for the case of an equilateral triangle.

the plane of the triangle. We want to find the effect of the combined operations GAG^{-1} on a point M. G^{-1} is a rotation by $2\pi/3$ in the negative sense. It brings b to the position b' coincident with a and M to M'. (All equal distances on the figure are marked off). A obviously leaves b in the position b' and shifts M' to the position M''. Finally, G the rotation by $2\pi/3$ brings b back to its original position and M'' to M'''. The result of GA_2G^{-1} is thus to shift M to M''', but it is evident that the same result is obtained directly by performing a rotation by π around b. Hence we actually have $GA_2G^{-1}=B_2$.

11. Transformation of an *n*-fold axis into itself

Assume that the n-fold axis coincides with the z axis of the coordinate system and let the positive sense of rotation be counterclockwise around the positive direction of z. Consider two lines l_1 and l_2 in the xy plane such that we go from l_1 to l_2 in the trigonometric sense through the angle $2\pi/n$. If the transformation G performed on the symmetry elements does not affect the relative positions of l_1 and l_2, l_1 can be brought to the position l_2 only by the operation C_n. In this case there will be no possibility of transforming C_n into C_n^{-1}. For example: every rotation is conjugate only to itself if the operation G transforming the symmetry element is a reflection in the xy plane, or an inversion, or more generally any improper rotation around the z axis. On the other hand, if the operation G is such that it interchanges l_1 and l_2 or changes l_1 to $-l_1$ (or l_2 to $-l_2$, but not both) it is possible to bring l_1 into the position l_2 by means of C_n^{-1} and to have C_n conjugate to C_n^{-1}. Among operations G of this kind are reflections in vertical planes bisecting (l_1l_2) and rotations by π around either l_1 or l_2.

12. General properties of symmetry groups

The preceding discussion concerning conjugate operations enables us to determine the *classes* without having to set up the multiplication table of the group. The different types of covering operations give the number of classes; the number of elements in each class is found by considering the number of equivalent symmetry elements corresponding to each operation.

With this geometrical interpretation it is easy to determine and classify all the possible types of symmetry groups. We shall consider first the problem of finding groups of higher symmetry by adding certain symmetry elements to lower symmetry groups. By analogy with $\{A\}$ which stands for the period of A, $\{A, B\}$ will represent *all* quantities of the type A^mB^n, where the order of A and B cannot be interchanged. Consider a group[11] $\mathfrak{G}$ with the system of symmetry elements $\mathfrak{g}$; we want to add to it a system of elements $\mathfrak{a}$ with the operation A corresponding to one of the elements a of $\mathfrak{a}$. What conditions must the system $\mathfrak{a}$ and the operation A satisfy in order that $\{\mathfrak{G}, A\}$ should constitute a new group? In any group the total system of symmetry elements transforms into itself under every operation of the group. The ensemble consisting of $\mathfrak{g}$ and $\mathfrak{a}$ will obviously satisfy this requirement if every power of A transforms $\mathfrak{g}$ into itself and every operation of $\mathfrak{G}$ brings $\mathfrak{a}$ into superposition with itself. If $\mathfrak{G}$ consists of the operations E, $G^{(1)}$, $G^{(2)}$, $\cdots G^{(n-1)}$, this means that corresponding to every operation $G^{(k)}$ and every power m of A there is another operation $G^{(p)}$ such that:

$$A^mG^{(k)}A^{-m}=G^{(p)} \quad \text{or} \quad A^mG^{(k)}=G^{(p)}A^m. \tag{12}$$

We may further note that if a, $a^{(1)}$ etc., are the equivalent elements of $\mathfrak{a}$ then there is an operation $G^{(k)}A(G^{(k)})^{-1}=A^{(1)}$ which has the same relationship to $a^{(1)}$ as A has to a. We can now prove that under these conditions $\{\mathfrak{G}, A\}$ actually represents a group. Since $\mathfrak{G}$ is a group and A a covering operation (corresponding to a), all[12] we have to show is that the product of any two operations, say $G^{(p)}A^m$ and $G^{(l)}A^r$ is contained in $\{\mathfrak{G}, A\}$. From Eqs. (12) and the group property of $\mathfrak{G}$, it follows that

$$\begin{aligned} G^{(p)}A^mG^{(l)}A^r &= A^mG^{(k)}G^{(l)}A^r = A^mG^{(s)}A^r \\ &= A^mG^{(s)}A^{-m}A^{r+m} = G^{(t)}A^{r+m}, \end{aligned} \tag{13}$$

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[11] Cf. the notation in §3.

[12] The covering operation of the type $A^mG^{(k)}$ is by Eqs. (12) equal to an element of $\{\mathfrak{G}, A\}$.

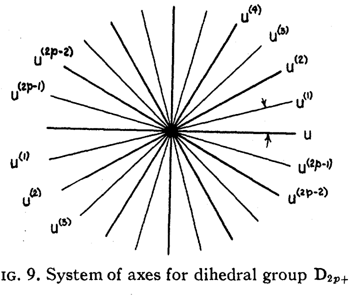

FIG. 9. System of axes for dihedral group $\mathbf{D}_{2p+1}$.

which by definition is contained in $\{\mathfrak{G}, A\}$. A and its powers may transform elements of $\mathfrak{G}$ into one another, which were nonequivalent with respect to the operations of $\mathfrak{G}$. Hence we need not expect that the classes of a rotation group should be identical with the classes of the group of the second kind derived from it. This will be the case, however, if $A=I$ for an inversion can only transform each single symmetry element into itself. Furthermore, we have seen in §11 that if an n-fold axis is transformed into itself by an inversion, each power of C_n remains conjugate only to itself. Since an inversion commutes with every other operation (§6, V), a class of the group $\{\mathfrak{G}, I\}$ is obtained from a class of $\mathfrak{G}$ by multiplying every conjugate element by I, for $G^{(k)}G^{(l)}(G^{(k)})^{-1}=G^{(n)}$ implies $G^{(k)}IG^{(l)}(G^{(k)})^{-1}=IG^{(n)}$. Hence $\{\mathfrak{G}, I\}$ has twice as many classes as $\mathfrak{G}$.

It may be shown that the method of construction presented here will actually lead to all the possible symmetry groups. Furthermore one can prove that if a group has more than one axis of symmetry of higher multiplicity than 2, its system of axes is identical with that of a regular polyhedron. The only regular polyhedra are the tetrahedron, the cube, the octahedron, the dodecahedron and the icosahedron. Of these the cube and octahedron have the same set of symmetry axes and the same is true of the icosahedron and dodecahedron. This restricts the number of possible groups of this type to a very few.

It might be pointed out in this connection that a regular polyhedron of n edges admits $2n$ covering operations of the first kind. This is due to the fact that any edge may be brought into superposition with any of the n others (including itself) in two different ways.

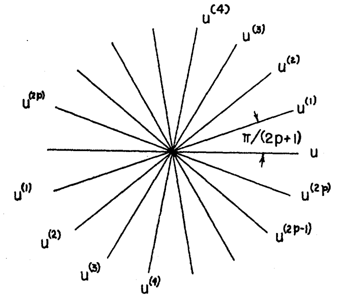

FIG. 10. System of axes for dihedral group $\mathbf{D}_{2p}$.

13. Classification of symmetry groups

This represents merely a tabulation. We shall start by considering first the groups of rotations and then add on to them symmetry elements of the second kind.

(A) ROTATION GROUPS

I. Cyclic groups $\boldsymbol{C}_n$

The simplest possible type of symmetry consists of just one n-fold axis c which is one-sided. The corresponding groups of operations are called *cyclic* and denoted by $\mathbf{C}_n=\{C_n\}$. Since all operations of a cyclic group are commutative, it has many classes as elements.

II. Dihedral groups $\boldsymbol{D}_n$

To construct a rotation group of higher order and symmetry we can add to the n-fold axis a perpendicular twofold axis u. According to V, §8 this postulates $n-1$ additional twofold axes $u^{(1)}, u^{(2)} \cdots u^{(n-1)}$ perpendicular to c; (the angle between two adjoining ones, is, of course, π/n). The resultant system obeys the symmetry requirement of §12. (It may be pointed out that this symmetry requirement could not possibly be satisfied unless the twofold axes were perpendicular to the n-fold one). Thus $\mathbf{D}_n=\{\mathbf{C}_n, U_2\}$.

To find the classes of $\mathbf{D}_n$ we note that in this case, according to §10, $C_n{}^k$ and $C_n{}^{-k}=C_n{}^{n-k}$ are conjugate to each other. The actual determination of the classes is different for groups of odd and even orders.

Consider first the group $\mathbf{D}_{2p+1}$. (See Fig. 9.) Successive rotations C_{2p+1} will bring the twofold axis u to coincide with the directions $u^{(2)}$,

$u^{(4)}\cdots u^{(2p)}$, $u^{(1)}$, $u^{(3)}\cdots u^{(2p-1)}$ and back to u. Hence all the twofold axes are equivalent and the $2p+1$ rotations by π corresponding to them are all in one class. Among the rotations around c there are $2p$ operations different from the identity which are conjugate to each other two by two. There are thus p classes of two elements each. The total number of classes is hence $p+2$.

Consider now a group of even order, $\mathbf{D}_{2p}$. (See Fig. 10.) Successive rotations C_{2p} will transform u to $u^{(2)}$, $u^{(4)}\cdots u^{(2p-2)}$, $-u$, $-u^{(2)}\cdots -u^{(2p-2)}$, u. No even-numbered axis can be transformed into an odd-numbered one; there are two non-equivalent sets of twfold axes and correspondingly two classes. Among the rotations around the $2p$-fold axis $C_{2p}{}^{p}=C_{2p}{}^{-p}=C_2$ is in a class by itself; the remaining $2p-2$ operations that are different from the identity are conjugate two by two. Hence the group $\mathbf{D}_{2p}$ has altogether $p+3$ classes.

An important special case is the group $\mathbf{D}_2$. It is usually known as the "Vierer" group and is symbolized by $\mathbf{V}$. Its system of three mutually perpendicular twofold axes is identical with the cartesian coordinate system.

III. Tetrahedral group, ***T***

This is the group of covering operations of the regular tetrahedron. It can be generated from the Vierer group by the addition of a system of equivalent threefold axes which will make the 3 twofold axes equivalent; (see Fig. 11). Thus: $\mathbf{T}=\{\mathbf{V}, C_3\}$. The tetrahedron has 4 threefold axes connecting each vertex with the center of the opposite face; the 3 twofold axes join the centers of opposite edges. (One axis of each kind is drawn in Fig. 12). The twofold axes being equivalent, the 3 rotations by π are in one class. Since in this case no operation transforms a threefold axis into itself, the rotations by $2\pi/3$ and $4\pi/3$ are in different classes and the total number of classes is 4.

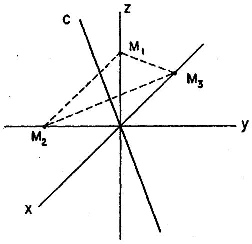

FIG. 11. A system of two and threefold axes.

IV. Octahedral group, ***O***

The octahedral group may be generated from **T** by adding a system of equivalent twofold axes. It is easier, however, to discuss the group on the basis of the symmetry elements of the cube or of the octahedron. A cube has 3 fourfold axes connecting the centers of opposite faces; the 4 main diagonals are threefold axes, and in addition to this there are 6 twofold axes which join the centers of opposite edges. Again only one axis of each kind is drawn in Fig. 13. It may easily be shown that all axes of the same multiplicity are equivalent and that all the rotations $C_n{}^k$ and $C_n{}^{n-k}$ are conjugate. Hence **O** has the following 5 classes: E, 8 rotations by $2\pi/3$, 6 rotations by $\pi/2$, 3 rotations by π around fourfold axes, and 6 rotations by π around twofold axes.

V. Icosahedral group ***P***

This particular symmetry type has no crystallographic application and it is doubtful whether it is needed for polyatomic molecules. It will, therefore, be mentioned only briefly for the sake of completeness. The group does not have any standardized symbol. **P** (for pentagonal dodecahedron which is one of the two polyhedra corresponding to the group) is suggested here; it has the advantage over Placzek's notation that it does not conflict with any other symbol. **P** consists of sixty operations; its symmetry elements are as follows: 6 fivefold axes, 10 threefold and 15 twofold ones. For more detailed results reference may be made to Speiser.[4]

(B) GROUPS OF THE SECOND KIND

A suitable reflection may be added to the rotation group $\mathfrak{G}$ to give rise to a new group $\{\mathfrak{G}, \sigma\}$. Since $\sigma^2=E$, these groups of the second kind will have the same number of improper as of proper rotations. It may be shown[13] that two groups $\{\mathfrak{G}, \sigma_1\}$ and $\{\mathfrak{G}, \sigma_2\}$ are identical if and only if $\sigma_1\sigma_2$ is a rotation contained in $\mathfrak{G}$, i.e., if the intersection of the two planes is a symmetry axis of $\mathfrak{G}$. It may also be shown that groups

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[13] Schoenflies, p. 80.

