Chapter

3 BASIC THEORY AND APPLICATIONS OF SYMMETRY REPRESENTATIONS (NON-ABELIAN SYMMETRY GROUPS)

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CHAPTER 3

BASIC THEORY AND APPLICATIONS OF SYMMETRY REPRESENTATIONS (NON-ABELIAN SYMMETRY GROUPS)

So far we have considered symmetry operations which commute with each other ($gh = hg$), i.e., groups which are Abelian. It has been shown how one can expand all operators of any Abelian group in combinations of a single set of orthogonal idempotent operators. Several examples have been given in which the Abelian idempotent operators help to solve physical problems.

However, many of the most interesting problems involve non-Abelian symmetry groups, that is, groups having some operators which do not commute. In Figure 3.1.1 the non-Abelian crystal point symmetries are listed and modeled. Note that half of the possible crystal symmetries and all of the larger groups are non-Abelian.

It will now be shown how to generalize the idea of the idempotent expansions to include these more complicated symmetry groups and related physical problems. The simplest examples that illustrate each point will be used in the development of this theory.

3.1 SIMPLEST EXAMPLES OF NON-ABELIAN SYMMETRY

A. Trigonal Symmetries C_{3v} and D_3

The smallest non-Abelian symmetries are the groups C_{3v} and D_3 with each having just six elements. C_{3v} is the full symmetry of the three-pendulum system which was discussed in Section 2.6. The theory there involved only the symmetry C_3, which is a subgroup of C_{3v} (the line between C_3 and C_{3v} in Figure 3.1.1 indicates that C_3 is contained in C_{3v}; i.e., $C_3 \subset C_{3v}$). The operators of C_{3v} which were neglected in Section 2.6 are the three vertical
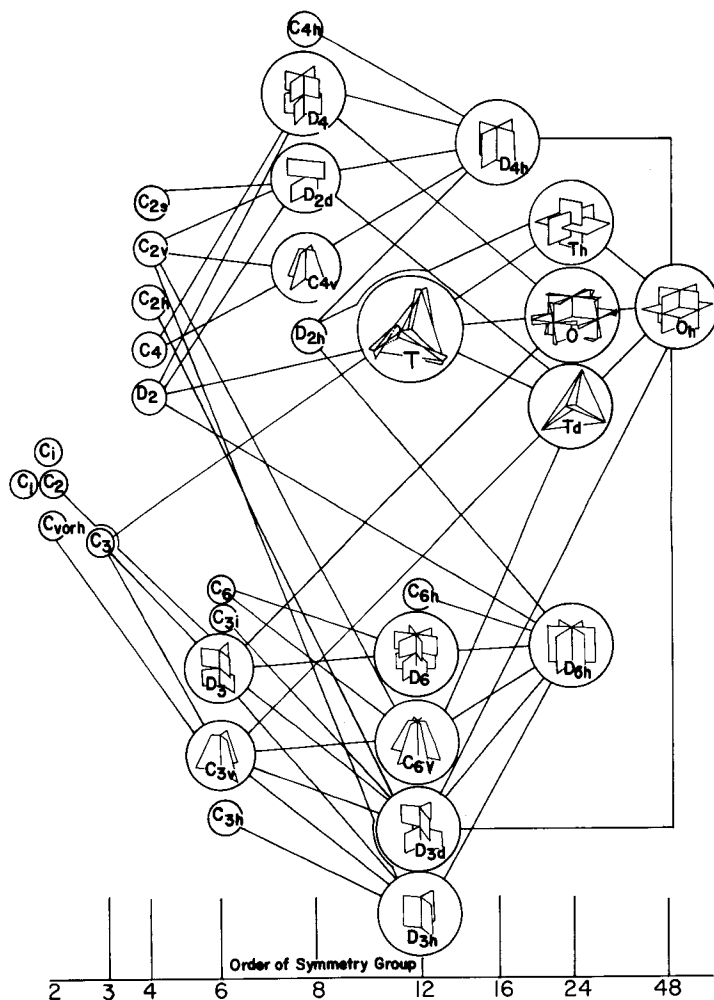
Figure 3.1.1 Crystal point symmetry groups. Models are sketched in circles for the 16 non-Abelian groups. (See also Figure 2.11.1.)

mirror-plane reflection operators labeled by σ_1, σ_2, and σ_3 in Figure 3.1.2. (See also Figure 3.1.3.) On the left-hand side of Figure 3.1.2 there are pictures of the pendulum bobs frozen in some nonequilibrium position state. Then the effect of the reflection operators on the positions of the pendulums are shown by the pictures in the center of Figure 3.1.2. The effect of σ_2 followed by σ_1 is a counterclockwise $120°$ rotation (r^2). These results may be expressed by the group product relations $(\sigma_1\sigma_2 = r)$ and $(\sigma_2\sigma_1 = r^2)$.

For non-Abelian groups, the order of the operations makes a big difference. We shall define a group product ab to mean b acts first, followed by a
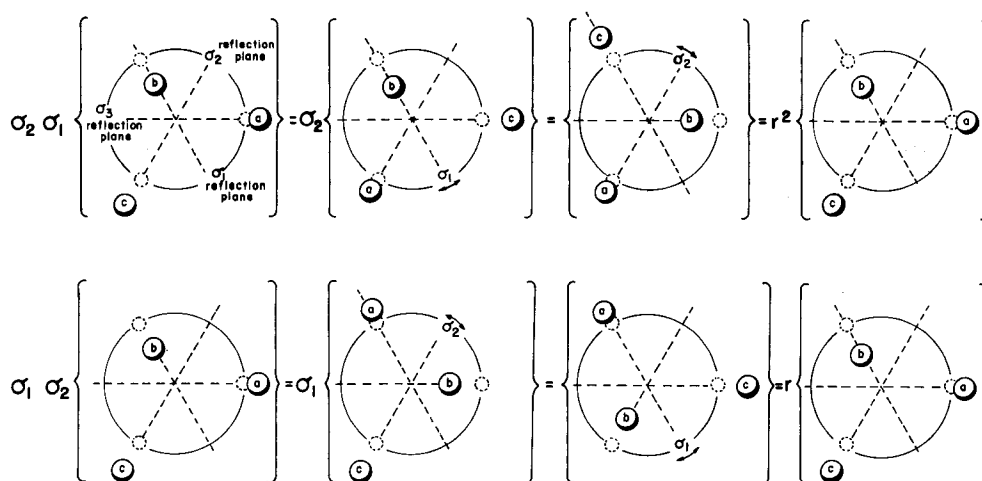
Figure 3.1.2 Effects of plane reflections on pendulum mass configuration. The effects of the products of reflection operations σ_1 and σ_2 taken in different orders are shown. Note that the reflection planes are fixed on the page, while the pendulum masses get moved.

on an operand sitting to the right of the operations. The complete multiplication table for all the C_{3v} operations is

	1	r	r^2	σ_1	σ_2	σ_3
1	1	r	r^2	σ_1	σ_2	σ_3
r	r	r^2	1	σ_3	σ_1	σ_2
r^2	r^2	1	r	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	1	r	r^2
σ_2	σ_2	σ_3	σ_1	r^2	1	r
σ_3	σ_3	σ_1	σ_2	r	r^2	1

$$(3.1.1)$$

By replacing the reflections σ_1, σ_2, and σ_3 with $180°$ rotations ρ_1, ρ_2, and ρ_3 around axes normal to the σ_j planes one obtains the symmetry group D_3. Objects of D_3 and C_{3v} symmetry are compared in Figure 3.1.3. Note that each reflection operation σ_j in C_{3v} is related to its rotational counterpart ρ_j in D_3 by the equations

$$\sigma_j = I\rho_j = \rho_j I, \qquad \rho_j = I\sigma_j = \sigma_j I, \qquad (3.1.2)$$
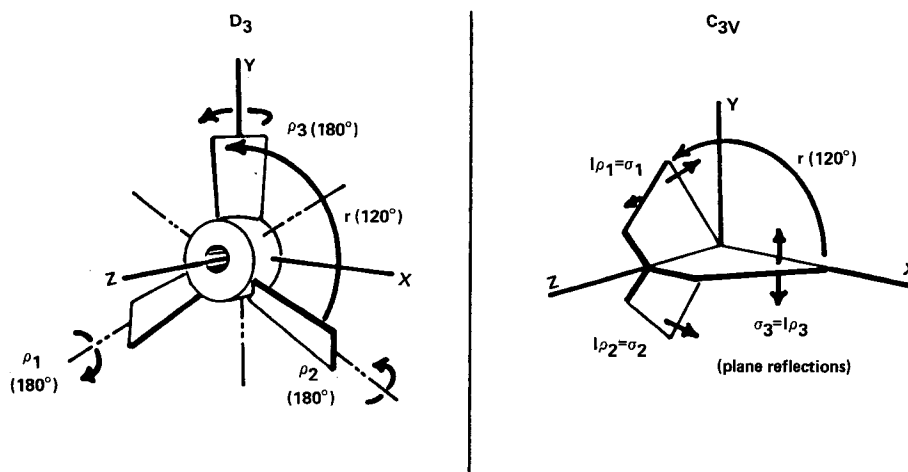
Figure 3.1.3   Pictorial comparison of D_3 and C_{3v} symmetry. A propeller having D_3 symmetry is shown next to a three-plane paddle having C_{3v} symmetry. The group operations are labeled by arrows, which indicate the effect they have. For example, ρ_3 is a 180° rotation around the y axis, while $I\rho_3 = \sigma_3$ is a reflection through the xz plane. (Here axes are fixed and the objects rotate.)

involving inversion I. [Recall Eq. (2.11.4).] Since I commutes with all point-group operations, the relation between D_3 and C_{3v} is easily established. For example, the product $(\sigma_1\sigma_2 = r)$ implies that $(I\rho_1 I\rho_2 = r)$ or $(\rho_1\rho_2 = r)$, since $I^2 = 1$. In this way one sees that D_3 has the same multiplication table, aside from a change in notation, as C_{3v}; i.e., D_3 is isomorphic to C_{3v}. Mathematicians have shown that there is only one abstract non-Abelian group of order 6.

B. Reflections and Hamilton's Turns

There are some easy ways to visualize and compute point-group products. Consider first the product of mirror reflections. Imagine two planes: an xz plane, and another ϕz plane which makes an angle ϕ with the xz plane while intersecting it along the z axis. The matrix representations of reflections σ_{xz} and $\sigma_{\phi z}$ may be obtained from geometry as shown in Figure 3.1.4. The effect of mirror reflections on the unit vectors $|x\rangle$ and $|y\rangle$ is shown. The reflection planes intersect along the z axis, which is normal to the figure. Hence, we have $\sigma_{\phi z}|z\rangle = |z\rangle$ for all angles ϕ.

The product of reflections represented in the $\{|x\rangle, |y\rangle\}$ basis is as follows:

$$\langle \sigma_{\phi z}\sigma_{xz}\rangle = \begin{pmatrix} \cos 2\phi & \sin 2\phi \\ \sin 2\phi & -\cos 2\phi \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} \cos 2\phi & -\sin 2\phi \\ \sin 2\phi & \cos 2\phi \end{pmatrix} = \langle R[2\phi]\rangle.$$

$$\langle \sigma_{xz} \rangle = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\langle \sigma_{\phi z} \rangle = \begin{pmatrix} \cos 2\phi & \sin 2\phi \\ \sin 2\phi & -\cos 2\phi \end{pmatrix}$$

$\sigma_{\phi z} | x \rangle = \cos 2\phi | x \rangle + \sin 2\phi | y \rangle$

$\sigma_{xz} | x \rangle = | x \rangle$

$\sigma_{xz} | y \rangle = -| y \rangle$

$\sigma_{\phi z} | y \rangle = \sin 2\phi | x \rangle - \cos 2\phi | y \rangle$

(a) xz—PLANE REFLECTION
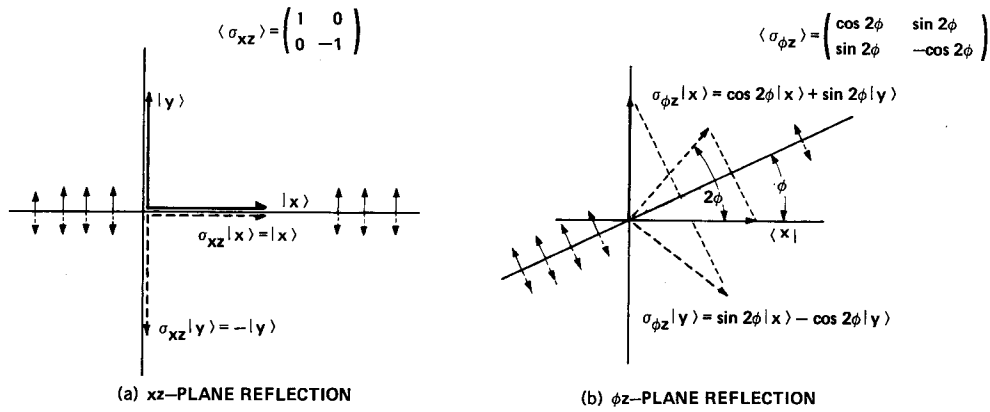
(b) ϕz—PLANE REFLECTION

Figure 3.1.4 Representations of mirror plane reflection operators (a) $\langle \sigma_{xz} \rangle$, (b) $\langle \sigma_{\phi z} \rangle$.

The result is a representation of a counterclockwise rotation by angle 2ϕ in the xy plane or around the z axis of intersection. This proves that a rotation $R[\omega]$ by angle ω about an axis $\hat{\omega}$ is a product of two planar reflections. The first reflection may be through any plane that contains $\hat{\omega}$. The second reflection is through a plane containing $\hat{\omega}$ and making an angle $\omega/2$ with the first plane as shown in Figure 3.1.5. The $\omega/2$ arc between the two normals N_1 and N_2 in the figure is called a HAMILTON-TURN vector.

The Hamilton-turn vector can be positioned anywhere on its great circle or equatorial arc. It is useful for computing products of rotations around different axes. Suppose a rotation $R[\omega']$ about axis ω' follows $R[\omega]$. Then
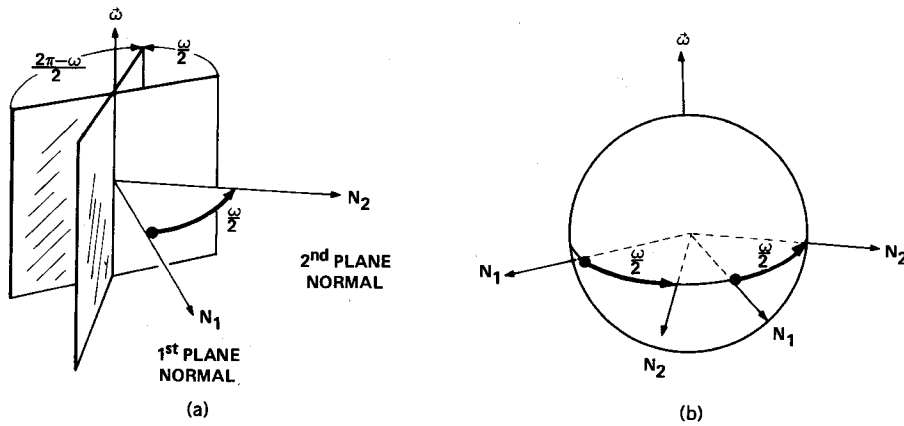

(a)

(b)

Figure 3.1.5 Hamilton's representation of rotation $R[\omega]$. (a) Two planes intersect with half the angle of the rotation. (b) Hamilton-turn great circle arc vectors on a unit sphere represent the rotation about the axis ω, which is orthogonal to their plane.

$$R[\omega'] \ R[\omega] = R[\omega'']$$

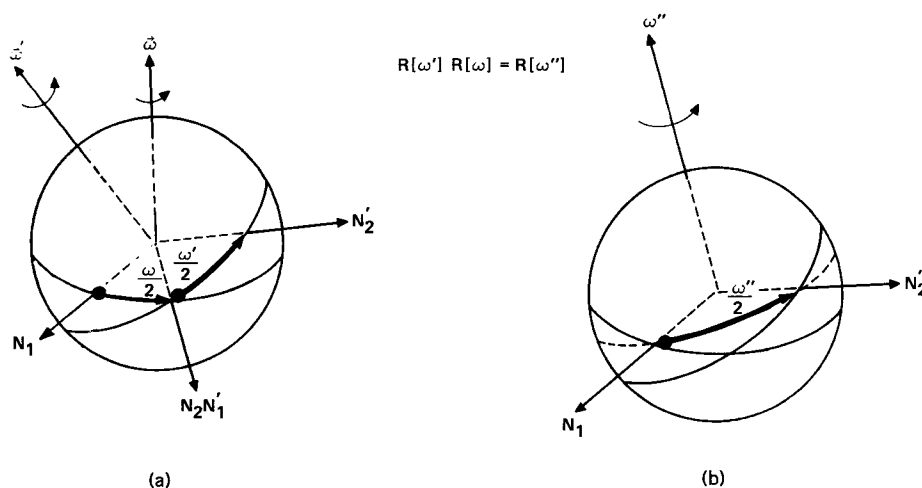(a)   (b)

Figure 3.1.6 Hamilton's construction for rotation group product $(R[\omega']R[\omega] = R[\omega''])$. (a) The head of arc vector $(\omega/2)$ for first rotation $R[\omega]$ meets tail of arc vector $(\omega'/2)$ for second rotation $R[\omega']$. (b) Resultant great circle arc vector $(\omega''/2)$ defines product rotation $R[\omega'']$.

one may move their Hamilton-turn vectors into a head-to-tail position at the arc intersection as shown in Figure 3.1.6(a). Then the N_2 and N'_1 normals and planes coincide and the corresponding reflections cancel. The great circle arc $\omega''/2$ between the first normal (N_1) for $R[\omega]$, and the second normal (N'_2) for $R[\omega']$ is the turn vector for the group product:

$$R[\omega''] = R[\omega']R[\omega].$$

This is shown in Figure 3.1.6(b). In other words, spherical vector addition with half-angle arcs is a key to understanding rotational point-group products. Furthermore, all point-group operations are either rotations (R) or rotations with an inversion (I) attached. Since inversion commutes with all rotations $(R \cdot I = I \cdot R)$ and squares to unity $(I^2 = 1)$, the entire point-group calculation reduces to Hamilton-turn addition.