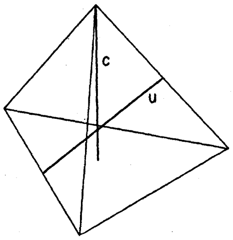

FIG. 12. A two and a threefold axis of the tetrahedral system.

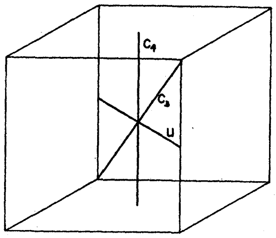

FIG. 13. A two, three and fourfold axis of the cube.

constructed by adding an inversion to a group of rotations are already contained among the $\{\mathfrak{S}, \sigma\}$ type, or else are identical with groups having an improper axis. It is convenient though, to indicate, whenever a group has a center of symmetry, for then according to §12 its classes may be obtained very simply from the corresponding group of rotations. These general statements are sufficient to determine all the groups which have symmetry elements of both the first and the second kind. We shall assume that the principal n-fold axis is vertical; h will denote a horizontal plane and v a vertical one. The addition of either one of these elements to a group of rotations will be symbolized by adding an h, respectively a v as subscript to the group symbol. The most important features of these groups will now be summarized.

VI. Cyclic groups $\mathbf{C}_{nh}$

By definition $\mathbf{C}_{nh} = \{\mathbf{C}_n, \sigma_h\}$. All the operations of this group are commutative;[14] it has as many classes as elements. According to III, §8, the groups of even order have a center of symmetry. The group $\mathbf{C}_{1h}$ is sometimes denoted by $\mathbf{C}_s$.

VII. Cyclic groups $\mathbf{C}_{nv}$

These groups contain n vertical symmetry planes (see II, §8). The operations consist of the n rotations and the n reflections. By a reasoning analogous to the one used in the case of the dihedral groups it may be shown that for n even the n symmetry planes form two nonequivalent sets, while for n odd all the planes are equivalent. Also, by §11, C_n^k and C_n^{n-k} are conjugate to each other. Hence $\mathbf{C}_{2pv}$ has the following $p+3$ classes: E, 2 sets of p reflections each, a rotation by π and $p-1$ sets each consisting of two rotations. Similarly the group $\mathbf{C}_{2p+1,\,v}$ has $p+2$ classes.

VIII. The groups $\mathbf{S}_n$

There are groups of operations whose only symmetry element is an improper n-fold axis. $\mathbf{S}_n = \{S_n\}$ and the groups are Abelian. It may be shown very easily by writing $S_n = C_n\sigma_h$ and considering all the elements of $\mathbf{S}_n$, that for certain values of n, the improper n-fold axis is equal to simpler symmetry elements. Thus:

$$\mathbf{S}_{2p+1} = \{\mathbf{C}_{2p+1}, \sigma_h\} = \mathbf{C}_{2p+1,\,h};$$
$$\mathbf{S}_{4p+2} = \{\mathbf{C}_{2p+1}, I\} = \mathbf{C}_{2p+1,\,i}.^{15}$$

No such relation exists, however, for $\mathbf{S}_{4p}$.

IX. Dihedral groups $\mathbf{D}_{nh}$

If a horizontal plane is added to a dihedral group of rotations, its presence postulates[16] n vertical planes going through the twofold axes. Since $\mathbf{D}_n$ consists of $2n$ operations, $\mathbf{D}_{nh}$ will have $4n$ of them. The additional operations are obviously the n reflections in the n vertical planes and the n improper rotations (among them is included the improper rotation by an angle zero, i.e., the reflection in the horizontal plane). The new symmetry elements do not transform any of the symmetry axes into one another that were nonequivalent before. Hence the rotations of $\mathbf{D}_{nh}$ will be divided into classes in the same way they were in the case of $\mathbf{D}_n$. The vertical planes are again equivalent if n is odd and divided into two sets if n is even. If C_n^k and C_n^{-k} are conjugate to

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[14] See IV, §6.

[15] This last symbol is part of the standard crystallographic notation.

[16] See statement IIa, §8.

each other, i.e., if for any operation G of the group $GC_n{}^kG^{-1}=C_n{}^{-k}$, then $GS_n{}^kG^{-1}=G\sigma_hC_n{}^kG^{-1}=G\sigma_hG^{-1}GC_n{}^kG^{-1}=G\sigma_hG^{-1}C_n{}^{-k}=\sigma_hC_n{}^{-k}=S_n{}^{-k}$; because σ_h can only be conjugate to itself since there is no plane equivalent to h. The improper rotations are also conjugate two by two. Hence $\mathbf{D}_{nh}$ has twice as many classes as $\mathbf{D}_n$, i.e., $\mathbf{D}_{2p+1h}$ has $2p+4$ classes and $\mathbf{D}_{2ph}$ has $2p+6$.

X. Dihedral groups $\mathbf{D}_{nd}$

Since $\mathbf{D}_{nh}$ contains already vertical planes going through the twofold axes, the only other way a vertical plane could be added to $\mathbf{D}_n$ and still transform the system of axes into itself would be to have it bisect the angle of the twofold axes (Fig. 8 or Fig. 9). This plane is called d (for diagonal). Again one plane of this type postulates $n-1$ additional ones. These diagonal planes reflect two adjoining twofold axes into one another, hence in this case the twofold axes are equivalent both for even and odd values of n. Similarly all the planes are also equivalent. Since the angle between a plane and an axis is always an odd multiple of $\pi/2n$ (even multiples give the angle between two planes or two axes), in the case of n odd, one of the planes is always perpendicular to one of the twofold axes. Hence for $n=2p+1$, the system has a center of symmetry.

The $4n$ operations of $\mathbf{D}_{nd}$ are the n rotations around the n-fold axis, the n rotations by π around the axes u, $u^{(1)}$ etc., the n reflections in the diagonal planes, and another set of n operations of the type $G=U_2\sigma_d$. To obtain these in a more customary form, we consider a vertical plane v going through the axis u. Then, according to Eqs. (10), $U_2=\sigma_h\sigma_v$ and $G=U_2\sigma_d=\sigma_h\sigma_v\sigma_d$. Since the two planes v and d intersect in the n-fold axis and the angle (v, d) is an odd multiple of $\pi/2n$, $\sigma_v\sigma_d=C((2k+1)2\pi/n)$ and $G=\sigma_hC_{2n}{}^{2k+1}=S_{2n}{}^{2k+1}(k=1, \cdots n-1)$. By analogy with the case of $\mathbf{D}_{nh}$, we find that $S_{2n}{}^{2k+1}$ and $S_{2n}{}^{-2k-1}$ are conjugate to each other.

From the preceding discussion we obtain the following classes for $\mathbf{D}_{2pd}$.

E, a rotation by π around the $2p$-fold axis, $p-1$ classes of conjugate rotations, one class of $2p$ rotations by π, one class of $2p$ reflections, and p classes of conjugate improper rotations; altogether $2p+3$ classes.

Since $\mathbf{D}_{2p+1d}$ has a center of inversion, it has twice as many classes as $\mathbf{D}_{2p+1}$, i.e., $2p+4$. For details, reference may be made to Section II.

XI. Tetrahedral group, $\mathbf{T}_d$

The six symmetry planes of $\mathbf{T}_d=\{\mathbf{V}_d, C_3\}$ pass through an edge and the median lines of the two opposite faces, and each contains one of the threefold axes. Since the plane of symmetry is vertical with respect to the threefold axis, the rotations C_3 and $C_3{}^{-1}=C_3{}^2$ will be conjugate to each other.[17] Also the twofold axes of $\mathbf{T}$ are now equivalent improper fourfold axes since the generating group is $\mathbf{V}_d$. We obtain then the following classes for $\mathbf{T}_d$:

E, a class of 8 rotations around threefold axes, a class of 6 reflections, a class of 6 improper rotations around fourfold axes, and a class of 3 rotations by π around these improper axes, altogether 5 classes.

XII. The group $\mathbf{T}_h$

This group is derived from $\mathbf{V}_d$ by the addition of a threefold axis, quite similarly to the construction of $\mathbf{T}$ from $\mathbf{V}$; $\mathbf{T}_h=\{\mathbf{V}_h, C_3\}$. Since $\mathbf{V}_h$ has a center of inversion, $\mathbf{T}_h$ will have one too, i.e., $\mathbf{T}_h=\{\mathbf{T}, I\}$ and its 8 classes can be obtained directly from those of $\mathbf{T}$. The standard notation $\mathbf{T}_h$ for this group is somewhat misleading, for as a rule h is perpendicular to the principal axis, i.e., the axis of greatest multiplicity, while in this case it is perpendicular to a twofold axis. Furthermore, it is evident that the geometry of a tetrahedron does not allow a center of symmetry, so that this so-called tetrahedral group is not a group of covering operations of the tetrahedron.

XIII. Octahedral group, $\mathbf{O}_h$

From the discussion of the symmetry of the cube, we see that any symmetry plane h will contain 2 fourfold axes and 2 twofold ones. Hence[18] its presence postulates both v and d planes and there is no other way of constructing a group of the second kind from the group $\mathbf{O}$. $\mathbf{O}_h$ has a center of symmetry, so that its 10 classes are immediately known from those of $\mathbf{O}$.

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[17] See §11.

[18] See statement II, §8.

XIV. Icosahedral group, $\mathbf{P}_h$

This group also has a center of inversion, the plane h being perpendicular to the twofold axis.

(C) CONTINUOUS GROUPS

In addition to the finite groups, three infinite groups must be considered. They are called $\mathbf{D}_\infty$, $\mathbf{C}_{\infty v}$, and $\mathbf{D}_{\infty h}$ and are analogous to $\mathbf{D}_n$, $\mathbf{C}_{nv}$ and $\mathbf{D}_{nh}$. The four group postulates may be extended to include an infinite number of elements[19] and the other concepts such as characters irreducible representations, etc., follow in a logical manner.

Consider the rotations around a fixed z axis by the angle φ, which may take an infinity of values between 0 and 2π. This group, in analogy with the cyclic groups is called the two-dimensional pure rotation group, $\mathbf{C}_\infty$, and is Abelian. It is a sub-group of the two-dimensional rotary reflection group, $\mathbf{C}_{\infty v}$ which is formed by the addition of a plane of reflection passing through the z axis. In this case, the rotations by $\pm\varphi$ form a single class as shown before,[20] and the extended group is not Abelian.

The group $\mathbf{D}_\infty$ is isomorphous with this group, but in place of the plane of reflection, there is a twofold axis of rotation, perpendicular to the z axis.

The group $\mathbf{D}_{\infty h}$ contains in addition to the infinite number of rotations about the z axis and the twofold axis of rotation, a center of inversion. It thus has twice as many classes and may be written:

$$\mathbf{D}_{\infty h} = \{\mathbf{D}_\infty, I\}.$$

14. Correlation between molecules and symmetry groups

When coordinating a molecule to one of the symmetry groups enumerated above, we must be careful to use the most complete group which will transform into one another the equivalent atoms, i.e., atoms which are identical and occupy geometrically equivalent positions. The incomplete group allows an asymmetry in the potential field around each atom as will be shown on the following example. Consider the molecule X_3, with its three atoms at the vertices of an equilateral triangle. We might represent the potential field symbolically by means of lines of force. Then if we take just $\mathbf{C}_3$ as the symmetry group of the molecule, a potential distribution shown in Fig. 14 is permissible geometrically, even though obviously quite impossible physically.

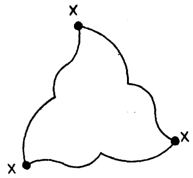

FIG. 14. A figure with the proper symmetry $\mathbf{C}_3$.

15. Introduction to the theory of representations

Since we have identified the elements of the symmetry groups with certain definite geometrical operations, we should be able to find for them analytical expressions, the so-called *representations*. In this section we shall discuss the geometrical meaning of representations and indicate to what extent geometrical intuition can serve as a guide in finding them.

Instead of actually specifying the group operations we could obviously indicate the numerical value of some quantity associated with the symmetrical figure for each one of the operations. For example, in the cyclic group $\mathbf{C}_n$ we could, starting from some arbitrarily chosen point, represent each operation C_n^k by the value of the corresponding angle of rotation. Thus:

$$\begin{array}{cccccc} E & C_n & C_n^2 & C_n^3 & \cdots & C_n^{n-1} \\ 0 & 2\pi/n & 4\pi/n & 6\pi/n & \cdots & 2\pi(n-1)/n. \end{array}$$

The disadvantage of this "representation" is that the corresponding group operation is not multiplication but addition combined with taking the residue from an integral multiple of 2π; e.g., $4\pi/5+8\pi/5=2\pi+2\pi/5$.