In Chapter 5 the half-angle $(\omega/2)$ will be connected with spin-$\frac{1}{2}$. [Recall the half-angles that occur in Eq. (1.1.3).] Electrons and half-integral spin particles have the disturbing property of turning up with a negative (-1) phase after a "full" rotation by 2π or $360°$. For these particles a rotation by (ω) is (-1) times a rotation by $-(2\pi - \omega)$. The Hamilton-turn method distinguishes the latter rotation by a clockwise supplementary arc of length $(\pi - \omega/2)$, as shown in Figure 3.1.5. This aids in the understanding of "double-group" theory, which will be discussed in Chapter 5.
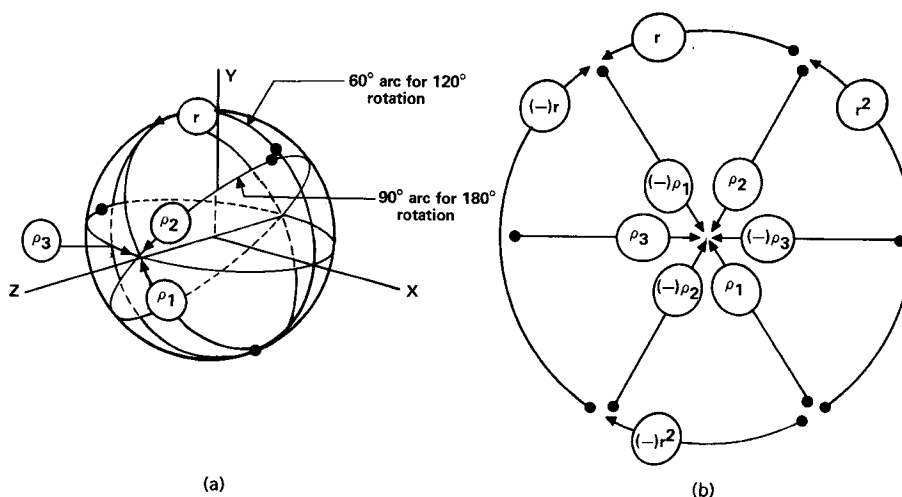
(a)   (b)

Figure 3.1.7   Geometrical definition of symmetry group D_3. (a) Hamilton arc vectors are drawn for rotations r, i_1, and i_3. (b) Group nomogram is obtained by projecting (a) onto the xy plane.

The D_3 or C_{3v} group table of Eq. (3.1.1) may be replaced by a geometrical nomogram. The Hamilton-turn arcs for D_3 rotations are drawn into place in Figure 3.1.7(a), following the conventions established by Figure 3.1.3. A view down the z axis is shown in Figure 3.1.7(b). Note that the supplementary arcs designated by a $(-)$ symbol are included there. Vector addition is accomplished by visually sliding the arc vectors into desired positions. For example, note the product

$$(-)\rho_1 r = \rho_2,$$

which is given by the uppermost sector of Figure 3.1.7(b). By ignoring the $(-)$ and changing ρ_j to σ_j one obtains the product $(\sigma_1 r = \sigma_2)$ in agreement with the C_{3v} table. [Recall Eq. (3.1.1).]

C. Laboratory and Body Reference Frames

For future work it is important to notice that it makes a difference how one defines the "reference frame" for molecular point-group operations. The rotation axes and reflection planes can be imagined to be attached to the stars, or more prosaically, to a fixed "laboratory" coordinate system x, y, and z. This was done in Figure 3.1.2. Consider now an alternative definition of operators $\underline{\sigma}_i$ made by fixing all these axes and planes to the "body" frame of the pendulums, as in Figure 3.1.8. However, note that a change of the multiplication rules will result, since each operator changes the laboratory position of all planes or axes except its own.
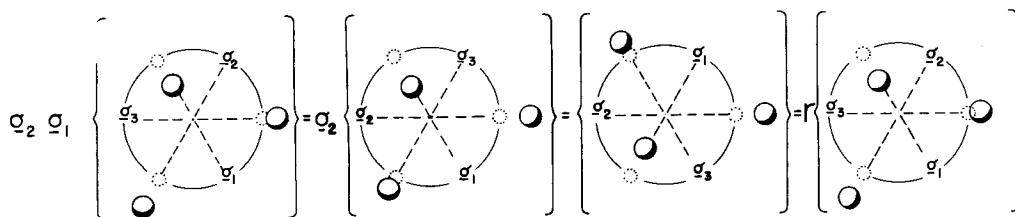
Figure 3.1.8 Effects of body-fixed plane reflections on pendulum mass configuration.

At the beginning of Chapter 5 a convenient relation is established between operators defined in laboratory and body frames. It is shown that if each body operator is identified with the *inverse* of a laboratory operator, then the original multiplication rules are recovered.

For the Abelian "fan-blade" group D_2 (recall Figure 2.1.1), or for any symmetry involving just inversions or rotations by 180°, it makes no difference whether the rotation axes are imbedded in the object or fixed in space as far as the multiplication table is concerned.

D. Tetragonal Symmetries C_{4v} and D_4

C_{4v} and D_4 are isomorphic crystal point symmetry groups of order 8. They are symmetries of a square pyramid and a square fan blade, respectively, as shown in Figure 3.1.9.

You should use this analogous symmetry to help you understand the theory of Sections 3.2–3.6. Each time some theory or application of C_{3v} symmetry is given you should work out the same for C_{4v} without looking at the answers in Section 3.6.
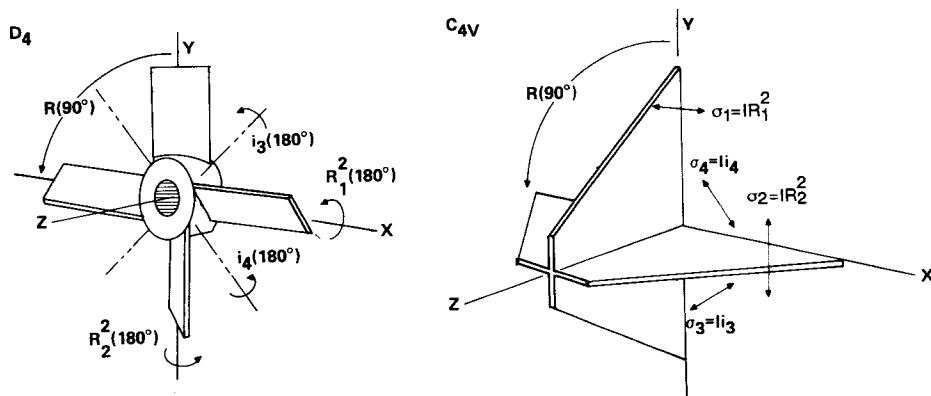

Figure 3.1.9 Pictorial comparison of D_4 and C_{4v} symmetry.

This sort of on-the-job training will make the difficult non-Abelian algebra easier to learn and remember. You should begin by constructing a Hamilton nomogram and group table for D_4 and C_{4v}. (See Problem 3.3.1.).

3.2   FIRST STAGE OF NON-ABELIAN SYMMETRY ANALYSIS

The idempotent theory developed in Chapters 1 and 2 always works when the operators commute, but it appears at first not to be applicable to non-Abelian groups. However, an interesting trick allows the theory to work for the noncommutative cases, as well. First one assembles the elements of the group C_{3v} into categories of operations which look more or less alike. Let category c_1 be the identity **1** by itself, category $c_2 = \{r, r^2\}$ be the 120° rotations, and category $c_3 = \{\sigma_1, \sigma_2, \sigma_3\}$ include all reflections. Then, if one defines the operators c_j to be the sums,

$$c_1 = 1, \qquad c_2 = r + r^2, \qquad c_3 = \sigma_1 + \sigma_2 + \sigma_3, \qquad (3.2.1a)$$

of operators within each category, it turns out that these c_j commute with each other $[c_j c_k = c_k c_j]$. Their multiplication structure is obtained by selectively "condensing" the group table in Eq. (3.1.1). The c_j multiplication table that follows is derived by simply counting up the elements in the rectangular sections of Eq. (3.1.1):

$$
\begin{array}{c|ccc}
 & c_1 & c_2 & c_3 \\
\hline
c_1 & c_1 & c_2 & c_3 \\
c_2 & c_2 & 2c_1 + c_2 & 2c_3 \\
c_3 & c_3 & 2c_3 & 3c_1 + 3c_2
\end{array}
\qquad (3.2.1b)
$$

Since the c_j operators are mutually commutative, it is possible to generate a set of idempotents from them. This is done in Section 3.2.B, but first, a general theory of c_j operators is given in the following section.

A. Class Operators

In general the categories c_j are called CLASSES, the c_j are CLASS OPERATORS, and their multiplication structure represents the CLASS ALGEBRA. The formal definition of a class is the following.

Definition Elements g and g' are in the same class c_j of group G if there are any elements h in G such that $g = hg'h^{-1}$.

The observation that categories of elements such as $\{\sigma_1, \sigma_2, \sigma_3\}$ "look alike" means that, for example, σ_2 or σ_3 can be replaced by σ_1. One may state this more precisely by group equations such as $(r\sigma_3 r^{-1} = \sigma_1)$. One translation of this equation is "r transforms σ_3 into σ_1." The transformation of σ_3 by r has the fore-and-aft form which operator transformations should have. [Recall Eq. (1.1.23).] Figure 3.1.3 shows rather clearly that r transforms σ_3 into σ_1. Another way to read $(r\sigma_3 r^{-1} = \sigma_1)$ is to note that by turning around with r^{-1} then doing σ_3, and finally returning with r, one obtains the same operation as σ_1.

It is easy to see that a class operator $c_g = g + g' + \cdots$ made by summing all the elements of a class must commute with every element h of the group in question. The following equation:

$$h^{-1} c_g h = h^{-1}(g + g' + \cdots)h = c_g \qquad (3.2.2)$$

follows from the class definition and the fact that $h^{-1} g h = h^{-1} g' h$ if and only if $g = g'$. Inverting this yields

$$c_g h = h c_g. \qquad (3.2.3)$$

Roughly speaking, the classes show the symmetry of the symmetry group. Equation (3.2.3) guarantees that each c_g commutes with all symmetry operators. In addition, any product $c_g c_l$ or linear combination $\alpha c_g + \beta c_l$ will commute with everything in the group.

The Hamilton-turn diagrams are helpful for describing class structure. Suppose rotation operator R' is obtained from another rotation operator R through the transformation by a third rotation T; i.e.,

$$R' = TRT^{-1}. \qquad (3.2.4)$$

Then the Hamilton arcs of R and R' must be opposite sides of a spherical parallelogram, as indicated by shading as shown in Figure 3.2.1. Note that one diagonal of the parallelogram consists of two t arcs. The arc length of this diagonal is equal to the angle of the T rotation according to Hamilton's half-angle rule.

Given a transformation equation (3.2.4), it is possible that several or many transformation operators $\{T, U, V, \ldots\}$ transform R into R'. For each operator Q which commutes with R, one has

$$QRQ^{-1} = R. \qquad (3.2.5)$$

Substituting this into Eq. (3.2.4) gives

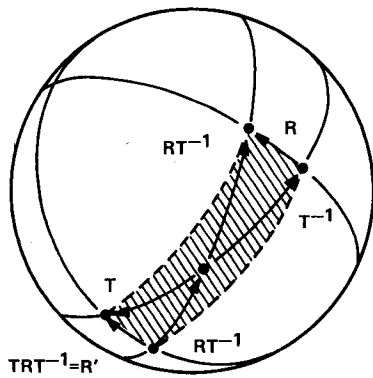$$R' = TQRQ^{-1}T^{-1} = URU^{-1}, \qquad (3.2.6a)$$

Figure 3.2.1 Showing class equivalence using Hamilton's vectors. Operation R is equivalent to $R' = TRT^{-1}$.

where

$$U = TQ,$$

$$U^{-1} = Q^{-1}T^{-1}. \tag{3.2.6b}$$

Thus each operator Q that commutes with R gives one more operator $U = TQ$ which transforms R into R'.

The set of all operators Q in a group G which commute with a given R form a subgroup $\{N_R = 1, Q, \ldots\}$ of G. This N_R is the "symmetry group" of R and is called its NORMALIZER. N_R includes R and all powers of R, and sometimes several inversion or reflection operators as well. The set of all operators $TN_R = \{T, TQ, \ldots\} = \{T, U, \ldots\}$ made by left multiplication by T on N_R is called the (left) COSET of subgroup N_R. Coset TN_R contains T and all operators which transform R into a particular operator $R' = TRT^{-1}$ in its class.

For example, the normalizer of r in C_{3v} is the subgroup $C_3 = \{1, r, r^2\}$. The subgroup C_3 and its coset $\sigma_1 C_3 = \{\sigma_1, \sigma_2, \sigma_3\}$ divide C_{3v} into two parts, and so there are only two elements $\{r, r^2\}$ in the class c_r of r. For another example, the normalizer of σ_1 in C_{3v} is the subgroup $C_v = \{1, \sigma_1\}$. The subgroup $C_v = \{1, \sigma_1\}$ and cosets $rC_v = \{r, \sigma_3\}$ and $r^2 C_v = \{r^2, \sigma_2\}$ divide the group C_{3v} into three parts, and so there are three elements $\{\sigma_1, \sigma_2, \sigma_3\}$ in the class c_σ of σ_1.

It is left as an exercise to prove generally that a normalizer of operator h contains a number $({}^\circ N_h)$ of elements which evenly divides the order $({}^\circ G)$ of the group. Furthermore, the fraction

$$^\circ c_h = ({}^\circ G)/({}^\circ N_h) \tag{3.2.7}$$

is the number of elements in the class c_h of h. These statements belong to LAGRANGE'S theorems.

For the analysis of a symmetry group or algebra it is helpful to define the ALL-COMMUTING or CENTRAL operators $\{\mathbb{C}, \mathbb{C}', \ldots\}$. These are any operators

$$\mathbb{C} = \sum_{g} \gamma_{g} g \qquad (3.2.8)$$

in the group algebra which commute with all group operators $[\mathbb{C}h = h\mathbb{C}]$. By averaging over all group operators using commutativity $[\mathbb{C} = h\mathbb{C}h^{-1}]$ we obtain

$$\mathbb{C} = (1/{}^{\circ}G) \sum_{h} h\mathbb{C}h^{-1} = (1/{}^{\circ}G) \sum_{g} \gamma_{g}\left(\sum_{h} hgh^{-1}\right). \qquad (3.2.9)$$

By appealing to Lagrange's theorem and Eq. (3.2.7) one derives

$$\mathbb{C} = (1/{}^{\circ}G) \sum_{g} \gamma_{g}{}^{\circ}N_{g}c_{g} = \sum_{g} (\gamma_{g}/{}^{\circ}c_{g})c_{g}. \qquad (3.2.10)$$

This proves that any all-commuting operator $\mathbb{C}$ must be a linear combination of class operators. The $\mathbb{C}$'s make up the commutative class algebra for which the c_{g}'s are a basis. Since any product $c_{g}c_{h}$ belongs to the algebra it must be a combination,

$$c_{g}c_{h} = \sum_{j} \gamma_{gh}^{j} c_{j}, \qquad (3.2.11)$$

of c_{g}'s, as well. The coefficients γ_{gh}^{j} are called algebraic STRUCTURE CONSTANTS.