Obviously we could select in this way any number of quantities but it turns out that the resulting representations are not independent of each other. One requirement for a suitable representation is that it should have as its group operation either ordinary or matrix multiplication. Thus, in the example above, if instead of giving the value of the angle we chose the complex coordinate of a point on the unit circle, we

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[19] For the details of continuous groups and their theory, see Wigner, Chapter X, page 97.

[20] See §11; also Section VII, this §.

would get as the coordinate of this point under successive transformations:

$$\begin{array}{ccccc} E & C_n & C_n^2 & \cdots & C_n^{n-1} \\ 1 & e^{2\pi i/n} & e^{4\pi i/n} & \cdots & e^{2\pi(n-1)i/n}; \end{array}$$

which would be a satisfactory group representation.

If we take as our numerical quantity, a system of unit vectors directed along the symmetry axes, it would be an invariant under all operations. This case might be represented by ascribing the identity (for simplicity just the number 1) to every group element. This particular representation is obviously possible for every group. Consider now the example of a dihedral group, $\mathbf{D}_n$. Take a point on the n-fold axis c at unit distance from the plane of the twofold axes. Every rotation around c would leave this point unchanged so that we can represent each one of them by 1. The rotations by π bring this point below the plane; to them we can ascribe the number -1.

These examples suggest that we could in general consider the three coordinates xyz of a point on the unit sphere and see what happens to them under various operations. If the operation G shifts M to the position M_g with the coordinates:

$$x_g = g_{11}x + g_{12}y + g_{13}z; \quad y_g = g_{21}x + g_{22}y + g_{23}z; \quad z_g = g_{31}x + g_{32}y + g_{33}z$$

the nine numbers $g_{11}, g_{12} \cdots g_{33}$ can be assigned to G as its representations. The only way, however, to have these nine numbers obey simple multiplication is to take their matrix:

$$G \rightarrow \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}. \tag{14}$$

This intuitive method of finding representations makes clear their geometrical meaning but otherwise has some very serious drawbacks. There is too much arbitrariness in the selection of the numerical quantity associated with the symmetrical figure and no simple way to ascertain whether all possible representations have been found. Also we do not know whether the representations obtained are independent of one another. Still another objection is that no obvious meaning can be attached to representations by matrices of higher order than the third. As a result we have to use other more formal methods to obtain the representations in any but the simplest cases.

THEORY OF REPRESENTATIONS

16. Linear substitution groups

Since we are interested only in the symmetry groups, i.e., the groups of covering operations of symmetrical figures, we shall limit our study of the theory of representations to this special case. As a consequence, one should be very careful about extending any of the statements made here to groups of a more general nature.

The more formal method of finding the representations is based on a study of linear transformations. Consider a substitution of degree m:

$$\begin{aligned} x_1 &= a_{11}x_1' + a_{12}x_2' + \cdots + a_{1m}x_m', \\ x_2 &= a_{21}x_1' + a_{22}x_2' + \cdots + a_{2m}x_m' \\ &\cdots\cdots\cdots\cdots \\ x_m &= a_{m1}x_m' + a_{m2}x_2' + \cdots + a_{mm}x_m' \end{aligned} \tag{15}$$

with the matrix A

$$A = \begin{pmatrix} a_{11}a_{12}\cdots a_{1m} \\ a_{21}a_{22}\cdots a_{2m} \\ \cdot\quad\cdot\quad\cdot\quad\cdot \\ a_{m1}a_{m2}\cdots a_{mm} \end{pmatrix}. \tag{16}$$

This may be written

$$x_i = \sum_{j=1}^{m} a_{ij}x_j', \quad (i = 1, 2 \cdots m), \tag{17}$$

or

$$X = AX', \tag{18}$$

where X stands for the vector with the components x_1, x_2, etc.

Assume that there are further substitutions of the same type, $X' = BX''$, $X'' = CX'''$, etc. These matrices obviously obey the associative law, $(AB)C = A(BC)$. If the set of matrices is finite and closed,[21] these together with the unity or identical substitution form a linear substitution group.

To distinguish specifically between an abstract element or operation R and the matrix of the transformation corresponding to it, we shall denote the matrix by $\Gamma(R)$. The representation consisting of the matrices $\Gamma(E)$, $\Gamma(A)$, etc., will

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[21] The set of matrices is said to be closed if the fundamental group property I is fulfilled.

be denoted by Γ; a superscript will be attached to Γ whenever the representation is irreducible.

Every finite group is isomorphous with some linear transformation group, and when this is found, the matrices $\Gamma(A)$, $\Gamma(B)$, and $\Gamma(AB)$ can be associated with the elements A, B, and AB of the finite group in such a way that:

if $\qquad AB=C,$

also $\qquad \Gamma(A)\Gamma(B)=\Gamma(AB)=\Gamma(C).$

It may be shown[22] that all representations can consist of unitary matrices only, i.e., of matrices for which $\Gamma(R)\dagger=\Gamma(R)^{-1}$; $\Gamma(R)\dagger$ indicates the transpose of the conjugate matrix of $\Gamma(R)$. If $\Gamma(R)_{ik}$ is the element in the ith row and kth column of $\Gamma(R)$, then the corresponding element of $\Gamma(R)\dagger$ is $\bar{\Gamma}(R)_{ki}$, where the bar designates the complex conjugate.

In case there is a different matrix for each element, the representation is said to be *faithful*. The isomorphism may, however, be of the general type in which one matrix represents several elements of the group. One multiple isomorphism of any group is the previously discussed case in which the matrix (1) is associated with each element.

17. Reducible representations

Suppose the matrix corresponding to one of the elements of the group has the general form (16). It is often possible to find such a transformation of coordinates that

$$\begin{aligned}
x_1'' &= a_{11}x_1' + \cdots + a_{1,\,n+1}x_{n+1}' + \cdots + a_{1m}x_m' \\
x_2'' &= a_{21}x_1' + \cdots \qquad\qquad\qquad\qquad + a_{2m}x_m \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
x_n'' &= a_{n1}x_1' + \cdots a_{n,\,n+1}x_{n+1}' + \cdots \\
&\qquad\qquad\qquad + a_{nm}x_m' \qquad (19) \\
x_{n+1}'' &= \qquad\qquad a_{n+1,\,n+1}x_{n+1}' + \cdots \\
&\qquad\qquad\qquad + a_{n+1,\,m}x_m' \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
x_m'' &= \qquad\qquad a_{m,\,n+1}x_{m+1}' + \cdots + a_{mm}x_m'.
\end{aligned}$$

This matrix has the form

$$\begin{pmatrix} P & Q \\ O & S \end{pmatrix}, \tag{20}$$

where P and S are square matrices of degree n and $(m-n)$, O is a zero matrix, and Q has $(m-n)$ columns and n rows but may also be a zero matrix. If a transformation can be found which will put *all* the matrices of a given representation in this form the representation is said to be *reducible*. It is always then possible[23] to continue the process by a convenient choice of axes until *every* matrix of the group has the appearance

$$\Gamma(R)=\begin{pmatrix} \Gamma^{(1)}(R) & O \\ O & \Gamma^{(2)}(R) \end{pmatrix}. \tag{21}$$

If there is no transformation which will in turn put every matrix $\Gamma^{(1)}(R)$ (or $\Gamma^{(2)}(R)$) in the form (21), then the set of matrices $\Gamma(R)$ is said to be completely reduced and $\Gamma^{(1)}(R)$, $\Gamma^{(2)}(R)$ are called the irreducible representations.

The h operations of a group may be acting on any number n of variables $x_1, x_2, \cdots x_n$. The complete representation of the group referred to these n variables will consist of matrices of n rows and columns. If we write such a matrix in reduced form, some of the matrices of the irreducible representation may occur more than once (and some may not come in at all), due to the fact that the number n is independent of the group. Matrix expressions of the type given by (21) will be symbolized by

$$\Gamma(R)=\sum a^{(i)}\Gamma^{(i)}(R) \tag{22}$$

where $a^{(i)}$ gives the number of times the irreducible matrix $\Gamma^{(i)}(R)$ occurs in the reduced form of $\Gamma(R)$. Instead of dealing with individual matrices, we could write the representation Γ in the same symbolic form:

$$\Gamma=\sum a^{(i)}\Gamma^{(i)}. \tag{23}$$

18. The character

The task of finding all the representations for any group is rather cumbersome for any but the simplest group. However, for most physical applications it is sufficient to know only the sum of the diagonal elements of the matrices. From any set of matrices representing a group, infinitely many new ones may be obtained by transforming with an arbitrary matrix, G

$$GEG^{-1}=E \qquad GBG^{-1}=B', \text{ etc.,}$$
$$GAG^{-1}=A'$$

and if

$$AB=C \qquad GAG^{-1}GBG^{-1}=GABG^{-1}=GCG^{-1}.$$

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[22] See Wigner, Chapter IX.

[23] See Wigner, Speiser, reference 4. An illustration of the complete reduction of the matrices for the group (7) may be found in Bauer, p. 79.

These transformed matrices therefore follow the same multiplication properties. The sum of the diagonal elements is also the same.

$$\text{Spur } AG=\sum_{ik}a_{ik}g_{ki}=\sum_{ki}g_{ki}a_{ik}=\text{Spur } GA$$

and Spur $GAG^{-1}=\text{Spur } AGG^{-1}=\text{Spur } A$.
The *spur* in this connection is called the *character* and designated by $\chi(R)$, where R stands for any element of the group. (Cf. $\Gamma(R)$.) The characters of matrices representing elements of the same class are identical.

19. Properties of the character

Some important properties of the character will now be presented without proof. For further details, the texts cited must be consulted.

I. If there are r classes for a finite group, there can only be r different irreducible representations, $\Gamma^{(1)}, \Gamma^{(2)}, \cdots, \Gamma^{(r)}$. The characters corresponding to $\Gamma^{(j)}$ will be symbolized by $\chi^{(j)}(R)$.

II. Class E is always represented by the unit matrix. The characters, $\chi^{(j)}(E)$ are thus equal to the dimension of the representation and constitute a divisor of the order of the group.

III. The dimensions of the representations can be determined from the relation:

$$[\chi^{(1)}(E)]^2+[\chi^{(2)}(E)]^2+\cdots+[\chi^{(r)}(E)]^2=h. \quad (24)$$

With r and h given, there will be a unique way[24] for all the symmetry groups of satisfying Eq. (24) with integers.

IV. The characters form an orthogonal system:

$$\sum_R \chi^{(j)}(R)\chi^{(j')}(R)=h\delta_{jj'}. \quad (25)$$

Not only the characters but also the representations are orthogonal. If f_i and f_j are the dimensions of the representations $\Gamma^{(i)}$ and $\Gamma^{(j)}$, then:

$$\sum_R \Gamma^{(i)}(R)_{\alpha\beta}\bar{\Gamma}^{(j)}(R)_{\mu\nu}=[h/(f_if_j)^{\frac{1}{2}}]\delta_{ij}\delta_{\alpha\mu}\delta_{\beta\nu}. \quad (26)$$

The characters $\chi(R)$ of the reducible representation are given by:

$$\chi(R)=\sum_{j=1}^{r}a^{(j)}\chi^{(j)}(R), \quad (27)$$

an expression analogous to Eq. (22) for the matrices of the representation. Eq. (27) determines the r numbers $a^{(j)}$ completely, for by forming the scalar product with $\bar{\chi}^{(j)}(R)$, summing over all group elements, and using the orthogonality property (25), we get:

$$a^{(j)}=(1/h)\sum_R \chi(R)\bar{\chi}^{(j)}(R); \quad (28)$$

or by summing over the classes:

$$a^{(j)}=(1/h)\sum_{i=1}^{r}\chi(\mathfrak{C}_i)\bar{\chi}^{(j)}(\mathfrak{C}_i)h_i, \quad (29)$$

where h_i is the number of elements in the class $\mathfrak{C}_i$.