B. Idempotent Analysis of Class Algebras

It is possible to write all the class operators c_{g} as a combination of a single set of idempotents P^{α}, as was done for Abelian groups of operators in Chapter 2. The only difference here is that the minimal equations are more complicated.

For example, using the C_{3v} class algebra table [Eq. (3.2.1b)] we find the minimal equation of c_{3}. This is the lowest-degree equation that involves just powers of c_{3}. [It may also involve $c_{1} = 1$; however, c_{1} may be thought of as the zeroth power $(c_{3})^{0}$.] The degree of the following equation is not yet high enough, since an unwanted $3c_{2}$ term appears:

$$(c_{3})^{2} = 3c_{1} + 3c_{2}.$$

Multiplying by c_3 again gives the desired minimal equation

$$(c_3)^3 = 3c_3 + 3c_2c_3 = 9c_3. \tag{3.2.12}$$

Note that the degree of a minimal equation for class operators cannot exceed the number of classes, since that is the dimension of the algebra. The cubic minimal equation for c_3 factors into the following form:

$$(c_3 - 31)(c_3 + 31)(c_3 - 01) = 0. \tag{3.2.13}$$

The three roots $c_3^{(1)} = 3$, $c_3^{(2)} = -3$, and $c_3^{(3)} = 0$ yield three idempotents $\mathbb{P}^1$, $\mathbb{P}^2$, and $\mathbb{P}^3$, respectively, when substituted into the general formula (1.2.15)

$$\mathbb{P}^\alpha = \prod_{\gamma \neq \alpha} (c_3 - c_3^{(\gamma)}1) \Big/ \prod_{\gamma \neq \alpha} (c_3^{(\alpha)} - c_3^{(\gamma)}). \tag{3.2.14}$$

The desired idempotents are given as follows.

$$\mathbb{P}^1 = \left[(c_3 + 31)(c_3 - 0)\right] \Big/ \left[(3 + 3)(3 - 0)\right] = \left[(c_3)^2 + 3c_3\right]\Big/18,$$

$$\mathbb{P}^1 = (c_1 + c_2 + c_3)/6 = \left(1 + r + r^2 + \sigma_1 + \sigma_2 + \sigma_3\right)/6,$$

$$\mathbb{P}^2 = (c_1 + c_2 - c_3)/6 = \left(1 + r + r^2 - \sigma_1 - \sigma_2 - \sigma_3\right)/6,$$

$$\mathbb{P}^3 = (2c_1 - c_2)/3 = (21 - r - r^2)/3. \tag{3.2.15}$$

The $\mathbb{P}^\alpha$ are called ALL-COMMUTING, CENTRAL, or CLASS idempotents of C_{3v}. The original class operators can be expanded in terms of all-commuting idempotents according to spectral decomposition, where

$$c_j = \sum_\alpha c_j^{(\alpha)} \mathbb{P}^\alpha,$$

$$c_j \mathbb{P}^\alpha = c_j^{(\alpha)} \mathbb{P}^\alpha. \tag{3.2.16}$$

The eigenvalues $c_1^{(\alpha)}$ and $c_2^{(\alpha)}$ are found by multiplying $\mathbb{P}^\alpha$ and c_1 and c_2, respectively, and $c_3^{(\alpha)}$ was given following Eq. (3.2.13). The C_{3v} class spectral decomposition has the following form:

$$1 \equiv c_1 = \mathbb{P}^1 + \mathbb{P}^2 + \mathbb{P}^3,$$

$$c_2 = 2\mathbb{P}^1 + 2\mathbb{P}^2 - \mathbb{P}^3,$$

$$c_3 = 3\mathbb{P}^1 - 3\mathbb{P}^2. \tag{3.2.17}$$

C. Does the Class Algebra Reduction Work in General?

We can easily prove that a decomposition such as the one for C_{3v} is possible for all finite groups. Since class operators commute, one can follow the procedure which worked for Abelian groups (recall Section 2.9), provided no minimal equation contains a repeated root. But suppose a root is repeated; that is, suppose that

$$(c - c^1\mathbf{1})(\cdots)(c - c^r\mathbf{1})^m(\cdots) = 0 \qquad (3.2.18)$$

was the MEq of c with $m \geq 2$ repeated roots. This would imply that one could construct a nonzero operator n,

$$n = (c - c^1\mathbf{1})(\cdots)(c - c^r\mathbf{1})^{m-1}(\cdots) \neq 0, \qquad (3.2.19)$$

which is NILPOTENT, i.e., an operator whose square is zero:

$$n^2 = 0. \qquad (3.2.20)$$

If nilpotent n acts on any combination $G = \Sigma \gamma_g g$ of group operators it yields an operator nG which is also nilpotent (note that $nG = Gn$ since n is in the class algebra):

$$nGnG = Gn^2G = 0. \qquad (3.2.21)$$

Now setting $G = n^\dagger$, and following the same arguments which are stated in Appendix C, we conclude that $n^\dagger n$ and finally n must be zero. A Hermitian operator cannot be nilpotent without being zero. Hence, a class operator can never have repeated roots; therefore, the class spectral decomposition is always possible.

Finally, the all-commuting or class idempotents can be seen to be unique for the same reasons that applied to Abelian groups (cf. Section 2.9). Also, they may be shown to be Hermitian (see Problem 1.2.7):

$$\mathbb{P}^{\alpha\dagger} = \mathbb{P}^\alpha. \qquad (3.2.22)$$

3.3 SECOND STAGE OF NON-ABELIAN SYMMETRY ANALYSIS

It is not possible that every operator in a non-Abelian group is a combination of the same set of idempotents. If this were so, then every operator would commute. Stated another way, the representations of noncommuting operators cannot *all* be transformed to diagonal matrices at once.

However, every non-Abelian group has some Abelian subgroups. For example, C_{3v} has the subgroup $C_3 = \{1, r, r^2\}$, $C_v = \{1, \sigma_1\}$, $C'_v = \{1, \sigma_2\}$, or $C''_v = \{1, \sigma_3\}$, which were mentioned before. (The lines leading back to

Abelian groups in Figure 2.1.1 indicate all the possibilities for each crystal symmetry.) The idea is to find the largest possible set of mutually commuting operators. Abelian subgroup operators commute with each other and with the all-commuting class operators. A reflection subgroup C_v and class operators taken together give four independent commuting operators σ_j, c_1, c_2, and c_3. By taking the cyclic subgroup C_3 one gets another set of four independent operators r, c_1, c_2, and c_3. (Note that r^2 is not linearly independent, since $r^2 = c_2 - r$.] The maximum number of independent mutually commuting operators which can be found in a group algebra is called the RANK of the algebra. The rank is the maximum number of operators that can be represented at once by diagonal matrices. It is up to the physicist to decide which Abelian subgroups he would like to represent by diagonal matrices. While one choice may be as good as another from a mathematical viewpoint, it can make a big difference in ease of computation and clarity of physical insight. Two very different choices C_3 or C_v exist within the C_{3v} symmetry. Since r in C_3 does not commute with σ_j in C_v, one cannot choose both. It will turn out that the C_3 choice yields moving-wave solutions, while a C_v choice yields standing-wave solutions.

For example, let us choose $C_v'' = \{1, \sigma_3\}$. This group has the familiar completeness relation

$$1 = P^+ + P^- = \tfrac{1}{2}(1 + \sigma_3) + \tfrac{1}{2}(1 - \sigma_3). \qquad (3.3.1)$$

When this is multiplied by the completeness relation [Eq. (3.2.17)] for the all-commuting idempotents [Eq. (3.2.15)] as is done in the following, a new and different set of idempotents will result:

$$1 = (P^+ + P^-)(\mathbb{P}^1 + \mathbb{P}^2 + \mathbb{P}^3), \qquad (3.3.2a)$$

$$1 = P^+\mathbb{P}^1 + P^-\mathbb{P}^1 + P^+\mathbb{P}^2 + P^-\mathbb{P}^2 + P^+\mathbb{P}^3 + P^-\mathbb{P}^3, \qquad (3.3.2b)$$

$$1 = \mathbb{P}^1 + 0 + 0 + \mathbb{P}^2 + P_1^3 + P_2^3 \qquad (3.3.2c)$$

In the last line we use the C_{3v} group table [Eq. (3.1.1)] to work out the products. The first and fourth products yield the original all-commuting $\mathbb{P}^1$ and $\mathbb{P}^2$, while the second and third products yield nothing. However, the last two terms yield a SPLITTING of the all-commuting $\mathbb{P}^3$ into two new and orthogonal idempotents,

$$P_1^3 = P^+\mathbb{P}^3 = \tfrac{1}{6}(1 + \sigma_3)(21 - r - r^2) = \tfrac{1}{6}(21 - r - r^2 - \sigma_1 - \sigma_2 + 2\sigma_3),$$
$$(3.3.3a)$$

$$P_2^3 = P^-\mathbb{P}^3 = \tfrac{1}{6}(1 - \sigma_3)(21 - r - r^2) = \tfrac{1}{6}(21 - r - r^2 + \sigma_1 + \sigma_2 - 2\sigma_3),$$
$$(3.3.3b)$$

where

$$\mathbb{P}^3 = P_1^3 + P_2^3. \qquad (3.3.3c)$$

This procedure has yielded four idempotents $\mathbb{P}^1$, $\mathbb{P}^2$, P_1^3, and P_2^3, which may be used to expand four mutually commuting operators c_1, c_2, c_3, and σ_3. The four idempotents are called IRREDUCIBLE or unsplittable idempotents, since they cannot be split further into sums of orthogonal idempotents. In general a group algebra of rank r has exactly r irreducible idempotents.

However, C_{3v} has six linearly independent operators in all. In order to expand the whole C_{3v} group we will need two more operators of some kind. It is not possible to find two more orthogonal idempotents, since C_{3v} is non-Abelian. The question is: What form should these two additional operators take?

We begin to see the answer to this by performing the following expansion of general C_{3v} operator g using Eq. (3.3.2c) twice:

$$g = 1g1 = \left(\mathbb{P}^1 + \mathbb{P}^2 + P_1^3 + P_2^3\right)g\left(\mathbb{P}^1 + \mathbb{P}^2 + P_1^3 + P_2^3\right), \quad (3.3.4a)$$

$$g = \mathbb{P}^1 g \mathbb{P}^1 + \mathbb{P}^2 g \mathbb{P}^2 + P_1^3 g P_1^3 + P_1^3 g P_2^3 + P_2^3 g P_1^3 + P_2^3 g P_2^3 \quad (3.3.4b)$$

In writing Eq. (3.3.4b) we ignore vanishing cross-terms such as

$$\mathbb{P}^1 g \mathbb{P}^2 = g \mathbb{P}^1 \mathbb{P}^2 = 0, \qquad \mathbb{P}^1 g P_1^3 = g \mathbb{P}^1 P_1^3 = 0,$$

which involve idempotents which are all-commuting. The first two terms involving all-commuting $\mathbb{P}^1$ and $\mathbb{P}^2$ in Eq. (3.3.4b) can be rewritten as

$$\mathbb{P}^1 g \mathbb{P}^1 = g \mathbb{P}^1 = \mathscr{D}^1(g)\mathbb{P}^1, \qquad \mathbb{P}^2 g \mathbb{P}^2 = g \mathbb{P}^2 = \mathscr{D}^2(g)\mathbb{P}^2, \quad (3.3.5)$$

using commutivity ($\mathbb{P}^1 g = g \mathbb{P}^1$), idempotency, $\mathbb{P}^1 \mathbb{P}^1 = \mathbb{P}^1$, and the group eigenvector properties of $\mathbb{P}^1$ and $\mathbb{P}^2$, which follow from Eq. (3.2.15). Substituting, we find the eigenvalues

$$\mathscr{D}^1(1) = \mathscr{D}^1(r) = \mathscr{D}^1(r^2) = 1, \qquad \mathscr{D}^1(\sigma_1) = \mathscr{D}^1(\sigma_2) = \mathscr{D}^1(\sigma_3) = 1,$$

$$\mathscr{D}^2(1) = \mathscr{D}^2(r) = \mathscr{D}^2(r^2) = 1, \qquad \mathscr{D}^2(\sigma_1) = \mathscr{D}^2(\sigma_2) = \mathscr{D}^2(\sigma_3) = -1,$$

$$(3.3.6)$$

and thereby account for the first two of the C_{3v} irreps. So far this is the same as an Abelian irrep derivation.

However, the third C_{3v} irrep is different. Its properties are derived from the last four terms of the form $P_i^3 g P_j^3$ in Eq. (3.3.4b). The diagonal terms $P_i^3 g P_i^3$ turn out to be proportional to the original irreducible idempotents as

follows:

$$P_1^3 g P_1^3 = \mathscr{D}_{11}^3(g) P_1^3, \qquad P_2^3 g P_2^3 = \mathscr{D}_{22}^3(g) P_2^3.$$

The new terms $P_i^3 g P_j^3$ turn out to be proportional to two IRREDUCIBLE NILPOTENT projectors $P_{ij}^3 = P_{ji}^{3\dagger}$,

$$P_1^3 g P_2^3 = \mathscr{D}_{12}^3(g) P_{12}^3, \qquad P_2^3 g P_1^3 = \mathscr{D}_{21}^3(g) P_{21}^3,$$

which satisfy

$$P_{12}^3 P_{21}^3 = P_1^3, \qquad P_{21}^3 P_{12}^3 = P_2^3,$$

as well as nilpotency,

$$P_{12}^3 P_{12}^3 = 0 = P_{21}^3 P_{21}^3.$$

The proportionality coefficients $\mathscr{D}_{ij}^\alpha(g)$ expressed in matrix form

$$\mathscr{D}^\alpha(g) = \begin{pmatrix} \mathscr{D}_{11}^\alpha(g) & \mathscr{D}_{12}^\alpha(g) \\ \mathscr{D}_{21}^\alpha(g) & \mathscr{D}_{22}^\alpha(g) \end{pmatrix}$$

comprise the third irrep $\mathscr{D}^3$ of C_{3v}:

$$\mathscr{D}^3(1) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \mathscr{D}^3(r) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix},$$

$$\mathscr{D}^3(r^2) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}, \qquad \mathscr{D}^3(\sigma_1) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix},$$

$$\mathscr{D}^3(\sigma_2) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}, \qquad \mathscr{D}^3(\sigma_3) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \qquad (3.3.7)$$

These coefficients will be derived in the following section. It is more important now to appreciate the general form of non-Abelian group reduction.

Each non-Abelian group operator g may be expressed as a combination

$$g = \sum_\alpha \sum_{ij}^{l^\alpha} \mathscr{D}_{ij}^\alpha(g) P_{ij}^\alpha \qquad (3.3.8)$$

of ELEMENTARY OPERATORS P_{ij}^α weighted by coefficients $\mathscr{D}_{ij}^\alpha$. Diagonal operators

$$P_{ii}^\alpha \equiv P_i^\alpha \qquad (3.3.9)$$

are just the l^α irreducible idempotents which were split from all-commuting $\mathbb{P}^\alpha$:

$$\mathbb{P}^\alpha = P_{11}^\alpha + P_{22}^\alpha + \cdots + P_{l^\alpha l^\alpha}^\alpha. \qquad (3.3.10)$$

Off-diagonal operators are defined by

$$P_{ij}^\alpha = P_i^\alpha g P_j^\alpha / \mathscr{D}_{ij}^\alpha(g) = P_{ji}^{\alpha\dagger}, \qquad (3.3.11)$$

where nonzero $P_i^\alpha g P_j^\alpha$ may be found and normalized by coefficients $\mathscr{D}_{ij}^\alpha(g)$ to give

$$P_{ij}^\alpha P_{kl}^\beta = \delta^{\alpha\beta}\delta_{jk} P_{il}^\alpha. \qquad (3.3.12)$$

The orthonormality relation (3.3.12) can be understood if you always remember that P_{ij}^α carries orthogonal idempotents P_i^α and P_j^α as "bodyguards" on its left and right, respectively. When P_{ij}^α runs into P_{kl}^β, then P_{ij}^α's right-hand bodyguard P_j^α encounters the left-hand bodyguard P_k^β of P_{kl}^β. Annihilation occurs unless the guards are identical ($\alpha = \beta$ and $j = k$). Furthermore, one can show (Appendix D) that all operators $P_i^\alpha G P_j^\alpha$ with identical sets of bodyguards are indistinguishable, except for proportionality factors $\mathscr{D}_{ij}^\alpha(G)$; i.e.,

$$P_i^\alpha G P_j^\alpha = \mathscr{D}_{ij}^\alpha(G) P_{ij}^\alpha,$$

where $G = \sum_g \gamma_g g$ is any linear combination of group operators. If it happens that G is annihilated by its bodyguards, then let $\mathscr{D}_{ij}^\alpha(G) = 0$. The coefficients $\mathscr{D}$ are chosen so that Eq. (3.3.12) holds, whence they also satisfy group matrix representation relations:

$$\sum_j^{l^\beta} \mathscr{D}_{ij}^\beta(g)\mathscr{D}_{jk}^\beta(h) = \mathscr{D}_{ik}^\beta(gh). \qquad (3.3.13)$$

To prove the matrix relations first note the effect which a group operator (h) would have on the left bodyguard of P_{kl}^β. Equation (3.3.8) gives

$$hP_{kl}^\beta = \sum_\alpha \sum_{i,j}^{l^\alpha} \mathscr{D}_{ij}^\alpha(h) P_{ij}^\alpha P_{kl}^\beta,$$

and Eq. (3.3.12) gives

$$hP_{kl}^\beta = \sum_i^{l^\beta} \mathscr{D}_{ik}^\beta(h) P_{il}^\beta. \qquad (3.3.14)$$

This is the left-hand transformation rule, which holds for all group operators, including products such as (gh):

$$ghP_{kl}^{\beta} = \sum_{i}^{l^{\beta}} \mathscr{D}_{ik}^{\beta}(gh) P_{il}^{\beta}. \qquad (3.3.15)$$

However, this product is also equal to left operation by g onto Eq. (3.3.14):

$$ghP_{kl}^{\beta} = \sum_{j}^{l^{\beta}} \mathscr{D}_{jk}^{\beta}(h) g P_{jl}^{\beta}$$

$$= \sum_{j}^{l^{\beta}} \mathscr{D}_{jk}(h) \sum_{i}^{l^{\beta}} \mathscr{D}_{ij}^{\beta}(g) P_{il}^{\beta}$$

$$= \sum_{i}^{l^{\beta}} \left[\sum_{j}^{l^{\beta}} \mathscr{D}_{ij}^{\beta}(g) \mathscr{D}_{jk}^{\beta}(h) \right] P_{il}^{\beta}.$$

Equating the coefficient in brackets to $\mathscr{D}_{ik}^{\beta}(gh)$ in Eq. (3.3.15) yields Eq. (3.3.13).