20. Direct products

We shall introduce now a new concept. Consider two vectors X and Y with the components $x_1, x_2\cdots x_n$ and $y_1, y_2\cdots y_m$. We can associate with them another vector Z which would have for its components the products $x_iy_k(i=1\cdots n)$, $k=1\cdots m)$. We want to determine the transformation F such that:

$$Z=FZ' \quad (30)$$

would follow from

$$X=GX' \quad \text{and} \quad Y=TY'. \quad (31)$$

If:

$$x_i=\sum g_{i\alpha}x_\alpha' \quad \text{and} \quad y_k=\sum t_{k\beta}y_\beta' \quad (32)$$

then

$$x_iy_k=\sum_{\alpha\beta}g_{i\alpha}t_{k\beta}x_\alpha'y_\beta', \quad (33)$$

and

$$g_{i\alpha}t_{k\beta}=f_{ik,\ \alpha\beta} \quad (34)$$

is the element in the ik row and $\alpha\beta$ column of F. This matrix with mn rows and columns is called the *direct product* of G and T and is written

$$F=G\times T. \quad (35)$$

The relation between the individual elements is given by Eq. (34). The character of F is

$$\chi(F)=\sum_{i,k}f_{ik,\ ik}=\sum_{i,k}g_{ii}t_{kk}=\sum_i g_{ii}\sum_k t_{kk}=\chi(G)\chi(T). \quad (36)$$

Consider now a group $\mathfrak{A}$ with the n elements: $A_1, A_2,\cdots A_n$ and another group $\mathfrak{B}$ with the m elements $B_1, B_2,\cdots B_m$; let all the A's commute with all the B's. If we multiply every element of

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[24] The solution, however, is by no means unique for other types of groups.

$\mathfrak{A}$ with every element of $\mathfrak{B}$, we obtain a new set of *nm* elements, which may be shown to constitute a group. In fact, for every value of j, k, j' and k', we have

$$A_jB_k\cdot A_{j'}B_{k'}=A_jA_{j'}B_kB_{k'}=A_{j''}B_{k''}. \tag{37}$$

Similarly, we may show that the other group postulates are also obeyed. This extended group of *nm* elements is called the direct product of $\mathfrak{A}$ and $\mathfrak{B}$ and is symbolized by $\mathfrak{A}\times\mathfrak{B}$. We are interested in finding the representations of the direct product from the representations of the individual factors. From the preceding discussion concerning vectors we can conclude that if we have two typical matrices $\Gamma(A_j)$ and $\Gamma(B_k)$, then

$$\Gamma(A_jB_k)=\Gamma(A_j)\times\Gamma(B_k). \tag{38}$$

This expression is not to be confused with

$$\Gamma(A_jA_k)=\Gamma(A_j)\Gamma(A_k)=\Gamma(A_l)\quad \text{if}\quad A_jA_k=A_l. \tag{39}$$

This last equation refers to two matrices of the same representations for two elements of a group, the product of which is by definition again an element of the group. On the other hand, in Eq. (38) nothing is specified about the matrices $\Gamma(A_j)$ and $\Gamma(B_k)$ and A_jB_k, an element of the group $\mathfrak{A}\times\mathfrak{B}$, is not equal to any other element of that group.

We are interested chiefly in the characters of the irreducible representations of the direct product. The results for the complete representations are given by Eq. (36). For Abelian groups, where all representations are of the first degree, the procedure for finding the characters of the direct product is particularly simple. If $\chi(A_j)$ and $\chi(B_k)$ are the characters for typical elements of the component groups, the corresponding character in the direct product is $\chi(A_j)\chi(B_k)$. This is true also in the general case for non-Abelian groups if one representation is of the first degree and another of the nth degree. The representation of the product will also be of the nth degree and if the component representations are irreducible, the representation of the product is also irreducible. However, if both representations are of higher degree than one, the resulting product is reducible. The reduction is readily made if the table of characters for the two groups is known, for multiplication of one set of characters by another will give a sum of characters already contained in the table and this can always be uniquely resolved into its irreducible parts.

Examples of the use of these rules are easily shown with the group $\mathbf{C}_{\infty v}$, whose characters may be found in Table III. The following results are obtained:

$$\begin{aligned}
&A_1\times A_1=A_2\times A_2=A_1,\\
&A_1\times A_2=A_2,\\
&A_1\times E_k=A_2\times E_k=E_k && k>0,\\
&E_k\times E_k=A_1+A_2+E_{2k} && k>0,\\
&E_k\times E_j=E_{k+j}+E_{k-j} && j,\ k>0;\ j\neq k.
\end{aligned}$$

For notation see next paragraph.

21. Tables of characters

For methods of obtaining the characters, reference should be made to group theoretical texts. Tables of characters for some of the point groups were first given by Bethe[25] and then more completely by Wigner[4]. In Tables I and II we give the characters in a general form and explicitly for the infinite groups and the 32 point groups of interest in molecular structure. They are also given by Mulliken and Tisza[26] but our tables follow the arrangement of Wigner so that they may be used with the results of Wilson,[27] the only

TABLE I. *General form of characters for the isomorphous groups* $\mathbf{D}_n$ *and* $\mathbf{C}_{nv}$ *with n odd;* $p=(n-1)/2$, $\varphi=2\pi/n$.

$\mathbf{D}_n$	E	$2C_n^p$	$\cdots$	$2C_n^1$	nC_2
$\mathbf{C}_{nv}$	E	$2C_n^p$	$\cdots$	$2C_n^1$	$n\sigma_v$
A_1	1	1	$\cdots$	1	1
A_2	1	1	$\cdots$	1	-1
E_1	2	$2\cos p\varphi$	$\cdots$	$2\cos\varphi$	0
E_2	2	$2\cos 2p\varphi$	$\cdots$	$2\cos 2\varphi$	0
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
E_p	2	$2\cos p^2\varphi$	$\cdots$	$2\cos p\varphi$	0

TABLE II. *General form of characters for the isomorphous group* $\mathbf{D}_n$, $\mathbf{C}_{nv}$ *and* $\mathbf{S}_{nv}$ *with n even;* $p=n/2$.

$\mathbf{D}_n$	E	C_n^p	$2C_n^{p-1}$	$\cdots$	$2C_n^1$	pC_2	pC_2'
$\mathbf{C}_{nv}$	E	C_n^p	$2C_n^{p-1}$	$\cdots$	$2C_n^1$	$p\sigma_v$	$p\sigma_d$
$\mathbf{S}_{nv}$	E	S_n^p	$2S_n^{p-1}$	$\cdots$	$2S_n^1$	$p\sigma_v$	pC_2
A_1	1	1	1	$\cdots$	1	1	1
A_2	1	1	1	$\cdots$	1	-1	-1
B_1	1	$(-1)^p$	$(-1)^{p-1}$	$\cdots$	-1	1	-1
B_2	1	$(-1)^p$	$(-1)^{p-1}$	$\cdots$	-1	-1	1
E_1	2	$2\cos p\varphi$	$2\cos(p-1)\varphi$	$\cdots$	$2\cos\varphi$	0	0
E_2	2	$2\cos 2p\varphi$	$2\cos 2(p-1)\varphi$	$\cdots$	$2\cos 2\varphi$	0	0
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
E_{p-1}	2	$2\cos p(p-1)\varphi$	$2\cos(p-1)^2\varphi$	$\cdots$	$2\cos(p-1)\varphi$	0	0

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[25] Bethe, Ann. d. Physik **3**, 133 (1929).

[26] Mulliken, Phys. Rev. **43**, 279 (1933); Tisza, Zeits. f. Physik **82**, 48 (1933).

[27] Wilson, J. Chem. Phys. **2**, 432 (1934).

TABLE III. *Characters for the 32 crystallographic point groups and for the infinite cyclic and dihedral groups.*

$\mathbf{C}_1$	E
A	1

$\mathbf{C}_i$	$\mathbf{C}_2$	$\mathbf{C}_{1h}\equiv\mathbf{C}_s$	E	I
			E	C_2
			E	σ_h
A_g	A; z	A'; x, y	1	1
A_u; x, y, z	B; x, y	A''; z	1	−1

$\mathbf{C}_3$	E	C_3	C_3^2
A	1	1	1
E	1	ω	ω^2
	1	ω^2	ω

$\omega=e^{2\pi i/3}$

$\mathbf{C}_{3h}=\mathbf{C}_3\times\sigma_h$
$\mathbf{C}_{3i}\equiv\mathbf{S}_6=\mathbf{C}_3\times I$

$\mathbf{C}_4$	E	C_2	C_4	C_4^3
$\mathbf{S}_4$	E	C_2	S_4	S_4^3
A; z	1	1	1	1
B	1	1	−1	−1
E; $x\pm iy$	1	−1	i	$-i$
	1	−1	$-i$	i

$\mathbf{C}_{4h}=\mathbf{C}_4\times I$

$\mathbf{C}_6$	E	C_6	C_3	C_2	C_3^2	C_6^5
A	1	1	1	1	1	1
B	1	−1	1	−1	1	−1
E_1	1	ω^2	ω^4	1	ω^2	ω^4
	1	ω^4	ω^2	1	ω^4	ω^2
E_2	1	ω	ω^2	−1	$-\omega$	$-\omega^2$
	1	$-\omega^2$	$-\omega$	−1	ω^2	ω

$\omega=e^{2\pi i/6}=-\omega^4$ $\mathbf{C}_{6h}=\mathbf{C}_6\times I$

$\mathbf{C}_{2h}$	$\mathbf{C}_{2v}$	$\mathbf{V}\equiv\mathbf{D}_2$	E	C_2	σ_h	I
			E	C_2	σ_v	σ_v'
			E	C_2^z	C_2^y	C_2^x
A_g	A_1; z	A_1	1	1	1	1
B_g	B_2; y	B_3; x	1	−1	−1	1
A_u; z	A_2	B_1; z	1	1	−1	−1
B_u; $x\pm iy$	B_1; x	B_2; y	1	−1	1	−1

$\mathbf{V}_h\equiv\mathbf{D}_{2h}=\mathbf{V}\times I$

$\mathbf{D}_3$	E	$2C_3$	$3C_2'$
$\mathbf{C}_{3v}$	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2; z	1	1	−1
E; $x\pm iy$	2	−1	0

$\mathbf{D}_{3d}=\mathbf{D}_3\times I$

$\mathbf{D}_4$	E	C_2	$2C_4$	$2C_2$	$2C_2'$
$\mathbf{C}_{4v}$	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
$\mathbf{V}_d\equiv\mathbf{D}_{2d}$	E	C_2	$2S_4$	$2C_2$	$2\sigma_d$
A_1	1	1	1	1	1
A_2; z	1	1	1	−1	−1
B_1	1	1	−1	1	−1
B_2	1	1	−1	−1	1
E; $x\pm iy$	2	−2	0	0	0

$\mathbf{D}_{4h}=\mathbf{D}_4\times I$

$\mathbf{D}_6$	$\mathbf{C}_{6v}$	$\mathbf{D}_{3h}$	E	C_2	$2C_3$	$2C_6$	$3C_2$	$3C_2'$
			E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$
			E	σ_h	$2C_3$	$2S_6$	$3C_2$	$3\sigma_v$
A_1	A_1; z	A_1'	1	1	1	1	1	1
A_2; z	A_2	A_2'	1	1	1	1	−1	−1
B_1	B_2	A_1''	1	−1	1	−1	1	−1
B_2	B_1	A_2''; z	1	−1	1	−1	−1	1
E_2	E_2	E'; $x\pm iy$	2	2	−1	−1	0	0
E_1; $x\pm iy$	E_1; $x\pm iy$	E''	2	−2	−1	1	0	0

$\mathbf{D}_{6h}=\mathbf{D}_6\times I$

$\mathbf{T}$	E	$3C_2$	$4C_3$	$4C_3'$
A	1	1	1	1
E	1	1	ω	ω^2
	1	1	ω^2	ω
T	3	−1	0	0

$\omega=e^{2\pi i/3}$
$\mathbf{T}_h=\mathbf{T}\times I$

$\mathbf{O}$	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
$\mathbf{T}_d$	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
E	2	−1	2	0	0
T_2	3	0	−1	1	−1
T_1; x, y, z	3	0	−1	−1	1

$\mathbf{O}_h=\mathbf{O}\times I$

$\mathbf{D}_\infty$	E	$2C(\varphi)$	C_2
$\mathbf{C}_{\infty v}$	E	$2C(\varphi)$	σ_v
A_1	1	1	1
A_2	1	1	−1
E_1	2	$2\cos\varphi$	0
E_2	2	$2\cos 2\varphi$	0
..	.	…	…
E_k	2	$2\cos k\varphi$	0
..	.	…	…

$\mathbf{D}_{\infty h}=\mathbf{D}_\infty\times I$

difference being the order in which the representations and classes are written down. If the irreducible representations themselves, rather than the characters are desired they may be found in a paper by Seitz.[28]

The standard mathematical symbolism, used in the earlier part of our paper has been replaced by that used by Placzek[29] and Mulliken. Nondegenerate states are indicated by A, B; double degeneracy by E and triple degeneracy by T. States A are symmetrical while states B are antisymmetrical to a rotation by $2\pi/n$ around the principal n-fold axis, which is always in the z

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[28] Seitz, Zeits. f. Krist. **A88**, 433 (1934).

[29] Placzek, *Handbuch der Radiologie*, 2 Auflage, Band VI, Teil II (Leipzig, Akad. Verlagsges., 1934), p. 205ff.

direction. Different states of similar symmetry to reflection in a plane perpendicular to the principal axis are indicated by superscripts ′ and ″ and subscripts g and u refer to symmetry and antisymmetry with respect to a center of inversion.

The symbols for the classes have been explained at some length in §13. The number standing before the symbol for the class indicates the number of elements in that class and the sum of these numbers is the order of the group.

In addition to the groups given explicity some others are given outside the tables as the direct product of two groups. Their characters may be found as described in §20 and in addition to the states of the original group, which are g states there are an equal number of u states.

To aid in finding the selection rules, the transformation properties of x, y, z or $x\pm iy$, z have also been given. Where two or more groups are isomorphous and the states are the same (example, $\mathbf{D}_4$, $\mathbf{C}_{4v}$ and $\mathbf{V}_d$) the characters for the coordinates refer to the first group in that table. To obtain them for the other groups, one must change the sign for improper rotations, for example z transforms like A_2 for $\mathbf{D}_4$ but like A_1 for $\mathbf{C}_{4v}$ and like B_2 for $\mathbf{V}_d$.

THEORY OF VIBRATIONS OF POLYATOMIC MOLECULES

22. Introductory remarks

The problem is now to apply our knowledge of the symmetry properties of the molecule to the determination of vibration frequencies and of normal modes of vibration. There are two separate phases to this problem. First, we can determine the number and types of fundamental frequencies. We also have to ascertain the general characteristics of higher vibrational states. Furthermore, this phase includes finding the degree of the equation of which some particular frequency is a root. After this is known, we can proceed to obtain explicit expressions for the frequencies in terms of the nuclear masses and of the constants of the forces acting between the atoms. The qualitative results obtained previously should enable us to solve this second part of the problem in the least cumbersome fashion.

23. Number and types of fundamental vibration frequencies

Assume that the problem has been solved and that the kinetic and potential energies are given in terms of the $3N$–6 normal coordinates Q by:

$$\begin{aligned} T&=\tfrac{1}{2}\sum_i \dot{Q}_i^2+\tfrac{1}{2}\sum_k \sum_{\alpha=1}^{f_k} \dot{Q}_{k\alpha}^2, \\ V&=\tfrac{1}{2}\sum_i \lambda_i Q_i^2+\tfrac{1}{2}\sum_k \lambda_k \sum_{\alpha=1}^{f_k} Q_{k\alpha}^2. \end{aligned} \tag{40}$$

The coordinates denoted by two subscripts are f_k-fold degenerate.[30] There are f_k of them corresponding to *one* frequency $\sqrt{\lambda_k}$; f_k is the multiplicity of this frequency. Let the molecule be subjected now to a symmetry (covering) operation R. This purely geometrical procedure cannot possibly affect the physical state of the molecule therefore T and V are both invariant under R. Since the state of vibration is also unchanged, the only effect R can have on a nondegenerate coordinate Q_i is either to leave it unchanged, or else transform it into its negative. Symbolically this may be written:

$$RQ_i=\pm Q_i. \tag{41}$$

The same result can be obtained purely algebraically, since it is evident from the form of the expressions (40) that replacing Q_i by $-Q_i$ will leave the quadratic forms T and V invariant. The degenerate variables $Q_{k\alpha}$ are not defined uniquely, i.e., certain linear so-called orthogonal combinations of them are still normal coordinates.

Take, as an illustration, the very simple case:

$$T=\tfrac{1}{2}(\dot{Q}_1^2+\dot{Q}_2^2) \qquad V=\tfrac{1}{2}\lambda(Q_1^2+Q_2^2).$$

Any combination of Q_1 and Q_2 of the type $Q_1'=Q_1 \sin\vartheta+Q_2\cos\vartheta$ and $Q_2'=-Q_1\cos\vartheta+Q_2\sin\vartheta$ will leave T and V unchanged, as may be verified very easily by substitution. Hence, by definition, Q_1' and Q_2' are also normal coordinates corresponding to the frequency $\sqrt{\lambda}$.

The condition of invariance for T and V is satisfied if R transforms *each* $Q_{k\alpha}$ into a combination of all the coordinates corresponding to the same frequency $\sqrt{\lambda_k}$;

$$RQ_{k\alpha}=\sum_{\beta=1}^{f_k}\Gamma(R)_{k\alpha\beta}Q_{k\beta}; \quad (\alpha=1,2\cdots f_k). \tag{42}$$

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[30] Of course, it may happen that all the frequencies are single, in which case the double summations would not appear.

We may take each normal coordinate as the numerical quantity discussed in §15, whose behavior under various operations R gives us a representation of the group. We see from Eq. (41) that the representations associated with nondegenerate coordinates can consist only of ±1. Similarly Eq. (42) indicates that the representation corresponding to the f_k degenerate coordinates will be in matrix form, the dimensions of the matrix being the same as the multiplicity of the frequency.

Different coordinates may behave similarly under the various proper and improper rotations of the group; they must then all have the same representation, and the corresponding frequencies will be of the same type. The number of frequencies of a given type will hence be given by the number of times the corresponding irreducible representation occurs in the reduced form of the *complete representation* of the group referred to a particular molecule. Formula (28) gives this number explicitly in terms of the character $\chi(R)$ of the complete representation and the characters $\chi^{(k)}(R)$ of the irreducible representations. Since the quantities $\chi^{(k)}(R)$ are known for every symmetry group, the problem consists in finding $\chi(R)$ for every operation R. To do this we start by studying a general type of *physical* motion of the molecule. We may express this motion in terms of the displacements of each nucleus from its equilibrium position. Let the state then be described by: $\delta x_1, \delta y_1, \delta z_1, \cdots \delta x_i, \delta y_i, \delta z_i, \cdots \delta x_n, \delta y_n, \delta z_n$. It is to be stressed that all numerical indices refer to *fixed positions in space* and are not attached to any specific nuclei.[31] Apply a linear transformation to this system of variables. In a general case the new displacements $\delta x'$, $\delta y'$, $\delta z'$ will be given by:

$$\begin{aligned}
\delta x_1' &= g_{11}^{(xx)}\delta x_1 + g_{11}^{(xy)}\delta y_1 + g_{11}^{(xz)}\delta z_1 + \cdots \\
&\quad + g_{1n}^{(xx)}\delta x_n + g_{1n}^{(xy)}\delta y_n + g_{1n}^{(xz)}\delta z_n, \\
\delta y_1' &= g_{11}^{(yx)}\delta x_1 + g_{11}^{(yy)}\delta y_1 + g_{11}^{(yz)}\delta z_1 + \cdots \\
&\quad + g_{1n}^{(yx)}\delta x_n + g_{1n}^{(yy)}\delta y_n + g_{1n}^{(yz)}\delta z_n, \\
\delta z_1' &= g_{11}^{(zx)}\delta x_1 + g_{11}^{(zy)}\delta y_1 + g_{11}^{(zz)}\delta z_1 + \cdots \\
&\quad + g_{1n}^{(zx)}\delta x_n + g_{1n}^{(zy)}\delta y_n + g_{1n}^{(zz)}\delta z_n, \\
&\cdots\cdots\cdots\cdots\cdots\cdots \\
\delta z_n' &= g_{n1}^{(zx)}\delta x_1 + g_{n1}^{(zy)}\delta y_1 + g_{n1}^{(zz)}\delta z_1 + \cdots \\
&\quad + g_{nn}^{(zx)}\delta x_n + g_{nn}^{(zy)}\delta y_n + g_{nn}^{(zz)}\delta z_n.
\end{aligned} \tag{43}$$

where the indices attached to the various g's are self-explanatory. The matrix of the g's is the representation of this particular transformation and

$$\sum_{j=1}^{N}(g_{jj}^{(xx)} + g_{jj}^{(yy)} + g_{jj}^{(zz)}), \tag{44}$$

is its character. Let the transformation be an operation R of the symmetry group of the molecule which shifts a particle from the position j to the position k. The physical motion of this nucleus has not been affected by R; the only thing that could have been changed is the orientation in space of its displacement. The analytical expression of this fact is that $\delta x_k'$, $\delta y_k'$, $\delta z_k'$ can be a function only of δx_j, δy_j, δz_j.

$$\begin{aligned}
\delta x_k' &= \Gamma(R)_{kj}^{(xx)}\delta x_j + \Gamma(R)_{kj}^{(xy)}\delta y_j + \Gamma(R)_{kj}^{(xy)}\delta z_j, \\
\delta y_k' &= \Gamma(R)_{kj}^{(yx)}\delta x_j + \Gamma(R)_{kj}^{(yy)}\delta y_j + \Gamma(R)_{kj}^{(yz)}\delta z_j, \\
\delta z_k' &= \Gamma(R)_{kj}^{(zx)}\delta x_j + \Gamma(R)_{kj}^{(zy)}\delta y_j + \Gamma(R)_{kj}^{(zz)}\delta z_j.
\end{aligned} \tag{45}$$

The only diagonal terms in the representation for R that will be different from zero are the ones corresponding to nuclei whose equilibrium position in space is not changed by R.

As an illustration consider the case of a triatomic molecule YX_2 with the undisturbed atoms occupying the vertices of an isosceles triangle. As we see in Fig. 15, a reflection in the plane v, will leave the equilibrium position of the Y atom unchanged, but will change the orientation of its displacement. Thus in evaluating $\chi(R)$ we can consider the effect of R on a displacement separately for each particle where equilibrium position is not affected. The explicit expressions of the type (45) which connect $\delta x_k'$ with δx_j etc., depend of course on the orientation of the symmetry element (corresponding to the covering operation R) with respect to the cartesian coordinate system. The sum of the diagonal elements is, however, an invariant.[32] It suffices hence to find it for a simple case. A covering operation can be either a proper or an improper rotation. Let R be a rotation by an angle φ around the axis z. The operation may as usual be symbolized by $C(\varphi)$; the corresponding linear substitution is:

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[31] This is, of course, obvious from a quantum-mechanical point of view.

[32] Cf. §18.

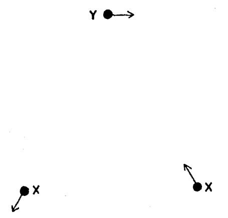

FIG. 15. Displacements of the nuclei of the YX_2 molecule from their equilibrium positions.

$$\begin{aligned} x' &= x\cos\varphi + y\sin\varphi, \\ y' &= -x\sin\varphi + y\cos\varphi, \\ z' &= z. \end{aligned} \tag{46}$$

The spur of $C(\varphi)$ is $1+2\cos\varphi$ and if u_C is the number of particles left unchanged by $C(\varphi)$, then the character of the complete representation of $C(\varphi)$ is: (we shall omit writing the angle φ wherever possible)

$$\chi(C) = u_C(1+2\cos\varphi). \tag{47}$$

If R is an improper rotation by φ around the z axis, $R \rightarrow S(\varphi)$, the equations of transformation are:[33]

$$\begin{aligned} x'' &= x\cos\varphi + y\sin\varphi, \\ y'' &= -x\sin\varphi + y\cos\varphi, \\ z'' &= -z, \end{aligned} \tag{48}$$

and the spur of $S(\varphi)$ is $-1+2\cos\varphi$. If, by analogy to the case of a proper rotation, we call the number of atoms left undisturbed by $S(\varphi)$, u_S, we obtain:

$$\chi(S) = u_S(-1+2\cos\varphi). \tag{49}$$

The characters given by the formulae (47) and (49) refer, however, to representations in terms of all the $3N$ variables. To get the character corresponding to the representation by means of the $3N$–6 normal coordinates, we have to subtract the characters of the motions of translation and rotation.

Consider first translation. The N vectors giving the displacements of the nuclei are by the laws of mechanics equivalent in this case to a resultant vector acting at the center of gravity of the molecule. The three components of this vector transform under R like any other displacements. Hence the character of a translation is $1+2\cos\varphi$ for $C(\varphi)$ and $-1+2\cos\varphi$ for $S(\varphi)$.