This is how a non-Abelian group is analyzed; each operator g is a combination of elementary operators, P_{ij}^{α}, whose multiplicative properties are, as the name implies, elementary. For example, each C_{3v} operator is a combination involving six terms:

$$g = \mathscr{D}^{1}(g)\mathbb{P}^{1} + \mathscr{D}^{2}(g)\mathbb{P}^{2} + \mathscr{D}_{11}^{3}(g)P_{11}^{3} + \mathscr{D}_{12}^{3}(g)P_{12}^{3} \\ + \mathscr{D}_{21}^{3}(g)P_{21}^{3} + \mathscr{D}_{22}^{3}(g)P_{22}^{3} \qquad (3.3.16)$$

and three sets of irreps. The analysis of non-Abelian groups is a generalization of that for Abelian groups. For Abelian groups all irreps are 1×1 matrices, whereas a non-Abelian group must have some irreps $\mathscr{D}^{\alpha}$ which are $l^{\alpha} \times l^{\alpha}$ matrices with $l^{\alpha} \geq 2$. For each (α) there are $(l^{\alpha})^{2}$ elementary operators. Since the number of elementary operators must equal the order $(^{\circ}G)$ of the group, we have

$$^{\circ}G = \sum_{\alpha} (l^{\alpha})^{2}. \qquad (3.3.17)$$

In the case of C_{3v} this number is $6 = 1^{2} + 1^{2} + 2^{2}$. The number of different types (α) of irreps equals the number of all-commuting idempotents ($\mathbb{P}^{\alpha} = \sum_{i} P_{ii}^{\alpha}$), which is the number of classes. In the following sections we shall show how the $\mathbb{P}^{\alpha}$, viz., Eq. (3.2.15), give directly the dimensions l^{α} of the irreps.

Now, while Abelian group irreps and elementary operators are all uniquely defined, those with $l_\alpha \geq 2$ for non-Abelian groups are not. For example, in C_{3v} we would have split $\mathbb{P}^3$ with idempotents from $C_3 = \{1, r, r^2\}$ instead of $C_v = \{1, \sigma_3\}$. However, the number l^α of P_i^α split from a given $\mathbb{P}^\alpha$ is fixed. Applying the three C_3 projectors $\{P^{0_3}, P^{1_3}, P^{2_3}\}$ to the all-commuting $\mathbb{P}^3$ yields only two nonzero idempotents,

$$P^{0_3}\mathbb{P}^3 = P^3(1 + r + r^2)/3 = 0,$$

$$P_1^3 = P^{1_3}\mathbb{P}^3 = \mathbb{P}^3(1 + \varepsilon^* r + \varepsilon r^2)/3 = (1 + \varepsilon^* r + \varepsilon r^2)/3,$$

$$P_2^3 = P^{2_3}\mathbb{P}^3 = \mathbb{P}^3(1 + \varepsilon r + \varepsilon^* r)/3 = (1 + \varepsilon r + \varepsilon^* r^2)/3. \quad (3.3.18)$$

Nevertheless, they differ markedly from the two operators obtained using $C_v = \{1, \sigma_3\}$ projectors in Eq. (3.3.3). They lead to a different but equivalent set of $\mathscr{D}^3$ irreps. We shall return to the significance of different choices shortly.

3.4 THEORY AND APPLICATION OF ELEMENTARY OPERATORS AND IRREPS

In order to demonstrate the theory and application of the non-Abelian symmetry C_{3v}, we shall eventually solve the equations for the mechanical system in Figure 3.4.1. However, the main objective of this section will be to derive and prove general relations which are followed by the elementary operators of a non-Abelian finite group $G = \{1, g, g', \ldots\}$. The analysis and application of multidimensional ($l^\alpha \geq 2$) irreps has a number of subtle features which are not present in Abelian symmetry analysis. However, once these are understood the application of the theory is just as easy as it was in the Abelian cases. You will soon be able to solve some very complicated problems with relatively little computation.

A. Group Space and the Regular Representation

In Figure 3.4.1 the coordinates $\langle g|x \rangle$ and unit vectors $|g\rangle$ are chosen in perfect correspondence to the symmetry group C_{3v}. Each group operation g acting on the first coordinate $\langle 1|x \rangle$ or vector $|1\rangle$ gives one of the others according to Eq. (3.4.1).

$$g|1\rangle = |g\rangle, \quad (3.4.1a)$$

$$\langle 1|g^\dagger = \langle g| = \langle 1|g^{-1}, \quad (3.4.1b)$$

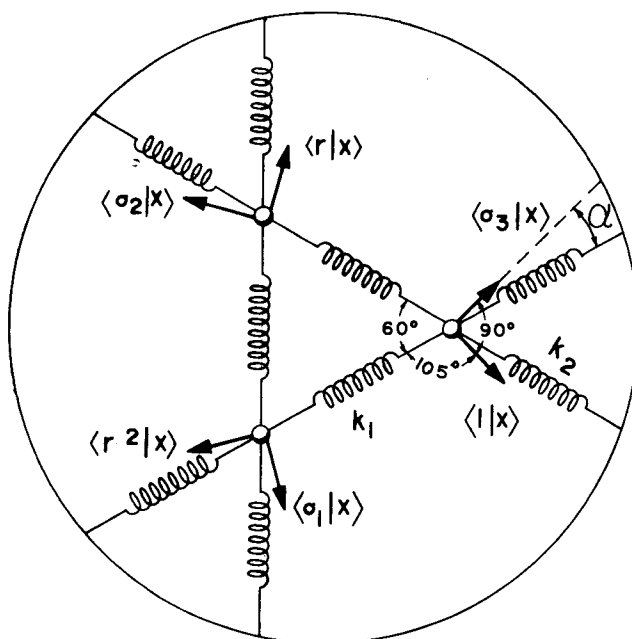$$\langle g|x\rangle = \langle 1|g^\dagger|x\rangle. \quad (3.4.1c)$$

Figure 3.4.1 Spring-mass model with C_{3v} symmetry. One coordinate degree of freedom exists for each symmetry operator in C_{3v}.

These vectors are defined to be orthonormal, as expressed by the following:

$$\langle g|h \rangle = \delta_{g,h} = \delta_{g^{-1}h,1},\qquad (3.4.2a)$$

$$\langle 1|g^{\dagger}h|1 \rangle = \delta_{g^{-1}h,1} = \langle 1|g^{-1}h|1 \rangle.\qquad (3.4.2b)$$

The group basis $\{|1\rangle, |g\rangle, \dots\}$ spans what is called the REGULAR REPRE-SENTATION $\mathscr{R}(g)$. This is defined in the following with the help of the two preceding equations:

$$\mathscr{R}_{hf}(g) = \langle h|g|f \rangle = \langle 1|h^{\dagger}gf|1 \rangle = \delta_{h^{-1}gf,1} = \delta_{g,hf^{-1}}.\qquad (3.4.3)$$

The regular representation exists quite independently of any physical system such as the one in Figure 3.4.1. In fact, you may construct each matrix $\mathscr{R}(g)$ directly from any group table in which the top row is arranged so that each position contains the inverse $f^{\dagger} = f^{-1}$ of the occupant of the corresponding left column position, as in the following. $\mathscr{R}(g)$ is then obtained by transcribing one (1) wherever g shows up and zero, $(0) \equiv (\cdot)$, elsewhere. For example,

$\mathscr{R}(r)$ is constructed as follows:

$$
\begin{array}{c|cccccc}
 & 1 & r^2 & r & \sigma_1 & \sigma_2 & \sigma_3 \\
\hline
1 & 1 & r^2 & r & \sigma_1 & \sigma_2 & \sigma_3 \\
r & r & 1 & r^2 & \sigma_3 & \sigma_1 & \sigma_2 \\
r^2 & r^2 & r & 1 & \sigma_2 & \sigma_3 & \sigma_1 \\
\sigma_1 & \sigma_1 & \sigma_3 & \sigma_2 & 1 & r & r^2 \\
\sigma_2 & \sigma_2 & \sigma_1 & \sigma_3 & r^2 & 1 & r \\
\sigma_3 & \sigma_3 & \sigma_2 & \sigma_1 & r & r^2 & 1 \\
\end{array}
\rightarrow \mathscr{R}(r) =
\begin{array}{cccccc}
|1\rangle & |r\rangle & |r^2\rangle & |\sigma_1\rangle & |\sigma_2\rangle & |\sigma_3\rangle \\
\end{array}
\begin{pmatrix}
\cdot & \cdot & 1 & \cdot & \cdot & \cdot \\
1 & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & 1 & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & 1 & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & 1 \\
\cdot & \cdot & \cdot & 1 & \cdot & \cdot \\
\end{pmatrix}.
$$

$$(3.4.4)$$

Note that the trace of the regular representation of all group operators g is zero, except for the identity $g = \mathbf{1}$, which has a trace equal to the order $^{\circ}G$ of the group:

$$\text{Trace } \mathscr{R}(g) = \delta_{g,1}{}^{\circ}G. \tag{3.4.5}$$

This is very important for later derivations.

Note also that group space vectors can be defined with respect to operator combinations $G = \Sigma \gamma_g g$ of group operators:

$$|G\rangle = G|1\rangle = (\gamma_1 \mathbf{1} + \gamma_g g + \cdots)|1\rangle = \gamma_1|1\rangle + \gamma_g|g\rangle \cdots, \tag{3.4.6a}$$

$$\langle G| = \langle 1|G^{\dagger} = \langle 1|(\gamma_1^* \mathbf{1} + \gamma_g^* g + \cdots) = \gamma_1^* \langle 1| + \gamma_g^* \langle g| + \cdots. \tag{3.4.6b}$$

For example, consider the operators $P_i^{\alpha} g P_j^{\alpha} = \mathscr{D}_{ij}^{\alpha}(g) P_{ij}^{\alpha}$. If you change (g) in $P = P_i^{\alpha} g P_j^{\alpha}$ it is unchanged according to Appendix D except for an overall factor $\mathscr{D}_{ij}^{\alpha}(g)$. Let us suppose $\mathscr{D}_{ij}^{\alpha}(g)$ are still unknown, and define $|\hat{P}\rangle$ so that the overall factor is absorbed in normalization of the vector. Let

$$|\hat{P}_{ij}^{\alpha}\rangle \equiv P_{ij}^{\alpha}|1\rangle / (N_{ij}^{\alpha})^{1/2}, \tag{3.4.7a}$$

where the normalization factor N_{ij}^{α} is determined by

$$\langle \hat{P}_{ij}^{\alpha}|\hat{P}_{ij}^{\alpha}\rangle = 1 \tag{3.4.7b}$$

to within a phase.

For C_{3v} one can easily calculate the operators $P_i^{\alpha} g P_j^{\alpha}$ for select g, and by normalizing one finds the corresponding vectors $|\hat{P}_{ij}^{\alpha}\rangle$. Actually, the first four operators have been derived once before. [See Eqs. (3.3.3) and equations following (3.3.4).] The latter two equations are worked out in the following

using the group table in Eq. (3.4.4):

$$\mathbb{P}^1 \mathbb{1} \mathbb{P}^1 = \mathbb{P}^1 = \tfrac{1}{6}\left(1 + \mathbf{r} + \mathbf{r}^2 + \sigma_1 + \sigma_2 + \sigma_3\right),$$

$$\mathbb{P}^2 \mathbb{1} \mathbb{P}^2 = \mathbb{P}^2 = \tfrac{1}{6}\left(1 + \mathbf{r} + \mathbf{r}^2 - \sigma_1 - \sigma_2 - \sigma_3\right),$$

$$P^3_{11} \equiv P^3_1 \mathbb{1} P^3_1 = P^3_1 = \tfrac{1}{6}\left(2\mathbb{1} - \mathbf{r} - \mathbf{r}^2 - \sigma_1 - \sigma_2 + 2\sigma_3\right),$$

$$P^3_{22} \equiv P^3_2 \mathbb{1} P^3_2 = P^3_2 = \tfrac{1}{6}\left(2\mathbb{1} - \mathbf{r} - \mathbf{r}^2 + \sigma_1 + \sigma_2 - 2\sigma_3\right),$$

$$\mathscr{D}^3_{12}(\sigma_2)P^3_{12} = P^3_1\sigma_2 P^3_2 = \tfrac{1}{4}\left(0 - \mathbf{r} + \mathbf{r}^2 - \sigma_1 + \sigma_2 + 0\right),$$

$$\mathscr{D}^3_{21}(\sigma_2)P^3_{21} = P^3_2\sigma_2 P^3_1 = \tfrac{1}{4}\left(0 + \mathbf{r} - \mathbf{r}^2 - \sigma_1 + \sigma_2 + 0\right).$$

By assembling these coefficients into vectors and then normalizing so that $\langle \hat{P}|\hat{P}\rangle = 1$, one obtains the following:

$$\langle \hat{P}^1| \leftrightarrow \frac{1}{\sqrt{6}}\overline{1\ 1\ 1\ 1\ 1\ 1}, \qquad\qquad \langle \hat{P}^3_{22}| \leftrightarrow \frac{1}{2\sqrt{3}}\overline{2 - 1 - 1\ 1\ 1 - 2},$$

$$\langle \hat{P}^2| \leftrightarrow \frac{1}{\sqrt{6}}\overline{1\ 1\ 1 - 1 - 1 - 1}, \qquad \langle \hat{P}^3_{12}| \leftrightarrow \frac{1}{2}\overline{0 - 1\ 1 - 1\ 1\ 0},$$

$$\langle \hat{P}^3_{11}| \leftrightarrow \frac{1}{2\sqrt{3}}\overline{2 - 1 - 1 - 1 - 1\ 2}, \qquad \langle \hat{P}^3_{21}| \leftrightarrow \frac{1}{2}\overline{0\ 1 - 1 - 1\ 1\ 0}.$$

$$(3.4.8)$$

Pictures of these vectors are drawn in Figure 3.4.2, as they represent motions of the system in Figure 3.4.1. Let us now study these pictures in order to understand the P^α_{ij} operators.