Let the displacements of the N particles now be such that they result in a physical rotation of the molecule as a whole. This state may be expressed by means of an angular momentum l acting on some point with the coordinates x, y, z. The three components of the angular momentum are:

$$\begin{aligned} l_x &= y\delta z - z\delta y, \\ l_y &= z\delta x - x\delta z, \\ l_z &= x\delta y - y\delta x. \end{aligned} \tag{50}$$

It may be shown (by means of general theorems about angular momenta or in a very straightforward if inelegant fashion by direct substitution) that l transforms under a rotation $C(\varphi)$ around the z axis in the following way:

$$\begin{aligned} l_x' &= l_x\cos\varphi + l_y\sin\varphi, \\ l_y' &= -l_x\sin\varphi + l_y\cos\varphi, \\ l_z' &= l_z. \end{aligned} \tag{51}$$

The effect of $S(\varphi)$ on the other hand is expressed by:

$$\begin{aligned} l_x'' &= -l_x\cos\varphi - l_y\sin\varphi, \\ l_y'' &= l_x\sin\varphi - l_y\cos\varphi, \\ l_z'' &= l_z, \end{aligned} \tag{52}$$

the character of the motion of rotation is thus $1+2\cos\varphi$ for $C(\varphi)$ and $1-2\cos\varphi$ for $S(\varphi)$.

Hence the character of the representation referring to the $3N$–6 normal coordinates

$$\begin{aligned} \Xi(C) &= \chi(C) - 2(1+2\cos\varphi) \\ &= (u_C-2)(1+2\cos\varphi), \end{aligned} \tag{53}$$

$$\begin{aligned} \Xi(S) &= \chi(S) - (-1+2\cos\varphi) \\ &\quad - (1-2\cos\varphi) = \chi(S) \\ &= u_S(-1+2\cos\varphi). \end{aligned} \tag{54}$$

Combining formulae (53) and (54), we obtain the number of times, $a^{(k)}$, a given representation, say $\chi^{(k)}$ occurs in the complete ($3N$–6) dimensional representation as:

$$\begin{aligned} a^{(k)} = (1/h)\{&\sum_C (u_C-2)(1+2\cos\varphi_C)\chi^{(k)}(C) \\ &+ \sum_S u_S(-1+2\cos\varphi_S)\chi^{(k)}(S)\}. \end{aligned} \tag{55}$$

---

[33] Wigner uses the expression "Drehspiegelung" which usually means rotary reflection to denote an operation known as perversion, i.e., a rotation followed by an inversion. A perversion by the angle φ is equal to an improper rotation by the angle $\pi+\varphi$. This difference has to be taken into account when comparing the formulae given here with those of Wigner.

The first summation extends over all proper rotations and the second over all the improper ones. The subscripts C and S have been added to φ to stress the fact that a different angle is involved for different terms in the summation. Since the quantities u, φ, and $\chi^{(k)}$ are identical for all conjugate elements, we can multiply the expressions under the summation sign by the number of elements in each class and sum only over the number of classes. (Cf. Eq. (29).)

To illustrate the preceding discussion we shall treat in detail the case of the ZYX_3 molecule, which has the shape shown in Fig. 17; this is the structure of CCl_3H, CH_3Br, etc. The symmetry group is $\mathbf{C}_{3v}$. We arrange in a table the characters of the group, the quantities φ_R and u_R for ($R=C(\varphi)$ and $R=S(\varphi)$); then $\pm 1+2\cos\varphi_R$ depending as to whether the rotation is a proper or an improper one. From these we obtain $\chi(R)$ and $\Xi(R)$.

	E	$2C_3$	$3\sigma_v$
$\chi^{(1)}$	1	1	1
$\chi^{(2)}$	1	1	-1
$\chi^{(3)}$	2	-1	0
φ_R	0	$2\pi/3$	0
u_R	5	2	3
$\pm 1+2\cos\varphi_R$	3	0	1
$\chi(R)$	15	0	3
Ξ	9	0	3

Now we apply formula (55) and obtain:

$$a^{(1)}=3 \qquad a^{(2)}=0 \qquad a^{(3)}=3.$$

Hence molecule ZYX_3 will have three frequencies corresponding to the representation $\chi^{(1)}$ and three corresponding to $\chi^{(3)}$. Frequencies of this last type of symmetry will be doubly degenerate.

24. Irreducible representations and states of the molecule

So far the preceding treatment has been purely classical. However, to discuss overtones we must introduce the quantum-mechanical point of view. As is well known[34] the energy of a molecule considered as a system of uncoupled harmonic oscillators with the fundamental frequencies $\omega_1, \omega_2 \cdots \omega_k$ is given by:

$$E=h\sum\omega_i(v_i+\tfrac{1}{2}), \tag{56}$$

and each set of numerical values assigned to the quantum numbers $v_1, v_2, \cdots v_k$ defines a state. We want to investigate the symmetry properties of such a state, denoted by n, i.e., the irreducible representation of the eigenfunction ψ_n associated with it. The explicit expression for ψ will depend on the potential function; the symmetry properties, however, are obviously something more fundamental. The irreducible representation of a state will be independent of the specific form of the Hamiltonian, provided the latter is invariant with respect to all the operations of the group. Hence we may investigate the simplest case, a system of uncoupled harmonic oscillators. The eigenfunction written in terms of the normal coordinates $Q_1 \cdots Q_j$, $Q_{i\alpha}$ etc., is:

$$\psi=\left[\exp\left(-\tfrac{1}{2}\sum c_iQ_i^2-\tfrac{1}{2}\sum_j c_j\sum_\alpha Q_{j\alpha}^2\right)\right] \times\Big\{\prod_i H_{v_i}(c_iQ_i)\Big\}\Big\{\prod_j\prod_\alpha H_{v_\alpha}(c_jQ_{j\alpha})\Big\}, \tag{57}$$

where Π, as usual, designates a product, $H_{v_i}(c_iQ_i)$ is a Hermitian polynomial of degree v_i in c_iQ_i, and $c_i=(2\pi\omega_i/h)^{\frac{1}{2}}$. The double subscripts refer, as before, to degenerate frequencies.

The exponential term is obviously invariant with respect to every symmetry operation, thus we have only to investigate the transformation properties of the product of Hermitian polynomials. Its representation is a direct product of the representations for the individual polynomials and the character is a product of their characters. For nondegenerate coordinates the following relations hold (as may be proved by referring to explicit formulas for Hermitian polynomials):

$$RH_{v_i}(c_iQ_i)=H_{v_i}(c_iQ_i) \quad \text{if } RQ_i=Q_i \tag{58a}$$

and

$$RH_{v_i}(c_iQ_i)=(-1)^{v_i}H_{v_i}(c_iQ_i) \quad \text{if } RQ_i=-Q_i. \tag{58b}$$

These give immediately the character of the product in the first bracket. For degenerate coordinates, the treatment is more complicated. If f_j is the degree of degeneracy, then for every value of j:

$$\prod_{\alpha=1}^{f} H_{v_\alpha}(c_jQ_{j\alpha})=\text{const. } Q_{j1}^{v_1}Q_{j2}^{v_2}\cdots Q_{jf}^{v_f} + \text{lower degree terms}, \tag{59}$$

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[34] For details concerning the quantum-mechanical treatment of the harmonic oscillator, reference may be made to any text on quantum mechanics.

where we omit the subscript on f. All terms for which the sum of the powers of the various Q's is the same, are of equal degree and they transform into one another under any operation of the group. The highest degree term gives the product of Hermitian polynomials unambiguously and so it is sufficient to know its transformation properties which will be the same as for the product. The characters for various values of f and

$$v=\sum_{\alpha=1} v_\alpha$$

of the product are given by the following formulas:[35]

$$\begin{aligned}
\chi_v(R)&=[\chi(R)]^v \quad \text{for } f=1, \text{ i.e., no degeneracy,}\\
\chi_v(R)&=\tfrac{1}{2}[\chi_{v-1}(R)\chi(R)+\chi(R^v)] \quad \text{for } f=2,\\
\chi_v(R)&=\tfrac{1}{3}\{2\chi(R)\chi_{v-1}(R)-\tfrac{1}{2}\chi_{v-2}(R)[\chi(R)]^2\\
&\quad+\tfrac{1}{2}\chi(R^2)\chi_{v-2}(R)+\chi(R^v)\} \quad \text{for } f=3. \qquad (60)
\end{aligned}$$

In the case of $\chi_1(R)$, we omit writing the subscript. In this symbolic notation $\chi_0(R)\equiv 1$ and $\chi_{-k}(R)\equiv 0$. The higher degrees of degeneracy $f=4$ and $f=5$ occur only for icosahedral groups; for explicit expressions for these cases, reference may be made to Tisza.[35]

25. The degree of the equation giving the fundamental frequencies

It remains only to determine the degree of the equation in λ. From the preceding discussion we would expect to obtain frequencies of the same type as the roots of the same equation and different type frequencies as the roots of different equations. Furthermore we might expect that a frequency with a f_i-fold degeneracy would come in as a root of multiplicity f_i, i.e., that the equation determining it would be repeated f_i times. We can actually prove this intuitional reasoning to be correct.

To do this we consider expression (4) for the potential energy:

$$V=\tfrac{1}{2}\sum_{i,j} K_{ij}s_is_j.$$

The same arguments hold for the kinetic energy function. Assume that the variables s have been chosen in a way to satisfy the symmetry requirements of the group, i.e., equations of the type (41) and (42). These variables which involve neither the masses nor the force constants might be called *geometrical symmetry* coordinates.[36]

Consider now any two nondegenerate variables, s_a and s_b, which belong to different irreducible representations. Among the operations of the group there is at least one R such that $Rs_a=s_a$, while $Rs_b=-s_b$, for if this were not the case s_a and s_b would belong to the same irreducible representation. The operation R thus transforms the product s_as_b into its negative, and the condition of invariance for V cannot be satisfied unless the coefficient of this product term vanishes.

For degenerate coordinates we shall make explicit use of the formalism of group theory. If every operation R of the group leaves a quantity s_ms_n invariant, i.e., if:

$$Rs_ms_n=s_ms_n, \qquad (61)$$

then, obviously:

$$\sum_R Rs_ms_n=hs_ms_n, \qquad (62)$$

where h is the order of the group. Conversely if Eq. (62) does not hold for any product s_ms_n, we may conclude that the latter is not invariant with respect to every operation of the symmetry group and hence cannot occur in the expressions for the kinetic and potential energies. Consider now two representations $\Gamma^{(i)}$ and $\Gamma^{(k)}$ with the respective dimensions f_i and f_k. Let $s_{i\alpha}$ and $s_{k\beta}$ be any two geometrical symmetry coordinates belonging to these representations; the equation of transformation for their product is

$$Rs_{i\alpha}s_{k\beta}=\sum_{\gamma,\,\eta}\Gamma^{(i)}(R)_{\alpha\gamma}\Gamma^{(k)}(R)_{\beta\eta}s_{i\gamma}s_{k\eta}. \qquad (63)$$

Summing with respect to R and making use of the orthogonality relations (26), we obtain

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[35] L. Tisza, Zeits. f. Physik **82**, 48 (1933).

[36] These geometrical symmetry coordinates are not to be confused with the *symmetry* coordinates introduced by Howard and Wilson, J. Chem. Phys. **2**, 630 (1934). These latter variables are functions of the masses and indicate motions which conserve angular and linear momentum. Their dependence on the masses makes their use very inconvenient for any isotope effect calculations.

$$\sum_R R s_{i\alpha} s_{k\beta} = \sum_R \sum_{\gamma,\,\eta} \Gamma^{(i)}(R)_{\alpha\gamma} \Gamma^{(k)}(R)_{\beta\eta} s_{i\gamma} s_{k\eta}$$

$$= \sum_{\gamma,\,\eta} s_{i\gamma} s_{k\eta} \sum_R \Gamma^{(i)}(R)_{\alpha\gamma} \Gamma^{(k)}(R)_{\beta\eta}$$

$$= \sum_{\gamma,\,\eta} s_{i\gamma} s_{k\eta} \delta_{ik} \delta_{\alpha\beta} \delta_{\gamma\eta} h/\surd(f_i f_k)$$

$$= \sum_{\gamma} s_{i\gamma} s_{k\gamma} \delta_{ik} \delta_{\alpha\beta} h/\surd(f_i f_k) \quad (64)$$

since all quantities are essentially real. It follows that no cross products may occur between coordinates belonging to different representations or between degenerate coordinates transforming according to different rows of the same matrix. If we have two coordinates, say $s_{i\alpha}$ and $s_{i\alpha}'$ which transform according to the same row of the matrix $\Gamma^{(i)}(R)$ of an irreducible representation, then according to Eq. (26),

$$\sum_R R s_{i\alpha} s_{i\alpha}' = \sum_{\gamma=1}^{f_i} (h/f_i) s_{i\gamma} s_{i\gamma}'. \quad (65)$$

Thus the product $s_{i\alpha} s_{i\alpha}'$ is itself not invariant, however, if we sum over all the f_i possible values of α, we obtain

$$\sum_R \sum_{\alpha=1}^{f_i} s_{i\alpha} s_{i\alpha}' = h \sum_{\gamma=1}^{f_i} s_{i\gamma} s_{i\gamma}'. \quad (66)$$

Hence $$\sum_{\alpha=1}^{f_i} s_{i\alpha} s_{i\alpha}'$$

is invariant with respect to every transformation of the group even though the individual terms are not. This means that all the products of the type $s_{i\alpha} s_{i\alpha}'$ have to come in with the same coefficient and that the potential function is the same function of $s_{i\alpha}$ as of $s_{i\beta}$.

Since the Hamiltonian written in terms of the geometrical symmetry coordinates does not contain any cross product terms between coordinates belonging to different representations, the determinantal equation (6) has the form shown in Fig. 16, where the solid blocks refer to irreducible representations and all the terms outside them are zero. Furthermore, the dimensions of any particular block, i.e., the degree of the resulting equation in λ is equal to the number of linearly independent symmetry coordinates associated with that representation. Corresponding to a representation of f_i dimensions there will be f_i identical blocks.

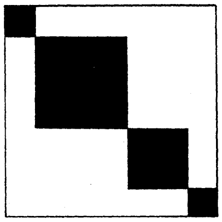

FIG. 16. Determinantal equation in reduced form.

26. The explicit solution of the vibration problem

The actual solution of any vibration problem requires a knowledge of the geometrical symmetry coordinates. For nondegenerate cases, these may be determined very easily; we simply choose such displacements of the atoms that will remain invariant under certain covering operations and transform into their negative under certain others, depending on whether the character of the operation is ±1 in this particular representation. Usually there may be an infinite number of sets of coordinates satisfying the symmetry requirements. However, only a small number of these will be linearly independent; we determine the number of coordinates corresponding to a given representation by the methods described in §23. Among the infinitely many sets, we select those that are most convenient for computation purposes. The procedure will be made clear in the case of the ZYX_3 molecule, which has been shown to have three doubly degenerate and three nondegenerate frequencies. We shall indicate both the algebraic and geometrical methods of finding the geometrical symmetry coordinates. The nondegenerate case corresponds to the representation $\Gamma^{(1)}$, where all the characters are $+1$. Hence all the coordinates should be invariant both with respect to rotations around the threefold axis and to reflections in the perpendicular planes. If we number the X atoms 1, 2, and 3 and assign the numbers 4 and 5, respectively, to Z and Y, then our nondegenerate coordinates will be linear combinations of the mutual displacements of the particles, the δq_{ij}'s, which are invariant with

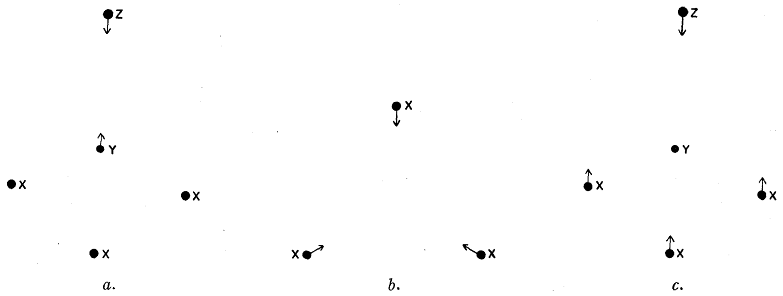

FIG. 17. Geometrical symmetry coordinates for the parallel vibrations of the molecule ZYX_3.

respect to all permutations of the numbers 1, 2, and 3. For example, we could choose

$$s_1=\delta q_{45},\quad s_2=\delta q_{14}+\delta q_{24}+\delta q_{34},$$
$$s_3=\delta q_{12}+\delta q_{13}+\delta q_{23},$$

or any linear combinations of these three. On proceeding purely geometrically, we could select the displacements indicated in Figs. 17*a*, *b*, and *c*. Fig. 17*c* shows the motions in the plane of the X atoms.

The construction of degenerate coordinates with the suitable symmetry is usually somewhat more laborious. However, the following remarks should prove helpful in any special problem. We shall limit the discussion to two and threefold degeneracy, since these are, apparently, the only ones important physically. Hence we may always assume our variables to be mutually orthogonal. For all the groups, the entire set of symmetry elements intersects in a line (example $\mathbf{C}_{3v}$) or in a point, which need not, however, be a center of inversion (cf. $\mathbf{T}_d$). If any atom is located at the point or on the line of intersection, then its equilibrium position is not affected by any of the group operations. The three components of its displacement transform under all the operations of the group like the components of a vector; the transformation matrices constitute a representation.[37] Hence the components of the displacement of such an atom form a set of degenerate geometrical symmetry coordinates. If there are more sets of degenerate variables belonging to a given representation than there are atoms on the line of intersection of the symmetry elements, we must use other methods of obtaining them. From the preceding set, we know the actual matrices of the representation and not only the characters as given by the tables, and this should greatly facilitate the problem. Also in some cases the solution may have been worked out for a molecule with the same symmetry but with a smaller number of atoms than the problem under consideration, so that we can use the results obtained there. We shall again illustrate the preceding remarks on the case of the ZYX_3 molecule. The three vertical symmetry planes of the $\mathbf{C}_{3v}$ group intersect in the z axis, the axis of threefold rotation. The Z and Y atoms are located on this line, hence their displacement in the x and y directions are geometrical symmetry coordinates. For the third variable belonging to this two-dimensional representation, we can make use of the result for the X_3 molecule.[38] The coordinates are shown in Figs. 18*a*, *b* and *c*.

With the knowledge of symmetry coordinates the problem is practically solved. We could write the potential energy expression V of required symmetry with arbitrary constants A, B, etc., in terms of the variables s_1, s_2, etc. From the discussion in §25, it follows that V is the sum of the most general quadratic forms in the coordinates associated with one representation. Since a quadratic form in n variables has $n(n+1)/2$

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[37] If the z axis is the only axis with a multiplicity $n\geqq 3$, then δz always transforms like ± 1, and there is no representation of higher degree than the second.

[38] The results for X_3 may themselves be obtained from those for YX_2 with the symmetry group $\mathbf{C}_v$, where all the representations are one-dimensional.

coefficients, for a molecule with r representations and b_i frequencies belonging to $\Gamma^{(i)}$, the total number of constants in the potential energy expression is

$$\sum_{i=1}^{r} b_i(b_i+1)/2.$$

However, since our physical and chemical ideas of intramolecular forces are bound up with the distances between the atoms, we may have to start by expressing V in terms of the δq_{ij} (cf. Eq. (1)) and then transforming to the variables s. This transformation gives us the connection between the general constants A, B, etc., and the "physical" constants $k_{iji'j'}$.

To obtain the expression for the kinetic energy, it may prove necessary to go through the very general and rather elaborate procedure sketched in the introduction.[39] However, in many cases it is possible to find T directly in terms of the variables s by means of simple dynamical theorems.

Knowing both T and V, we only have to expand the determinantal equation (6) to have the complete solution of the vibration problem.

Selection Rules

27. Frequencies active in the infrared

Let the electric moment of the molecule have the three components X, Y and Z. The probability of a transition from a state n to a state m is known to be proportional to:

$$P_{nm}^2 = X_{nm}^2 + Y_{nm}^2 + Z_{nm}^2, \tag{67}$$

where X_{nm} is a matrix element and is given by:

$$X_{nm} = \int \bar{\psi}_n X \psi_m d\tau. \tag{68}$$

If $P_{nm}=0$, the transition cannot occur but if $P_{nm} \neq 0$, while $X_{nm}=Y_{nm}=0$, the radiation is polarized in the z direction. To find the selection rules, we must determine for which values of n and m, the matrix elements will be different from zero.

The x component of the electric dipole moment is $\sum e_i x_i$, where e_i is the charge on the ith particle, x_i the x component of its distance from some fixed point, and the summation extends over *all the nuclei and all the electrons*. In this form, however, we cannot possibly use X for any calculations, since we do not know the electronic eigenfunctions. As an approximation, we may consider the dipole moment to be a function of the effective charges and displacements of the various atoms. It will be taken for granted that the electric moment, like the potential energy, has the same symmetry as the geometrical configuration; and we shall assume that if we expand it as a Taylor's series in terms of the displacements, all the terms beyond the linear ones may be neglected as being small. All the selection rules to be derived are based on this assumption which seems to be valid for diatomic molecules and hence is probably a good approximation to the polyatomic case. Since we are not interested in the permanent electric moment, we shall write:

$$X = \sum e_i \delta x_i, \tag{69}$$

or more conveniently in terms of the normal coordinates:

$$X = \sum \epsilon_i^{(x)} Q_i. \tag{70}$$

The summation is over all $3N$ normal coordinates, but the ones due to translation and rotation are of no importance and may be discarded. It is more convenient to study the electric moment, P itself rather than just one of its components, and so we shall write:

$$P = \sum \epsilon_i Q_i. \tag{71}$$

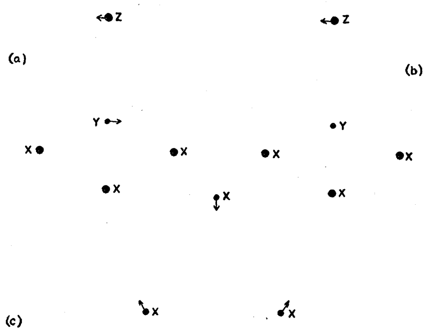

FIG. 18. Geometrical symmetry coordinates for the perpendicular vibrations of the molecule ZYX$_3$.

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[39] For a more detailed discussion of this method of finding the expression for the kinetic energy, reference may be made to J. E. Rosenthal, Phys. Rev. 45, 538 (1934).

In general, to evaluate integrals of the type (68) as functions of the $\epsilon_i^{(x)}$'s etc., we must know the wave functions ψ_m and ψ_n explicitly, and whenever the intramolecular forces are not harmonic, this may involve a long and laborious perturbation calculation. However, if we are interested only in the vanishing or nonvanishing of the matrix elements X_{nm}, we can determine that from symmetry considerations alone.

We shall begin by studying the transformation properties of the electric moment P under the various operations of the group. By definition P is a vector, hence it transforms as (46) under a rotation and as (48) under an improper rotation. Hence its character is either

$$\chi_P(C)=1+2\cos\varphi_C \tag{72}$$

or

$$\chi_P(S)=-1+2\cos\varphi_S. \tag{73}$$

We could investigate the transformation properties of P starting with expression (71). Purely formally we would get:

$$\Gamma_P(R)=\sum a_P^{(i)}\Gamma^{(i)}(R) \tag{74}$$

and

$$\chi_P(R)=\sum a_P^{(i)}\chi^{(i)}(R). \tag{74a}$$

The a_P's in these equations may be determined in the usual case by inspection. The quantities $\pm 1+2\cos\varphi$ are found for each class and they will be a sum of characters contained in the group. As an example, these quantities for the group C_{3v} are 3, 0, 1. This is immediately seen to be A_1+E, so $a^{(1)}=a^{(3)}=1$; $a^{(2)}=0$. The numerical value of $a_P^{(i)}$ indicates how many normal coordinates belonging to the irreducible representation occur in Eq. (71).

We have thus transformation properties of the electric moment. Since Γ_P is three-dimensional, it can consist either of 3 one-dimensional representations, 1 one-dimensional and 1 two-dimensional, or 1 three-dimensional one. It should be pointed out that the transformation properties of the electric moment depend exclusively on the symmetry group of the molecule and not on the number of atoms in it.

The components X, Y and Z of P transform like the corresponding coordinates, x, y and z. Hence in the case of the two-dimensional representations it is more convenient to consider $X\pm iY$, rather than X or Y separately. For three-dimensional representations, we would have to consider linear combinations of X, Y and Z. However, if we disregard the icosahedral groups which do not seem to have any physical application, three-dimensional representations occur only for the tetrahedral or octahedral groups. There the x, y, and z directions are equivalent so that $X=Y=Z$. In any case, we may associate a component of the electric moment with one of its irreducible representation.

We consider now the integral (68). At first, we shall limit the discussion to the case of transitions from the normal state only.

$$X_{n0}=\int\bar{\psi}_n X\psi_0 d\tau. \tag{75}$$

The eigenfunction of the ground state remains by definition invariant under every operation of the group. These operations must also leave integral (75) unaffected. This is possible (cf. the detailed discussion in §20) if and only if ψ_n and X transform alike under every operation. Thus if we know the irreducible representations of X, we also know immediately all the states that are active in the infrared.