The first two motions corresponding to $|\mathbb{P}^1\rangle$ (expansion) and $|\mathbb{P}^2\rangle$ (rotation or libration) have obvious symmetry properties. The interpretation of the $|P^3_{ij}\rangle$ is more subtle, particularly in regard to the left index (i) and the right index (j). An index equal to 1 or 2 denotes symmetry or antisymmetry, respectively. [Recall Eqs. (3.3.3).] The states $|P^3_{1j}\rangle$ and $|P^3_{2j}\rangle$ are symmetric and antisymmetric, respectively, to reflection σ_3 through the x plane of Figure 3.4.2. The $|P^3_{ij}\rangle$ states are eigenvectors of σ_3. Since σ_3 runs into the left-hand bodyguard P^3_i, the left-hand index determines the overall reflection parity of the state. The eigenrelation

$$\sigma_3|P^3_{ij}\rangle = \sigma_3 P^3_{ij}|1\rangle = (-1)^{i-1}|P^3_{ij}\rangle$$

follows from the definition

$$\sigma_3 P^3_i = -(-1)^i P^3_i = P^3_i \sigma_3$$

of the irreducible idempotents.
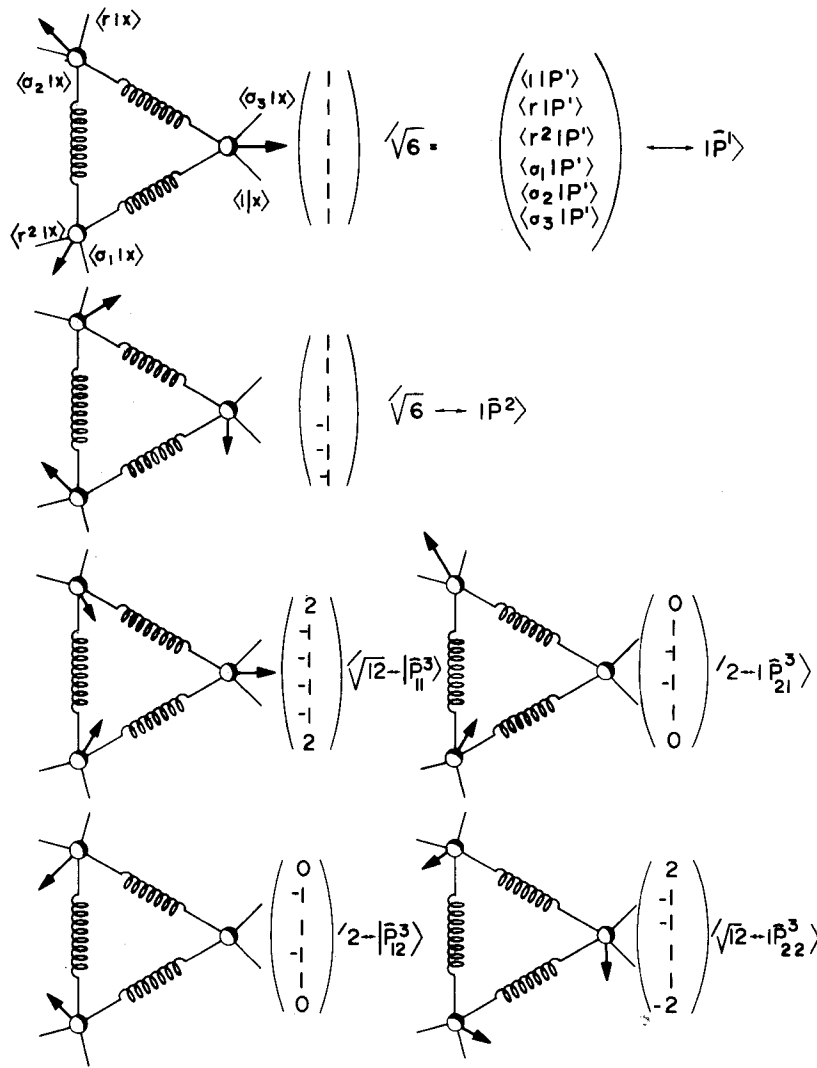
Figure 3.4.2 States of motion corresponding to C_{3v} P operators.

However, the right-hand index determines the *local* reflection symmetry properties of the motion. Note that each mass in state $|P_{i1}^3\rangle$ remains on its local reflection plane, while each mass in state $|P_{i2}^3\rangle$ moves perpendicularly to its local plane if it moves at all. State $|P_{i1}^3\rangle$ and $|P_{i2}^3\rangle$ are made of locally symmetric and antisymmetric motions, respectively. The right-hand index determines local symmetry since the right-hand bodyguard P_j^3 first encounters the local state $|1\rangle$ in the projection

$$P_{ij}^3|1\rangle = P_{ij}^3 P_j|1\rangle = P_{ij}^3|P_j\rangle,$$

where

$$P_j = \left(1 - (-1)^j \sigma_3\right)/2.$$

P_{ij}^3 acting on $|P_j\rangle$ gives a combination of states $g|P_j\rangle$ correspond.ng to similar motion of the other masses. But each state $g|P_j\rangle$ obeys a local symmetry equation

$$g\sigma_3 g^{-1} g|P_j\rangle = -(-1)^j g|P_j\rangle$$

equivalent to the initial equation

$$\sigma_3|P_j\rangle = -(-1)^j|P_j\rangle.$$

Note that vectors $|\hat{P}_{ij}^\alpha\rangle$ in Figure 3.4.2 are mutually orthogonal. This is a general result. To prove it first note that the scalar product in the following is zero if $i \neq k$, or $\alpha \neq \beta$:

$$\left\langle \hat{P}_{ij}^\alpha | \hat{P}_{kl}^\beta \right\rangle = \langle 1|P_{ij}^{\alpha\dagger}P_{kl}^\beta|1\rangle / \left(N_{ij}^\alpha N_{kl}^\beta\right)^{1/2} = \langle 1|P_{ji}^\alpha P_{kl}^\alpha|1\rangle \delta^{\alpha\beta} / \left(N_{ij}^\alpha N_{kl}^\alpha\right)^{1/2}$$

$$= \langle 1|P_{jl}^\alpha|1\rangle \delta_{ik}\delta^{\alpha\beta} / \left(N_{ij}^\alpha N_{kl}^\alpha\right)^{1/2}. \tag{3.4.9}$$

Now the matrix $\mathscr{R}(P_{jl}^\alpha)$ is nilpotent for $j \neq l$, since $\mathscr{R}(P_{jl}^\alpha)\mathscr{R}(P_{jl}^\alpha) = \mathscr{R}(P_{jl}^\alpha P_{jl}^\alpha) = \mathscr{R}(0)$. Therefore, $\mathscr{R}(P_{jl}^\alpha)$ has all zero eigenvalues and zero trace. Therefore $\langle 1|P_{jl}^\alpha|1\rangle$ must be zero if $j \neq l$ according to Eq. (3.4.5), since P_{jl}^α, being traceless, does not have any component of the unit operator **1**. This gives the scalar product result,

$$\left\langle \hat{P}_{ij}^\alpha | \hat{P}_{kl}^\alpha \right\rangle = \langle 1|P_{jj}^\alpha|1\rangle \delta^{\alpha\beta}\delta_{ik}\delta_{jl}/N_{ij}^\alpha = \delta^{\alpha\beta}\delta_{ik}\delta_{jl}. \tag{3.4.10a}$$

In general, normalization does not depend on the left-hand indices:

$$N_{ij}^\alpha \equiv N_j^\alpha = \langle 1|P_{jj}^\alpha|1\rangle. \tag{3.4.10b}$$

We find a simple formula for N_j^α in the next section.

B. Deriving and Using P_{ij} and $\mathscr{D}_{ij}(g)$

If we change our basis from the old regular representation vectors $\{\cdots |g\rangle \cdots\}$ to the new ones $\{\cdots |\hat{P}_{ij}^\alpha\rangle \cdots\}$, some simplifications will occur. The transformation will reduce or "almost diagonalize" the regular representation $\mathscr{R}$ matrices, and it will reduce the acceleration matrix $\langle a\rangle$ which describes the motion of the system in Figure 3.4.1.

To understand these two occurrences is to understand the heart of non-Abelian symmetry analysis, and so let us study them carefully. In addition, a general method for deriving irreps $\mathscr{D}_{ij}^\alpha$ will be shown, as well as

some justification of the previous assumptions made about irreps and the elementary P_{ij} operators.

(a)   Reducing the Regular Representation

The representation of a symmetry operator g in this new basis $\{ \cdots |P_{ij}^{\alpha}\rangle \cdots \}$ takes a simpler form, as shown by the following:

$$\langle \hat{P}_{ij}^{\alpha} | g | \hat{P}_{kl}^{\beta} \rangle = \langle 1 | P_{ji}^{\alpha} g P_{kl}^{\beta} | 1 \rangle / \sqrt{N_j^{\alpha} N_l^{\beta}}$$

$$= \langle 1 | P_{ji}^{\alpha} P_i^{\alpha} g P_k^{\alpha} P_{kl}^{\alpha} | 1 \rangle \delta^{\alpha\beta} / \sqrt{N_j^{\alpha} N_l^{\alpha}}$$

$$\text{(using idempotency: } P_i^{\alpha} = P_i^{\alpha} P_i^{\alpha})$$

$$= \mathscr{D}_{ik}^{\alpha}(g) \langle 1 | P_{ji}^{\alpha} P_{ik}^{\alpha} P_{kl}^{\alpha} | 1 \rangle \delta^{\alpha\beta} / \sqrt{N_j^{\alpha} N_l^{\alpha}} \qquad \text{[using Eq. (3.3.11)]}$$

$$= \mathscr{D}_{ik}^{\alpha}(g) \langle 1 | P_{jl}^{\alpha} | 1 \rangle \delta^{\alpha\beta} / \sqrt{N_j^{\alpha} N_l^{\alpha}} \qquad \text{[using Eq. (3.3.12)]}.$$

Finally, using the preceding equation (3.4.10) there results

$$\langle \hat{P}_{ij}^{\alpha} | g | \hat{P}_{kl}^{\beta} \rangle = \mathscr{D}_{ik}^{\alpha}(g) \delta^{\alpha\beta} \delta_{jl}. \qquad (3.4.11)$$

It is instructive to see an example of this wherein the $\mathscr{D}_{ik}^{\alpha}$ are evaluated. Consider the C_{3v} vector $r|P_{11}^3\rangle$ below. The group multiplication table gives the following vector and its regular representation.

$$
\begin{aligned}
r|\hat{P}_{11}^3\rangle &= r(2 \cdot 1 - r - r^2 - \sigma_1 - \sigma_2 + 2\sigma_3)|1\rangle/2\sqrt{3} \\
&= (2r - r^2 - 1 - \sigma_3 - \sigma_1 + 2\sigma_2)|1\rangle/2\sqrt{3} \\
&= (-|1\rangle + 2|r\rangle - |r^2\rangle - |\sigma_1\rangle + 2|\sigma_2\rangle - |\sigma_3\rangle)/2\sqrt{3} \leftrightarrow
\begin{pmatrix} -1 \\ 2 \\ -1 \\ -1 \\ 2 \\ -1 \end{pmatrix} \Bigg/ 2\sqrt{3}
\end{aligned}
$$

$$(3.4.12a)$$

By computing the scalar products of this vector with $|\hat{P}_{11}^3\rangle$ and $|\hat{P}_{21}^3\rangle$ we see that it is the following combination of them:

$$
\begin{pmatrix} -1 \\ 2 \\ -1 \\ -1 \\ 2 \\ -1 \end{pmatrix} \Bigg/ 2\sqrt{3} = -\frac{1}{2} \begin{pmatrix} 2 \\ -1 \\ -1 \\ -1 \\ -1 \\ 2 \end{pmatrix} \Bigg/ 2\sqrt{3} + \frac{\sqrt{3}}{2} \begin{pmatrix} 0 \\ 1 \\ -1 \\ -1 \\ 1 \\ 0 \end{pmatrix} \Bigg/ 2 \quad (3.4.12b)
$$

This is an example of the left-hand transformation rule first stated in Eq. (3.3.12):

$$r|\hat{P}_{11}^3\rangle = \left(-\frac{1}{2}\right)|\hat{P}_{11}^3\rangle + \left(\frac{\sqrt{3}}{2}\right)|\hat{P}_{21}^3\rangle = \mathscr{D}_{11}^3(r)|\hat{P}_{11}^3\rangle + \mathscr{D}_{21}^3(r)|\hat{P}_{21}^3\rangle. \quad (3.4.12c)$$

The rule for the second component is derived similarly:

$$r|\hat{P}_{21}^3\rangle = \left(\frac{-\sqrt{3}}{2}\right)|\hat{P}_{11}^3\rangle + \left(-\frac{1}{2}\right)|\hat{P}_{21}^3\rangle = \mathscr{D}_{12}(r)|\hat{P}_{11}^3\rangle + \mathscr{D}_{22}(r)|\hat{P}_{21}^3\rangle.$$

$$(3.4.13)$$

Together, the last two equations give the (3)-type irrep matrix of operator r for 120° rotation:

$$\mathscr{D}^3(r) = \begin{pmatrix} \mathscr{D}_{11}^3(r) & \mathscr{D}_{12}^3(r) \\ \mathscr{D}_{21}^3(r) & \mathscr{D}_{22}^3(r) \end{pmatrix} = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}. \quad (3.4.14)$$

In general a set of vectors $\{|P_{1j}^\alpha\rangle, |P_{2j}^\alpha\rangle, \ldots\}$ are said to be PARTNERS IN AN (α) IR BASIS when their symmetry transformation is the following:

$$g|P_{ij}^\alpha\rangle = \sum_{k=1}^{l^\alpha=2} \mathscr{D}_{ki}^\alpha(g)|P_{kj}^\alpha\rangle. \quad (3.4.15)$$

Note that the transformation (g) mixes only partners belonging to the same right-hand index j of local symmetry.

In Figure 3.4.3 there is shown a physical picture of the sort of transformation in Eq. (3.4.12c). This picture shows how an x motion that is rotated 120° by r is a combination of itself and a y motion with coefficients $(-1/2)$ and $(\sqrt{3}/2)$ respectively. At this point you may realize that we have just gone through what could very well be the world's most complicated derivation of $\cos(120°) = -\frac{1}{2}$ and $\sin(120°) = \sqrt{3}/2$. The same goes for the other $\mathscr{D}^3$ components which were given in Eq. (3.4.14) and (3.3.7).

This shows one of the main ideas of symmetry analysis. Only a few key numbers such as the $\mathscr{D}$ coefficients are needed for analysis in a virtual infinity of different problems. The necessary coefficients are usually easy to derive from simple physical considerations. The P-operator mathematics exists to expedite the theory and its applications. It also provides derivations for cases in which physical intuition fails.

Generally, one will be given the $\mathscr{D}_{ij}^\alpha$ coefficients and need to derive the P_{ij}^α operators instead of the other way around. Let us now derive a formula for P_{ij}^α. To begin this, observe the form of the regular representation of operators
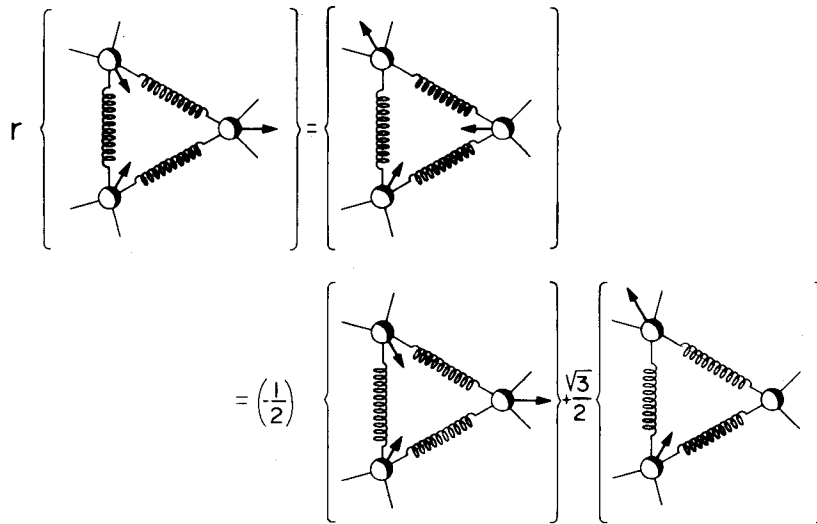
Figure 3.4.3 Pictorial representation of transformation $r|P_{11}^3\rangle = -\frac{1}{2}|P_{11}^3\rangle + (\sqrt{3}/2)P_{21}^3$.

in the basis of the $\{\cdots |P_{ij}^\alpha\rangle \cdots\}$ according to Eq. (3.4.11):

$$
\mathscr{R}(g) =
\begin{array}{c}
\\
\langle P^1| \\
\langle P^2| \\
\langle P_{11}^3| \\
\langle P_{21}^3| \\
\langle P_{12}^3| \\
\langle P_{22}^3|
\end{array}
\begin{pmatrix}
|P^1\rangle & |P^2\rangle & |P_{11}^3\rangle & |P_{21}^3\rangle & |P_{12}^3\rangle & |P_{22}^3\rangle \\
\mathscr{D}^1(g) & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \mathscr{D}^2(g) & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \mathscr{D}_{11}^3(g) & \mathscr{D}_{12}^3(g) & \cdot & \cdot \\
\cdot & \cdot & \mathscr{D}_{21}^3(g) & \mathscr{D}_{22}^3(g) & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \mathscr{D}_{11}^3(g) & \mathscr{D}_{12}^3(g) \\
\cdot & \cdot & \cdot & \cdot & \mathscr{D}_{21}^3(g) & \mathscr{D}_{22}^3(g)
\end{pmatrix}.
$$

$$(3.4.16)$$

In particular, the elementary operators in their own basis have a very simple form:

$$
\left\langle \hat{P}_{im}^\alpha \middle| P_{kl}^\beta \middle| \hat{P}_{jn}^\gamma \right\rangle = \delta^{\alpha\beta}\delta^{\gamma\beta}\delta_{ik}\delta_{jl}\delta_{mn}.
$$

The operator P_{ij}^3 is represented by unity at the (ij) position in each $\mathscr{D}^3$ block

matrix and zeros elsewhere:

$$\mathscr{R}(P_{11}^3) = \begin{bmatrix} 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 0 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & 0 & \cdot & \cdot \\ \cdot & \cdot & 0 & 0 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & 0 \\ \cdot & \cdot & \cdot & \cdot & 0 & 0 \end{bmatrix},$$

$$\mathscr{R}(P_{12}^3) = \begin{bmatrix} 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 0 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 0 & 1 & \cdot & \cdot \\ \cdot & \cdot & 0 & 0 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 0 & 1 \\ \cdot & \cdot & \cdot & \cdot & 0 & 0 \end{bmatrix}, \cdots . \tag{3.4.17}$$

All-commuting idempotents $\mathbb{P}^\alpha$ are represented by unit matrices in each $\mathscr{D}^\alpha$ block.

$$\mathscr{R}(\mathbb{P}^3) = \begin{bmatrix} 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 0 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & 0 & \cdot & \cdot \\ \cdot & \cdot & 0 & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & 0 \\ \cdot & \cdot & \cdot & \cdot & 0 & 1 \end{bmatrix},$$

$$\mathscr{R}(\mathbb{P}^2) = \begin{bmatrix} 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 0 & 0 & \cdot & \cdot \\ \cdot & \cdot & 0 & 0 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & 0 & 0 \end{bmatrix}, \cdots .$$

This form should be taken as one of the defining relations between irreps and the elementary operators. It is expressed more concisely by the following general equation:

$$\mathscr{D}_{ij}^\alpha(P_{kl}^\beta) = \delta^{\alpha\beta}\delta_{ik}\delta_{jl}. \tag{3.4.18}$$

This is needed in order to derive a formula for the elementary operators P_{jk}^α in terms of symmetry operators. Let us express an operator A, which is a sum of symmetry operators, as follows. [This uses the regular representation trace

relation in Eq. (3.4.5).]

$$A = \sum_g \{\text{TRACE } \mathscr{R}(g^\dagger A)/{}^\circ G\}g.$$

For $A = P_{jk}^\alpha$ one needs the trace of $\mathscr{R}(g^\dagger P_{jk}^\alpha)$. According to the left-transformation rule (3.4.15) one has

$$g^\dagger P_{jk}^\alpha = \sum_i^{l^\alpha} \mathscr{D}_{ij}^\alpha(g^\dagger)P_{ik}^\alpha = \sum_i \mathscr{D}_{ji}^{\alpha*}(g)P_{ik}^\alpha.$$

Substituting this in the preceding equation gives

$$A = P_{jk}^\alpha = \sum_g \sum_i^{l^\alpha} \mathscr{D}_{ji}^{\alpha*}(g)\{\text{Trace } \mathscr{R}(P_{ik}^\alpha)/{}^\circ G\}g.$$

A trace is independent of the choice of basis. The form of representations of P_{ik}^α in Eq. (3.4.17) make it clear that

$$\text{Trace } \mathscr{R}(P_{ik}^\alpha) = l^\alpha \delta_{ik}.$$

Substituting this in the equation for P_{jk}^α gives the desired result:

$$P_{jk}^\alpha = (l^\alpha/{}^\circ G)\sum_g \mathscr{D}_{jk}^{\alpha*}(g)g. \tag{3.4.19}$$

The normalization formula promised after Eq. (3.4.10) is found by using the fact that $\mathscr{D}_{ij}^\alpha(1) = \delta_{ij}$ in Eq. (3.4.19):

$$N_{ij}^\alpha = \langle 1|P_{jj}^\alpha|1\rangle = (l^\alpha/{}^\circ G) \equiv N^\alpha. \tag{3.4.20}$$

(b) *Reducing an Equation of Motion*   The first of six coupled equations of motion for the system in Figure 3.4.1 is given by

$$-\langle 1|\ddot{x}\rangle = \sum_g \langle 1|\mathbf{a}|g\rangle\langle g|x\rangle, \tag{3.4.21a}$$

where the first row of the acceleration matrix is the following:

$|g\rangle =$	$|1\rangle$	$|r\rangle$	$|r^2\rangle$	$|\sigma_1\rangle$	$|\sigma_2\rangle$	$|\sigma_3\rangle$
$\langle 1|\mathbf{a}|g\rangle =$	$\dfrac{(k_1+k_2)}{m}$	$\dfrac{k_1}{4m}$	$\dfrac{k_1}{4m}$	$\dfrac{k_1(2-\sqrt{3})}{4m}$	$\dfrac{k_1(2+\sqrt{3})}{4m}$	$\dfrac{k_1+2k_2\sin 2\alpha}{2m}$

$$\tag{3.4.21b}$$

A representation of the acceleration operator (**a**) in the $|P^\alpha_{ij}\rangle$ basis is derived as follows

$$\langle \hat{P}^\alpha_{ij} | \mathbf{a} | \hat{P}^\beta_{kl} \rangle = \langle 1 | P^\alpha_{ji} \mathbf{a} P^\beta_{kl} | 1 \rangle / \sqrt{N^\alpha N^\beta}$$

$$= \langle 1 | \mathbf{a} P^\alpha_{ji} P^\beta_{kl} | 1 \rangle / \sqrt{N^\alpha N^\beta} \qquad \text{(because of symmetry of } \mathbf{a} \text{ all } g \text{ commutute, } \mathbf{a}g = g\mathbf{a})$$

$$= \langle 1 | \mathbf{a} P^\alpha_{jl} | 1 \rangle \delta_{ik} \delta^{\alpha\beta} / N^\alpha \qquad \text{[using elementary operator properties in Eq. (3.3.12)].}$$

Finally, the Eqs. (3.4.19) and (3.4.20) for P_j and N give the reduced acceleration matrix components,

$$\langle \hat{P}^\alpha_{ij} | \mathbf{a} | \hat{P}^\beta_{kl} \rangle = \left(\sum_g \mathscr{D}^{\alpha*}_{jl}(g) \langle 1 | \mathbf{a} | g \rangle \right) \delta_{ik} \delta^{\alpha\beta}, \qquad (3.4.22)$$

which are shown explicitly in the following matrix:

$$m\langle \mathbf{a} \rangle = \begin{bmatrix}
\mathbf{a}^{(1)} & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \mathbf{a}^{(2)} & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \mathbf{a}^{(3)}_{11} & \mathbf{a}^{(3)}_{12} & \cdot & \cdot \\
\cdot & \cdot & \mathbf{a}^{(3)}_{21} & \mathbf{a}^{(3)}_{22} & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \mathbf{a}^{(3)}_{11} & \mathbf{a}^{(3)}_{12} \\
\cdot & \cdot & \cdot & \cdot & \mathbf{a}^{(3)}_{21} & \mathbf{a}^{(3)}_{22}
\end{bmatrix} \begin{matrix} |P^1\rangle \\ |P^2\rangle \\ |P^3_{11}\rangle \\ |P^3_{12}\rangle \\ |P^3_{21}\rangle \\ |P^3_{22}\rangle \end{matrix}$$

with column headers $|P^1\rangle \quad |P^2\rangle \quad |P^3_{11}\rangle \quad |P^3_{12}\rangle \quad |P^3_{21}\rangle \quad |P^3_{22}\rangle$

$$(3.4.23a)$$

where:

$$\mathbf{a}^{(1)} = 3k_1 + k_2(1 + \sin 2\alpha), \qquad \mathbf{a}^{(2)} = k_2(1 - \sin 2\alpha)$$

$$\mathbf{a}^{(3)}_{11} = \frac{3k_1}{4} + k_2(1 + \sin 2\alpha), \qquad \mathbf{a}^{(3)}_{12} = \frac{3k_1}{4}$$

$$\mathbf{a}^{(3)}_{21} = \frac{3k_1}{4}, \qquad \mathbf{a}^{(3)}_{22} = \frac{3k_1}{4} + k_2(1 - \sin 2\alpha). \quad (3.4.23b)$$

Note that the entire representation comes from just the first row of the original $\langle \mathbf{a} \rangle$ matrix in Eq. (3.4.21). Note also that the new representation leaves one with only a 2×2 matrix (this is repeated twice) to solve from the original 6×6 $\langle \mathbf{a} \rangle$ matrix. The $|P^1\rangle$ and $|P^2\rangle$ are already eigenvectors.

It is instructive to compare Eq. (3.4.11) with Eq. (3.4.22) and the matrix in Eq. (3.4.16) with the matrix in Eq. (3.4.23). In Eq. (3.4.11) one observes the
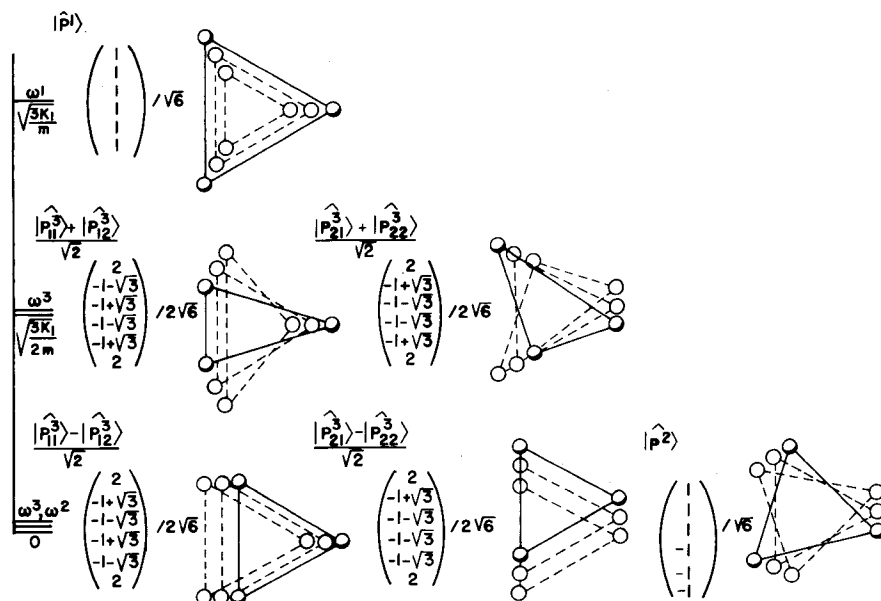
Figure 3.4.4 Standing-wave eigenvectors of C_{3v} spring-mass system.

factor δ_{jl} in the matrix element of symmetry operator g between $\langle P_{ij}^{\alpha}|$ and $|P_{kl}^{\beta}\rangle$, while in Eq. (3.4.22) the same matrix element of acceleration operator has a δ_{ik}. In the matrix Eq. (3.4.16) we find two identical block-diagonal matrices (D^3), where the first block connects states in one set $\{|P_{11}^3\rangle, |P_{21}^3\rangle\}$ of partners, while the second block connects the states in another set $\{|P_{12}^3\rangle, |P_{22}^3\rangle\}$ [recall Eq. (3.4.15)]. In the matrix Eq. (3.4.23) we also observe two identical block-diagonal matrices; only now the first block connects type-1 partners $(|P_{11}^3\rangle$ and $|P_{12}^3\rangle)$, while the second block connects type-2 partners $(|P_{21}^3\rangle$ and $|P_{22}^3\rangle)$.

When there is a repeated irrep $\mathscr{D}^3$ in any symmetry-analysis problem one has only to deal with the matrix connecting independent partners of type 1. This is so since the matrix for type 1 must be identical to that for type 2, ..., and type l^{α}. The degeneracy of each (α) eigenvalue will then be equal to the dimension l^{α} of irrep (α), since the eigenvalue equations are identical as well.

Figure 3.4.4 shows the eigenvectors of Eq. (3.4.23) with $k_2 = 0$. For this case there are three states with eigenvalue zero: the x, y translations and rotation. In molecular physics these are called NONGENUINE vibrations. The remaining three GENUINE vibration states are similar to those drawn in Figure 2.6.2. Indeed, the two degenerate states arising from the irreps D^{1_3} and D^{2_3} of C_3 now correspond to states arising from just one irrep D^3 of C_{3v}. The degeneracy exists because C_3 does not represent the full symmetry of the system.

(c) Moving-Wave or Circular Motions   The C_{3v} idempotents and irreps used in the preceding sections were derived by choosing representations of the reflection subgroup $C_v = \{1, \sigma_3\}$ to be diagonal. The problem can be done just as well using irreps for which rotation subgroup $C_3 = \{1, r, r^2\}$ is diagonal. However, instead of repeating the entire derivation, let us simply transform the C_v defined irrep $\mathscr{D}^3(r)$ [Eq. (3.4.14)] to diagonal form. Using the methods of Section 1.2 we quickly find that

$$\mathscr{D}^{3^0}(r) \equiv \mathscr{T}^\dagger \mathscr{D}^3(r)\mathscr{T} = \begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon^* \end{pmatrix} = \begin{pmatrix} \mathscr{D}^{1_3}(r) & 0 \\ 0 & \mathscr{D}^{2_3}(r) \end{pmatrix} \quad (3.4.24a)$$

reduces to a direct sum of C_3 irreps: $\varepsilon = e^{-2\pi i/3} \equiv \mathscr{D}^{1_3}(r)$ and $\varepsilon^* \equiv \mathscr{D}^{2_3}(r)$, using transformation

$$\mathscr{T} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -i/\sqrt{2} & i/\sqrt{2} \end{pmatrix}. \quad (3.4.24b)$$

Applying the same transformation to the $\mathscr{D}^3(\sigma_j)$ in Eq. (3.3.7) gives all nondiagonal reflection representations. $\mathscr{D}^{3^0}(\sigma_j) = \mathscr{T}^\dagger \mathscr{D}^3(\sigma_j)\mathscr{T}$, where

$$\mathscr{D}^{3^0}(\sigma_1) = \begin{pmatrix} 0 & \varepsilon^* \\ \varepsilon & 0 \end{pmatrix}, \quad \mathscr{D}^{3^0}(\sigma_2) = \begin{pmatrix} 0 & \varepsilon \\ \varepsilon^* & 0 \end{pmatrix}, \quad \mathscr{D}^{3^0}(\sigma_3) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$
$$(3.4.24c)$$

The preceding equations (3.4.24) define the CIRCULAR or MOVING-WAVE irreps $\mathscr{D}^{3^0}$ of C_{3v}. If you use them to solve the preceding eigenvibration problem the same eigenvalue must result, since $\mathscr{D}^3$ and $\mathscr{D}^{3^0}$ are equivalent. However, the columns of the transformation $\mathscr{T}$ in Eq. (3.4.24b) give quite different eigenvectors:

$$\left| \begin{matrix} (3) \\ 1_3 \end{matrix} \right\rangle = (1/\sqrt{2})\left| \begin{matrix} (3) \\ x \end{matrix} \right\rangle - (i/\sqrt{2})\left| \begin{matrix} (3) \\ y \end{matrix} \right\rangle,$$

$$\left| \begin{matrix} (3) \\ 2_3 \end{matrix} \right\rangle = (1/\sqrt{2})\left| \begin{matrix} (3) \\ x \end{matrix} \right\rangle + (i/\sqrt{2})\left| \begin{matrix} (3) \\ y \end{matrix} \right\rangle \quad (3.4.25)$$

if $|_x^{(3)}\rangle$ and $|_y^{(3)}\rangle$ are eigenvectors obtained in Figure 3.4.4. The new eigenstates correspond to a beautiful circular motion such as is depicted in Figure 3.4.5. However, this is just an $(x + iy)$ combination of x- and y-linear motion. Since x and y motions were degenerate any combination of them is allowed. This is related to the fact that degenerate $(l^\alpha \geq 2)$ irreps of non-Abelian groups are not uniquely defined.

$$|\overset{(3)}{\underset{x}{}}\rangle + i\,|\overset{(3)}{\underset{y}{}}\rangle$$
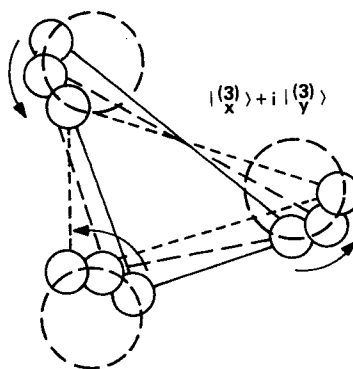
Figure 3.4.5 Moving-wave or circular form of type-3 eigenvector.