For the general case, we have as in §20 to make more explicit use of the formalism of group theory. The integral (68) will be invariant under all the elements of the group only if ψ_n and $X\psi_m$ transform alike and we know from §20 that if ψ_m transforms like $\Gamma^{(j)}(R)$ and X like $\Gamma^{(i)}(R)$, then the product $X\psi_m$ transforms like the direct product,

$$\Gamma^{(i)}(R)\times\Gamma^{(j)}(R)=\sum a^{(k)}\Gamma^{(k)}(R). \tag{76}$$

Physically this means that the quantity $X\psi_m$ may be considered to have different components each of which transforms according to an irreducible representation. The quantity $\bar{\psi}_n X\psi_m$ is invariant, i.e., $X_{nm}\neq 0$ and the transition is permitted if and only if the representation of $\bar{\psi}_n$ is contained among the representations on the righthand side of Eq. (76). Thus all we have to do is to find out which of the $a^{(k)}$ do not vanish. If we use the characters instead of the representations, we may write

$$\chi^{(i)}(R)\times\chi^{(j)}(R)=\sum_k a^{(k)}\chi^{(k)}(R). \tag{76a}$$

There are r such equations corresponding to the r classes. Usually, however, it is not necessary to solve these equations for the $a^{(k)}$ may be found by simple inspection.

An example, with the group $\mathbf{C}_{\infty v}$ will illustrate the use of the rules. Let us choose characters corresponding with state, A_1 and electric moment, Z which also transforms like A_1. The characters in both cases are 1, 1, 1 and forming the direct product, we have

$$Z\times A_1=A_1,$$

giving the selection rule, $A_1\rightarrow A_1$. For the state, A_2 we obtain $A_2\rightarrow A_2$, and for a state E_k, we have

$$Z\times E_k=E_k$$

and $$E_k\rightarrow E_k. \qquad k\neq 0$$

For an electric moment, $X\pm iY$, the characters are 2, 2 cos φ, 0. Multiplying by the characters for the states A_1, A_2 and E_k, we find the selection rules

$$A_1\rightarrow E_k$$
$$A_2\rightarrow E_k$$

and $$(X\pm iY)\times E_k=E_{k+1}+E_{k-1}$$

so, $$E_k\rightarrow E_{k'} \qquad k\pm k'=\pm 1.$$

28. The Raman effect

In order to determine the selection rules for the Raman effect, the integral

$$\alpha_{nm}=\int\bar{\psi}_n\alpha\psi_m d\tau$$

must be investigated, where α is the polarizability of the molecule. If this integral vanishes, the corresponding transition is forbidden just as in the infrared spectrum and symmetry consideration alone enable us to determine which lines are permitted in the same way as above for the infrared. The polarizability is a symmetric tensor of the second rank and thus has 6 components which transform under the proper and improper rotations of the group elements like the products of the corresponding vectors. When we use Eqs. (46) and (48) we find the equations of transformation to be:

$$\left.\begin{aligned}
\alpha_{zz}'&=\alpha_{zz},\\
(\alpha_{xx}'+\alpha_{yy}')&=(\alpha_{xx}+\alpha_{yy}),\\
(\alpha_{xx}'-\alpha_{yy}')&=(\alpha_{xx}-\alpha_{yy})\cos 2\varphi+2\alpha_{xy}\sin 2\varphi,\\
\alpha_{xy}'=\alpha_{yx}'&=-\tfrac{1}{2}(\alpha_{xx}-\alpha_{yy})\sin 2\varphi+\alpha_{xy}\cos 2\varphi,\\
\alpha_{xz}'=\alpha_{zx}'&=\pm\alpha_{xz}\cos\varphi\pm\alpha_{yz}\sin\varphi,\\
\alpha_{yz}'=\alpha_{zy}'&=\mp\alpha_{xz}\sin\varphi\pm\alpha_{yz}\cos\varphi,
\end{aligned}\right\}\quad(77)$$

where the upper (lower) signs are to be taken for proper (improper) rotations. Here, as in the case of the electric moment, it is found more convenient to take linear combinations of the components of the polarizability. If we sum the diagonal elements of Eq. (77), we obtain $2\pm 2\cos\varphi+2\cos 2\varphi$ with the plus (minus) sign for proper (improper) rotations and this is the character for α, which by analogy with Eq. (74) and (74a), enables us to determine to irreducible representations of the polarizability. These correspond as before directly to those states having active Raman frequencies. The lines are polarized in accordance with the subscripts on the components of the polarizability, whose matrix element does not vanish.

In addition to the selection rules, some further information about the Raman lines may be obtained from symmetry considerations. The polarizability may be written

$$\alpha=\alpha'+\alpha'',$$

where α' is called the average polarizability and α'' is a factor of anisotropy. These two parts are independent and additive for the polarizability and the molecule can be considered as a mixture of two kinds of molecules, part of them having the polarizability, α' and the rest having α''. If the incident light is polarized, molecules of the first kind will produce completely polarized scattered light but the molecules of the second type will result in scattered light polarized perpendicular to the direction of the original beam. If the scattered light is then investigated with a Nicol prism, parallel and perpendicular to the polarization of the incident light, the two parts of the polarizability may be distinguished. The ratio of the intensity of the two kinds of scattering is called the degree of depolarization and is given by

$$\rho=3\alpha''^2/(5\alpha'^2+4\alpha''^2) \qquad (78)$$

for linearly polarized light and for unpolarized light

$$\rho_n=2\rho/(1+\rho). \qquad (79)$$

From (78), it is seen that ρ varies between 0, where $\alpha''=0$ and $\frac{3}{4}$ where $\alpha'=0$. Under the rotational operations of the group, the quantity α' transforms like $\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$ and so will disappear unless this quantity is invariant. It is apparent that it will be invariant only for a totally symmetric state which corresponds with the identical representation of the groups. These have been designated A_1 in our tables and hence all permitted Raman lines except those for states A_1 will have $\rho=\frac{3}{4}$ and $\rho_n=6/7$.

The anisotropic factor of the polarizability transforms under the group in a more complicated way than α' and in the general case, nothing can be said about it from symmetry considerations. In the special case of cubic groups and for totally symmetric states, the symmetry is spherical and the anisotropy factor disappears. From Eq. (78) it is seen that

$$\rho=\rho_n=0.$$

For other cases of totally symmetric functions, we can only say that

$$0\leq\rho\leq\tfrac{3}{4}.$$

29. Tables for selection rules

The results for the selection rules may be collected together in a general set of tables. The transformation properties of the components of the electric moment and the polarizability will be found in Table IV. These states, as shown before are the frequencies active in the infrared or the Raman effect.

The overtone bands will be found in Table V, where a symbol like $[E_k]^v$ represents the vth overtone of the state, E_k and the irreducible parts are given. These have all been obtained from Eq. (60). It should be noted that E_k is only defined up to E_p or E_{p-1} (see Tables I and II). For $p=5$, for instance, $E_p=E_0$, $E_{p+1}=E_1$, $E_{p+2}=E_2$, $\cdots E_{p+5}=E_0$, $\cdots$.

The representation for the combination states, direct products of the irreducible representations, are given in Table VI. This is to be read as an ordinary multiplication table. The states are all commutative and the direct product of E_k and E_j, for instance will be found at the intersection of the row and column headed by those two symbols. One must apply the rules given above to decide which of the given states are active.

CONCLUSION

For the results of the application of group theory to vibrations, we refer to a paper by Wilson[34] in which he has tabulated the number of frequencies, degeneracy, selection rules and other properties for the normal vibrations of a large number of molecules. The molecules included, contain from three to nine atoms and comprise most of the ones which are liable to be observed experimentally. Explicit solutions, including isotopic shifts have been worked out by the group theoretical and other methods for molecules of the type YX_2, YX_3, YX_4, Y_6X_6 and some others, references to the papers being too numerous to mention here. The Raman effect has been discussed in great detail by Placzek,[29] who uses a method equivalent, but not identical with the group theory one.

Electronic states for many polyatomic molecules have been treated by Mulliken[26] in a series of papers, using the group theory method. Rotational states[40] have not been discussed at

TABLE IV. *Transformation properties of the components of the electric moment and of the polarization tensor.*

	$\mathbf{C}_i$	$\mathbf{C}_{1h}$	$\mathbf{C}_{nv}$[a]	$\mathbf{D}_n$[a]	$\mathbf{S}_{nv}$[b]	$\mathbf{O}$	$\mathbf{T}_d$
X, Y	A_u	A'	—	—	—	T_1	T_2
Z	A_u	A''	A_1	A_2[c]	B_1	T_1	T_2
$X\pm iY$	—	—	E_1[d]	E_1[c]	E_1	—	—
α	A_g	—	—	—	—	A_1+E+T_2	
α_{ii}, α_{xy}	—	A'	—	—	—	—	—
α_{xz}, α_{yz}	—	A''	E_1[d]	E_1	$E_{n/2-1}$	—	—
$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$	—	—	A_1	A_1	A_1	—	—
$\alpha_{xx}-\alpha_{yy}, \alpha_{xy}$	—	—	E_2[e]	E_2[e]	E_2	—	—

[a] $n=\infty$ or 2, 3, 4, $\cdots$

[b] $n=2, 3, 4, \cdots$

[c] for $n=2$; $A_2=B_1$; $E_1=B_2+B_3$

[d] for $n=2$; $E_1=B_1+B_2$

[e] for $n=4$; $E_2=B_1+B_2$; for $n=3$; $E_2=E_1$

TABLE V. *Overtones.*

$\mathbf{C}_i$, $\mathbf{C}_{1h}$;[a] $$[A']^{v_1}\times[A'']^{v_2}=A'^{v_1}\times A''^{v_2}=\begin{cases}A', & v_1 \text{ even}\\ A'', & v_1 \text{ odd}\end{cases}$$

Other groups:[b] $$[A_1]^v=A_1{}^v=A_1$$

$$[A_2]^v=A_2{}^v=\begin{cases}A_1, & v \text{ even}\\ A_2, & v \text{ odd}\end{cases}$$

$$[E_k]^v=\begin{cases}A_1+E_{2k}+E_{4k}+\cdots+E_{vk}, & v \text{ even}\\ E_k+E_{3k}+E_{5k}+\cdots+E_{vk}, & v \text{ odd}\end{cases}$$

For groups, $\mathbf{T}_d$ and $\mathbf{O}$, the E state transforms like the E state for $\mathbf{C}_{3v}$; for T states, see Tisza, reference 35.

[a] Combination bands are the same for these groups.

[b] Finite and continuous groups.

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[40] Casimir, *Rotations of a Rigid Body in Quantum Mechanics* (J. B. Wolters, Groningen, 1931); Jahn, Ann. d. Physik **23**, 529 (1935).

TABLE VI. *Combination bands.*

	A_1	A_2	E_1	$\cdots$	E_k	T_1	T_2
A_1	A_1	A_2	E_1	$\cdots$	E_k	T_1	T_2
A_2		A_1	E_1	$\cdots$	E_k	T_2	T_1
E_1			E_0+E_1	$\cdots$	$E_{k+1}+E_{\|k-1\|}$	T_1+T_2	T_1+T_2
$\cdot\cdot$	$\cdot\cdot$	$\cdot\cdot$	$\cdot\cdot$		$\cdot\cdot$	$\cdot\cdot$	$\cdot\cdot$
E_j					$E_{k+j}+E_{\|k-j\|}$	$\cdot\cdot$	$\cdot\cdot$
T_1						$A_1+E+T_1+T_2$	$A_2+E+T_1+T_2$
T_2							$A_1+E+T_1+T_2$

$E_0=A_1+A_2$ $E_{n/2}=B_1+B_2$
$B_1^2=B_2^2=A_1$ $B_1\times B_2=A_2$

great length but Wilson[41] has given the method for calculating the statistical weights of rotational levels and has applied it to several special molecules. The group theoretical method has been applied to many problems of diatomic molecules and atoms. A complete review of the subject and references to the original literature may be found in the books of van der Waerden[4] for the molecular case and Wigner[4] for the atomic one.

The advantage of the use of group theory in all problems of this kind may be summed up in the following remarks. To find the energy levels of a given system, one must, in general, solve the wave equation but this can be done exactly only in a few simple cases and even approximately only with some difficulty. On the other hand, the wave functions must be invariant to the interchange of equivalent electrons and nuclei as well as to certain rotations of the type considered here. In the language of group theory, the corresponding energy levels will then belong to the irreducible representations of the permutation group or the proper finite or continuous rotation group. From only a knowledge of the symmetry properties of the wave functions considerable information may be obtained about the energy levels without the necessity of solving a differential equation or performing a lengthy perturbation calculation.

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[41] Wilson, J. Chem. Phys. 3, 276 (1935).