The circular $(x \pm iy)$ bases will be excited by circular polarized radiation, as we will see ,in Chapters 4 and 6. They also result in the application of magnetic fields, Jahn-Teller distortions, and for rotating molecules.

3.5 CHARACTER FORMULAS

For Abelian symmetry analysis the number of repetitions or FREQUENCY of a given irrep $\mathscr{D}^\alpha$ is the number of states of that type still to be separated by means other than symmetry projection. The same is true for multidimensional irreps of non-Abelian groups because different substrates or partners of any irrep will give rise to identical equations. One has only to solve one set for each irrep (α) regardless of its dimension l^α.

Let us now derive some simple formulas for frequency of an irrep of a finite group in a given representation. These are called CHARACTER formulas. Characters of multidimensional irreps are the traces of the $\mathscr{D}^\alpha$ matrices as defined in the following:

$$\chi^\alpha(g) = \text{TRACE } \mathscr{D}^\alpha(g) = \sum_{i=1}^{l^\alpha} \mathscr{D}^\alpha_{ii}(g). \tag{3.5.1}$$

For Abelian groups irreps and characters are the same thing, since then $l^\alpha = 1$ always. Nevertheless, every formula given in this section can be applied to either Abelian or non-Abelian groups.

One property of the characters is that they are equal for any two symmetry operators g and g' that are equivalent or from the same class. If g is in the same class with g', then $g' = h^{-1}gh$ for some other symmetry operators h.

Representing this gives

$$\chi^\alpha(g') = \sum_i^{l^\alpha} \mathscr{D}_{ii}^\alpha(g') = \sum_{i,j,k}^{l^\alpha} \mathscr{D}_{ij}^\alpha(h^{-1}) \, \mathscr{D}_{jk}^\alpha(g) \, \mathscr{D}_{ki}^\alpha(h)$$

$$= \sum_{j,k}^{l^\alpha} \left(\sum_i^{l^\alpha} \mathscr{D}_{ki}^\alpha(h) \, \mathscr{D}_{ij}^\alpha(h^{-1}) \right) \mathscr{D}_{jk}^\alpha(g)$$

$$= \sum_j^{l^\alpha} \mathscr{D}_{jj}^\alpha(g),$$

and finally

$$\chi_{g'}^\alpha \equiv \chi^\alpha(g') = \chi^\alpha(g), \qquad (3.5.2)$$

for all g in the class c_g.

Recall the completeness relations between the all-commuting idempotents $\mathbb{P}^\alpha$ and the irreducible or elementary idempotents P_{ii}^α:

$$\mathbb{P}^\alpha = \sum_i P_i^\alpha = \sum_i P_{ii}^\alpha.$$

This leads to a formula for the all-commuting idempotents $\mathbb{P}^\alpha$ in terms of characters using the formula for P_{ii}^α given in Eq. (3.4.19):

$$\mathbb{P}^\alpha = \sum_i P_{ii}^\alpha = (l^\alpha/{}^\circ G) \sum_g \sum_i \mathscr{D}_{ii}^{\alpha*}(g) g$$

$$= (l^\alpha/{}^\circ G) \sum_g \chi^{\alpha*}(g) g.$$

Since the characters are the same for equivalent operators, the preceding sum can be reduced to a sum over just one element from each class $c_g = (g + g' + \cdots)$,

$$\mathbb{P}^\alpha = (l^\alpha/{}^\circ G) \left[\chi_g^{\alpha*}(g + g' + \cdots) + \chi_h^{\alpha*}(h + h' + \cdots) + \cdots \right],$$

or

$$\mathbb{P}^\alpha = (l^\alpha/{}^\circ G) \sum_{\substack{\text{classes} \\ c_g}} \chi_g^{\alpha*} c_g. \qquad (3.5.3)$$

This sum is a key to the derivation and application of characters.

A. Derivation of Irrep Characters

The algebra of classes discussed in Section 3.2 gives the all-commuting idempotents

$$\mathbb{P}^\alpha = \sum_{\substack{\text{classes} \\ c_g}} p_g^\alpha c_g \qquad (3.5.4)$$

as a sum of classes. For the example of C_{3v} we obtained

$$\mathbb{P}^1 = \tfrac{1}{6}c_1 + \tfrac{1}{6}c_2 + \tfrac{1}{6}c_3,$$

$$\mathbb{P}^2 = \tfrac{1}{6}c_1 + \tfrac{1}{6}c_2 - \tfrac{1}{6}c_3,$$

$$\mathbb{P}^3 = \tfrac{2}{3}c_1 - \tfrac{1}{3}c_2, \qquad (3.5.4)_x$$

in Eq. (3.2.15). Relating the p_g^α coefficients in Eqs. (3.5.4) to characters in Eq. (3.5.3) gives

$$\chi_g^{\alpha*} = p_g^\alpha (l^\alpha / {}^\circ G)^{-1}. \qquad (3.5.5)$$

To use this one must first determine the dimension l^α which is the trace or character of the irrep of the unit class:

$$\chi_1^\alpha = l^\alpha = \text{Trace } \mathscr{D}^\alpha(1). \qquad (3.5.6)$$

Solving Eq. (3.5.5) gives

$$l^\alpha = \left({}^\circ G p_1^{\alpha*}\right)^{1/2}. \qquad (3.5.7)$$

The first column of Eq. $(3.5.4)_x$ gives

$$l^1 = \left(6 \cdot \tfrac{1}{6}\right)^{1/2} = 1,$$

$$l^2 = \left(6 \cdot \tfrac{1}{6}\right)^{1/2} = 1,$$

$$l^3 = \left(6 \cdot \tfrac{2}{3}\right)^{1/2} = 2, \qquad (3.5.7)_x$$

which is the first column of the C_{3v} character table in Eq. (3.5.8). The other characters follow from Eqs. $(3.5.4)_x$ and (3.5.5):

$j =$	1	2: (r, r^2)	3: $(\sigma_1 \sigma_2 \sigma_3)$
$\chi_j^{A'} = \chi_j^{A_1} = \chi_j^1 =$	1	1	1
$\chi_j^{A''} = \chi_j^{A_2} = \chi_j^2 =$	1	1	-1
$\chi_j^E = \chi_j^3 =$	2	-1	0

$$(3.5.8)$$

The standard notation $(1) \equiv A_1$, $(2) \equiv A_2$, and $(3) \equiv E$ for D_3 and C_{3v} irreps will be used from now on. The notation $(1) \equiv A'$ and $(2) \equiv A''$ is sometimes used instead for C_{3v} irreps.

B. Applications of Characters

The power of character theory is great, since it is independent of your choice of basis. Since a matrix trace is invariant to such choice it does not matter how a Hamiltonian is represented or which equivalent version of irreps you chose. Furthermore, sums over symmetry operators are replaced by sums over classes of operators, which can amount to a considerable saving of labor.

Here one of the simplest C_{3v} examples consisting of the three-pendulum system of Section 2.6 will be reexamined using character theory. The character method is not noticeably easier for such a simple problem, but it is a good pedagogical example.

(a) Deriving Irrep Frequency Suppose you want to find out which an⋅ how many irreps would appear on the diagonal of a given representation $\mathscr{R}$ upon reduction. That is, suppose you want to know the FREQUENCY f^α of irreps $\mathscr{D}^\alpha$ in the complete reduction,

$$\mathscr{T}^\dagger \mathscr{R}(g) \mathscr{T} = f^\alpha \mathscr{D}^\alpha(g) \oplus f^\beta \mathscr{D}^\beta(g) \oplus \cdots , \qquad (3.5.9)$$

of $\mathscr{R}$. This reduction holds for all combinations of g including the all-commuting idempotents $\mathbb{P}^\alpha$. Substituting $\mathbb{P}^\alpha$ for g and taking the trace gives

$$\text{Trace } \mathscr{R}(\mathbb{P}^\alpha) = f^\alpha \cdot l^\alpha , \qquad (3.5.10)$$

since $\mathscr{D}^\beta(\mathbb{P}^\alpha)$ is a unit matrix if $\alpha = \beta$ and zero otherwise. The equation for f^α,

$$f^\alpha = (1/l^\alpha) \text{ Trace } \mathscr{R}(\mathbb{P}^\alpha)$$

$$= (1/{}^\circ G) \sum_{\substack{\text{classes} \\ c_g}} \chi_g^{\alpha*} \text{ Trace } \mathscr{R}(c_g),$$

$$f^\alpha = (1/{}^\circ G) \sum_{\substack{\text{classes} \\ c_g}} \chi_g^{\alpha*} {}^\circ c_g \text{ Trace } \mathscr{R}(g), \qquad (3.5.11)$$

follows from Eq. (3.5.3), where ${}^\circ c_g$ is the order of class c_g and g is any element in the class.

For the example we need only the traces of 1, r, and , say, σ_3. The first trace equals the number of pendulum coordinates: Trace $\mathscr{R}(1) = 3$. The r trace vanishes: Trace $\mathscr{R}(r) = 0$, since all coordinates are moved by r. One coordinate sits on each reflection plane; hence Trace $\mathscr{R}(\sigma_3) = 1$. The A_1

frequency is given by

$$f^{A_1} = (1/{}^{\circ}G)\left[\chi_1^{A_1^*}{}^{\circ}c_1 \cdot 3 + \chi_r^{A_1^*}{}^{\circ}c_r \cdot 0 + \chi_\sigma^{A_1^*}{}^{\circ}c_\sigma \cdot 1\right]$$
$$= (1/{}^{\circ}G)\left[3\chi_1^{A_1^*} + 3\chi_\sigma^{A_1^*}\right] = 1, \qquad (3.5.11a)_x$$

where the character table in Eq. (3.5.8) is used. Similarly, one has the other frequencies:

$$f^{A_2} = \tfrac{1}{6}\left[3\chi_1^{A_2^*} + 3\chi_\sigma^{A_2^*}\right] = 0, \qquad (3.5.11b)_x$$

$$f^{E} = \tfrac{1}{6}\left[3\chi_1^{E^*} + 3\chi_\sigma^{E^*}\right] = 1. \qquad (3.5.11c)_x$$

From this one learns that the C_{3v} pendulum system has one A_1 level and one E level. The latter is degenerate since $l^E = 2$.

(b) Deriving Eigenvalues Let us use C_{3v} characters to rederive the eigenvalues of the three-pendulum acceleration matrix

$$\langle \mathbf{a} \rangle = \begin{pmatrix} \langle 1|\mathbf{a}|1\rangle & \langle 1|\mathbf{a}|r\rangle & \langle 1|\mathbf{a}|r^2\rangle \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} = \begin{pmatrix} 2a+b & -a & -a \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix},$$
$$(3.5.12)$$

which was solved in Chapter 2. In this case one may assume that the basis which diagonalizes $\langle \mathbf{a} \rangle$ would bring $\langle \mathbb{P}^\alpha \rangle$ to diagonal form also. This form of $\langle \mathbb{P}^\alpha \rangle$ would have a unit submatrix at the same diagonal positions that hold α-type eigenvalues $a^\alpha = \left\langle {\alpha \atop i} \middle| \mathbf{a} \middle| {\alpha \atop i} \right\rangle$ of the $\langle \mathbf{a} \rangle$ matrix. Zeros would occur at all other positions of the $\langle \mathbb{P}^\alpha \rangle$ matrix. Given that frequencies f^{A_1} and f^E are unit from Eqs. $(3.5.11)_x$ one may derive the $\langle \mathbf{a} \rangle$ eigenvalues from the formula

$$a^\alpha = (1/l^\alpha)\,\mathrm{Trace}\,\langle \mathbf{a}\mathbb{P}^\alpha \rangle$$
$$= (1/{}^{\circ}G)\sum_g \chi^{\alpha^*}(g)\,\mathrm{Trace}\,\langle \mathbf{a}g \rangle.$$

Once again the sum may be simplified since the trace of $\langle t\mathbf{a}gt^{-1}\rangle$ is equal to the trace of $\langle \mathbf{a}g\rangle$. Since all symmetry operators commute with $\mathbf{a}$, one has that

$$\mathrm{Trace}\,\langle t\mathbf{a}gt^{-1}\rangle = \mathrm{Trace}\,\langle \mathbf{a}tgt^{-1}\rangle = \mathrm{Trace}\,\langle \mathbf{a}g'\rangle$$

does not depend on which element of class $c_g = \{g, g', \dots\}$ is used. There-

fore the a^α formula reduces to a sum

$$a^\alpha = (1/\,^\circ G) \sum_{\substack{\text{classes} \\ c_g}} \chi_g^{\alpha^*} c_g \, \text{Trace} \, \langle \mathbf{a}g \rangle \qquad (3.5.13)$$

over just one element from each class.

The trace in the formula can be evaluated in such a way that only the first row $\{\langle 1|\mathbf{a}|1 \rangle, \langle 1|\mathbf{a}|r \rangle, \ldots\}$ of an $\langle \mathbf{a} \rangle$ matrix is required. For the matrix in Eq. (3.5.12) we have

$$\begin{aligned}
\text{Trace} \, \langle \mathbf{a}g \rangle &= \langle 1|\mathbf{a}g|1 \rangle + \langle r|\mathbf{a}g|r \rangle + \langle r^2|\mathbf{a}g|r^2 \rangle \\
&= \langle 1|\mathbf{a}g|1 \rangle + \langle 1|r^{-1}\mathbf{a}gr|1 \rangle + \langle 1|r^{-2}\mathbf{a}gr^2|1 \rangle \\
&= \langle 1|\mathbf{a}|g \rangle + \langle 1|\mathbf{a}|r^{-1}gr \rangle + \langle 1|\mathbf{a}|r^{-2}gr^2 \rangle. \qquad (3.5.14)
\end{aligned}$$

Substituting in turn $g = 1$, r, and σ_3, one finds

$$\text{Trace} \, \langle \mathbf{a} \rangle = 3\langle 1|\mathbf{a}|1 \rangle = 3(2a + b),$$

$$\text{Trace} \, \langle \mathbf{a}r \rangle = 3\langle 1|\mathbf{a}|r \rangle = -3a,$$

$$\text{Trace} \, \langle \mathbf{a}\sigma_3 \rangle = \langle 1|\mathbf{a}|1 \rangle + \langle 1|\mathbf{a}|r \rangle + \langle 1|\mathbf{a}|r^2 \rangle = b,$$

where the symmetry definitions $\sigma_3|1 \rangle = |1 \rangle$, $\sigma_2|1 \rangle = |r \rangle$, and $\sigma_1|1 \rangle = |r^2 \rangle$ of pendulum coordinates are used in the last line. Substituting the traces into Eq. (3.5.13) gives

$$a^{A_1} = \tfrac{1}{6}\left[1 \cdot 3(2a + b) + 1 \cdot 2 \cdot (-3a) + 3b \right] = b,$$

$$a^E = \tfrac{1}{6}\left[2 \cdot 3(2a + b) - 1 \cdot 2 \cdot (-3a) + 0 \right] = 3a + b,$$

in agreement with the previous calculation [recall Eq. (2.6.10)].

If an irrep had been repeated with a frequency $f^\alpha \geq 2$ the character procedure may still be applied. However, one can only derive the *average* of the a^α eigenvalues $\{a^\alpha, a^{\alpha'}, a^{\alpha''}, \ldots\}$:

$$\begin{aligned}
\langle \mathbf{a} \rangle_{\text{average}}^\alpha &\equiv 1/f^\alpha \sum a^{\alpha'} \\
&= (1/\,^\circ Gf^\alpha) \sum_{\substack{\text{classes} \\ c_g}} \chi_g^{\alpha^*} \,^\circ c_g \, \text{Trace} \, \langle \mathbf{a}g \rangle. \qquad (3.5.15)
\end{aligned}$$

To find the individual eigenvalues and eigenvectors requires full P_{ij}^α projection operator techniques in general.

3.6 D_n AND C_{nv} SYMMETRY AND BLOCH WAVES

A discussion of Bloch waves and C_n symmetry was given in Section 2.12. Here the D_n and C_{vn} symmetry analysis of Bloch waves will be given. This should provide a clear physical picture of the meaning of various D_n irreps for arbitrary n as well as some other spectroscopic concepts.

A. Tetragonal Symmetry

The tetragonal symmetries C_{4v} or D_{4n} were introduced in Section 3.1 and Figure 3.1.9. There it was suggested that the reader perform all the derivations that were done for C_{3v} or D_3. (See Problem 3.1.1.) The results are given in the following and are followed by an interpretation of the irrep bases in terms of Bloch waves.

The D_4 Hamilton nomogram is shown in Figure 3.6.1, following the conventions established before in Figure 3.1.9. This facilitates the computation of the group table, which is given in the following. Note that the C_{4v} group table is obtained by replacing transverse 180° rotations $\{R_1^2, R_2^2, i_3, i_4\}$ by vertical-plane reflections $\{\sigma_1 = IR_1^2, \sigma_2 = IR_2^2, \sigma_3 = Ii_3, \sigma_4 = Ii_4\}$.

1	R^2	R	R^3	R_1^2	R_2^2	i_3	i_4
R^2	1	R^3	R	R_2^2	R_1^2	i_4	i_3
R	R^3	R^2	1	i_3	i_4	R_2^2	R_1^2
R^3	R	1	R^2	i_4	i_3	R_1^2	R_2^2
R_1^2	R_2^2	i_4	i_3	1	R^2	R^3	R
R_2^2	R_1^2	i_3	i_4	R^2	1	R	R^3
i_3	i_4	R_1^2	R_2^2	R	R^3	1	R^2
i_4	i_3	R_2^2	R_1^2	R^3	R	R_2^2	1

$$(3.6.1a)$$

1	c_2	c_R	c_1	c_3
	1	c_R	c_1	c_3
		$21 + 2c_2$	$2c_3$	$2c_1$
			$21 + 2c_2$	$2c_R$
				$21 + 2c_2$

$$(3.6.1b)$$

The class algebra table (3.6.1b) follows. Note that transverse 180° rotations R_1^2 and R_2^2 around x and y axes, respectively, belong in a different class than diagonal rotations i_3 and i_4.
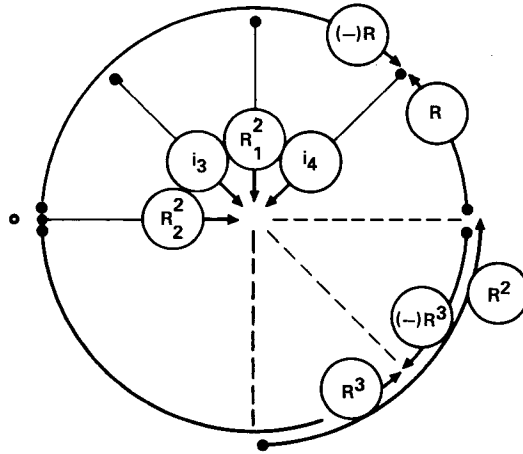
Figure 3.6.1 Hamilton turn nomogram for D_4 symmetry.

At least two minimal equations are needed to reduce the five-dimensiona' class algebra since all the c_j belong to one-, two-, or three-dimensional subalgebras. One finds $c_R^3 = 4c_R$ and $c_1^3 = 4c_1$, and combining the resulting idempotents gives the following five all-commuting idempotents:

$$\mathbb{P}^1 = \tfrac{1}{8}(1 + c_2 + c_R + c_1 + c_3),$$

$$\mathbb{P}^2 = \tfrac{1}{8}(1 + c_2 - c_R + c_1 - c_3),$$

$$\mathbb{P}^3 = \tfrac{1}{8}(1 + c_2 + c_R - c_1 - c_3),$$

$$\mathbb{P}^4 = \tfrac{1}{8}(1 + c_2 - c_R - c_1 + c_3),$$

$$\mathbb{P}^5 = \tfrac{1}{2}(1 - c_2). \tag{3.6.2}$$

Following Section (3.5.A) one converts the preceding $\mathbb{P}^\alpha$ to irrep characters:

C_{4v}				$(\sigma_1\sigma_2)$	$(\sigma_3\sigma_4)$
D_4	$j = 1,$	$(R^2),$	$(R, R^3),$	$(R_1^2 R_2^2),$	$(i_3 i_4)$
$\chi^{A'} = \chi^{A_1} = \chi_j^1 =$	1	1	1	1	1
$\chi^{B'} = \chi^{B} = \chi_j^2 =$	1	1	-1	1	-1
$\chi^{A''} = \chi^{A_2} = \chi_j^3 =$	1	1	1	-1	-1
$\chi^{B''} = \chi^{B_2} = \chi_j^4 =$	1	1	-1	-1	1
$\chi^{E} = \chi_j^E = \chi_j^5 =$	2	-2	0	0	0

$$\tag{3.6.3}$$

Conventional notation for D_4 irreps is given on the left-hand side of (3.6.3) along with an optional notation sometimes used for the isomorphic C_{4v} symmetry.

The A and B irreps all have dimension $l^{A_j} = 1 = l^{B_j}$, and so the idempotents $\mathbb{P}^{A_j}$ and $\mathbb{P}^{B_j}$ are irreducible as well as all-commuting. However, the E irrep has dimension $l^E = 2$, so the $\mathbb{P}^E$ idempotent must split it in two. How one splits $\mathbb{P}^E$ depends on one's choice of Abelian subgroups. One choice is the subgroup $C_4 = \{1, R, R^2, R^4\}$, which is analogous to the C_3 choice in the C_{3v} analysis. Multiplying $\mathbb{P}^E$ by a C_4 unit decomposition gives

$$\mathbb{P}^E = \mathbb{P}^E \mathbf{1} = \mathbb{P}^E (P^{0_4} + P^{1_4} + P^{2_4} + P^{3_4})$$
$$= 0 + \mathbb{P}^E P^{1_4} + 0 + \mathbb{P}^E P^{3_4}$$
$$= P^E_{1_4} + P^E_{3_4}, \tag{3.6.4a}$$

where

$$P^E_{1_4} = (\mathbf{1} - R^2 + iR - iR^3)/4,$$
$$P^E_{3_4} = (\mathbf{1} - R^2 - iR + iR^3)/4. \tag{3.6.4b}$$

This results in a complex set of E irreps analogous to the circular irreps of C_{3v}. Two examples are

$$\mathscr{D}^{\circ E}(R) = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}, \qquad \mathscr{D}^{\circ E}(R_1^2) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{3.6.5}$$

(Note that products of two elements can generate the whole group D_4; $\mathscr{D}^{\circ E}$ is defined by representing just two GENERATORS.) Since the circular or C_4-defined irreps $\mathscr{D}^{\circ E}$ are complex they give rise to moving-wave eigenstates in physical applications.

Standing-wave irreps result if one chooses to diagonalize one of the transverse 180° rotations, say R_1^2, or the Abelian subgroup $C_2 = \{1, R_1^2\}$. The unit decomposition of C_2 splits P^E as follows:

$$\mathbb{P}^E = \mathbb{P}^E \mathbf{1} = \mathbb{P}^E (P^1 + P^2)$$
$$= P^E_1 + P^E_2, \tag{3.6.6a}$$

where

$$P^E_1 = (\mathbf{1} - R^2 + R_1^2 - R_2^2)/4,$$
$$P^E_2 = (\mathbf{1} - R^2 - R_1^2 + R_2^2)/4. \tag{3.6.6b}$$

The resulting E irreps are the following real matrices.

$$\mathscr{D}^E(\mathbf{1}) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \mathscr{D}^E(R^2) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$\mathscr{D}^E(R) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \qquad \mathscr{D}^E(R^3) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix},$$

$$\mathscr{D}^E(R_1^2) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \mathscr{D}^E(R_2^2) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix},$$

$$\mathscr{D}^E(i_3) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \mathscr{D}^E(i_4) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}. \qquad (3.6.7)$$

Note that the whole subgroup $D_2 = \{1\,R_1^2 R_2^2 R^2\}$ is represented by diagonal matrices. Stated another way, the standing-wave E irrep is reduced with respect to $D_2 = \{1\,R_1^2 R_2^2 R^2\}$

$$\mathscr{D}^E(h \text{ in } D_2) = \left[\begin{array}{c|c} D^{B_1}(h) & 0 \\ \hline 0 & D^{B_2}(h) \end{array}\right] = D^{B_1}(h) \oplus D^{B_2}(h), \quad (3.6.8)$$

as well as $C_2 = \{1, R_1^2\}$.

$$\mathscr{D}^E(h \text{ in } C_2) = \left[\begin{array}{c|c} D^1(h) & 0 \\ \hline 0 & D^2(h) \end{array}\right] = D^1(h) \oplus D^2(h). \quad (3.6.9)$$

(Recall the irreps of D_2 labeled in Section 2.8.) Contrast this with the moving-wave irrep $\mathscr{D}^{\circ E}$, which is reduced instead with respect to $C_4 = \{1, R, R^2, R^3\}$.

$$\mathscr{D}^{\circ E}(h \text{ in } C_4) = \left[\begin{array}{c|c} D^{1_4}(h) & 0 \\ \hline 0 & D^{3_4}(h) \end{array}\right] = D^{1_4}(h) \oplus D^{3_4}(h). \quad (3.6.10)$$

The standing Bloch waves provide a simple picture of the D_4 irreps. The waves drawn in Figure 3.6.2 are a special case of the Bloch solutions described in Section 2.12.A and Figure 2.12.2. Note that (B) labels waves on the first Brillouin band boundaries as before, while A waves stand at the zeroth and second boundaries. Note that the subscripts 1 and 2 denote symmetry and antisymmetry, respectively, to the reversal R_1^2 around the first potential well; i.e., A_1 and B_1 are symmetric waves, while A_2 and B_2 are antisymmetric. In the character table (3.6.3) this is expressed by entries

$$\chi_{R_1^2}^{A_1} = 1 = \chi_{R_1^2}^{B_1}; \qquad \chi_{R_1^2}^{A_2} = -1 = \chi_{R_1^2}^{B_2}. \qquad (3.6.11)$$
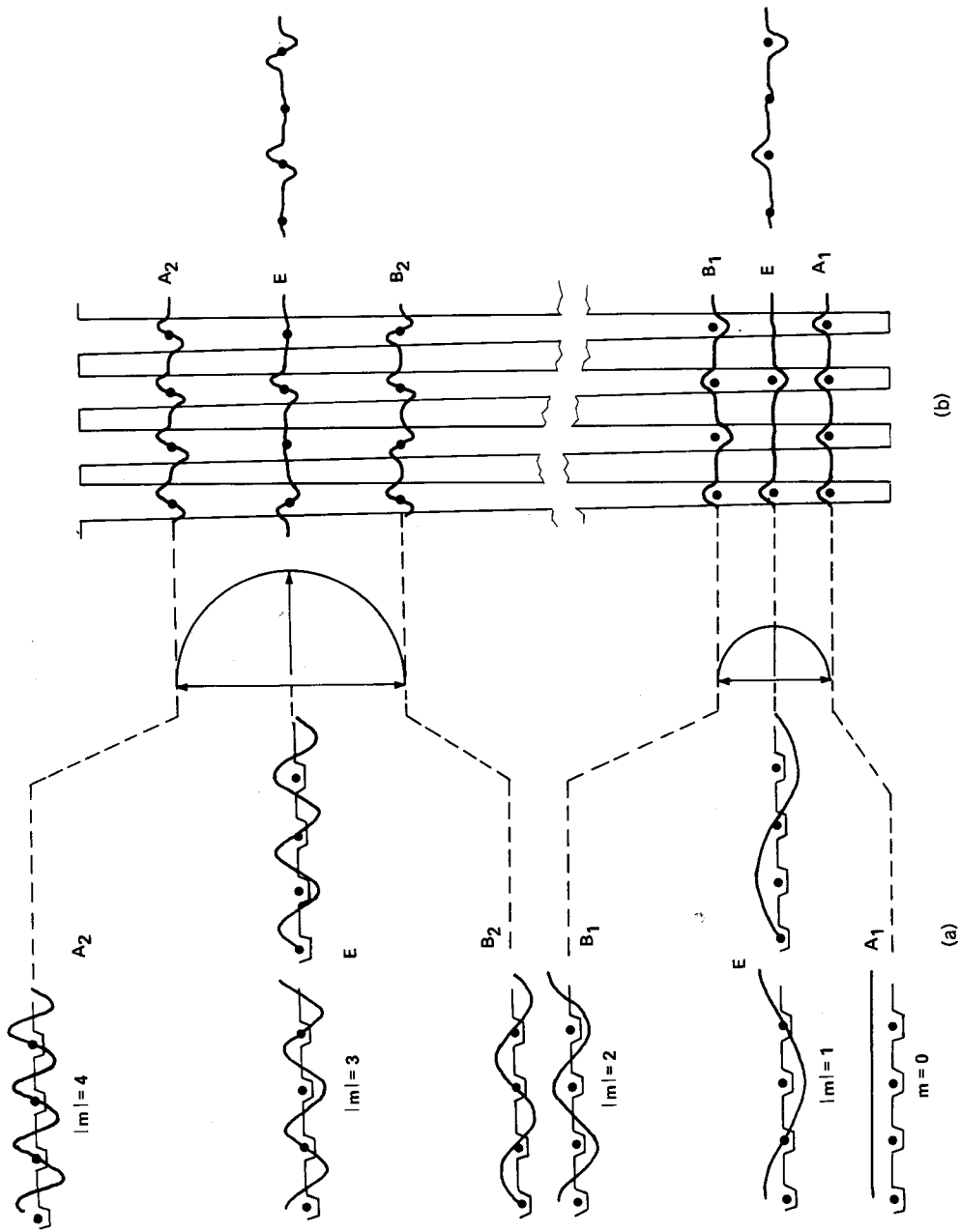
Figure 3.6.2 One-dimensional Bohr and Bloch waves in D_4 symmetry. (a) Weak D_4 potential. (b) Strong D_4 potential.

One could label standing cosine and sine standing-wave states similarly as χ_1^E and χ_2^E, respectively. However, do not forget that the E states are degenerate partner bases of a single irrep E. The E waves can slide their nodes to halfway or anywhere between wells without costing them energy, while the A and B waves cannot. Note that the B waves change sign under operation R (or R^3), which moves exactly one well spacing forward or backward. In the character table (3.6.3) this corresponds to the entries

$$\chi_R^{B_1} = -1 = \chi_R^{B_2}. \tag{3.6.12}$$

The A waves are unaffected by R or R^3, i.e.,

$$\chi_R^{A_1} = 1 = \chi_R^{A_2}. \tag{3.6.13}$$

As the potential wells of a D_4 symmetric potential grow deeper the form of the waves changes. This was explained in Section 2.12.A(c). However, as long as the D_4 symmetry is maintained the symmetry properties of a given level do not change. The states labeled A_1, B_1, etc., on the left-hand side of Figure 3.6.2 transform into corresponding states of the same label on the right-hand side. This transformation involves adding many higher harmonic-wave states which have that same symmetry label. The resulting spectrum will consist of repeating and alternating (A_1EB_1), (B_2EA_2), (A_1EB_1), (B_2EA_2),... clusters of D_4 levels in the limit of very deep wells. The lower-energy clusters become more nearly degenerate as the wells become deeper and their tunneling amplitudes S nearly vanish. Recall the discussion of Section 2.12.A(c). There D_n symmetry was implicitly assumed.

It remains to see what happens to a D_4 spectrum if symmetry is reduced to $D_4 = \{1, R, R^2, R^3\}$ or $C_2 = \{1, R_1^2\}$. A magnetic field placed along the z axis would reduce D_4 or C_{4v} symmetry to C_4, since transverse rotations R_j^2 or reflections σ_j do not leave such a field invariant. Similarly, if a field is put along the x axis, only C_2 symmetry remains.

The E irrep of C_{4v} or D_4 is not an irreducible representation of C_4. According to Eq. (3.6.10) it reduces to irreps of C_4,

$$\mathscr{D}^E \downarrow C_4 \simeq D^{1_4} \oplus D^{3_4}, \tag{3.6.14}$$

corresponding to two moving waves of wave number or momentum $m = 1$ and $m = 2 = -1$ modulo 4. The arrow ($\downarrow$) indicates SUBDUCTION or symmetry reduction, wherein a representation of a larger group is restricted to a subgroup. If the representation becomes reducible, or reduced as in Eq. (3.6.10), then the degeneracy of levels labeled by that representation may split. In this case Eq. (3.6.14) predicts that E levels will split in two as in Figure 3.6.3. This is elementary ZEEMAN SPLITTING for which the right-handed moving wave ($m = 1$ mod 4) has different energy than the left-handed ($m = -1$ mod 4) wave.
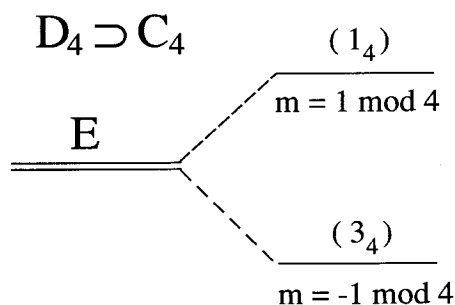
$$D_4 \supset C_4$$

Figure 3.6.3 Zeeman splitting of E level ($E \downarrow C_4 = (1_4) \oplus (3_4)$).

This is an important concept in symmetry analysis of spectroscopy. Energy-level splitting is associated with splitting of idempotents, viz., $\mathscr{D}^E \downarrow C_4 \simeq D^{1_4} + D^{3_4}$ is associated with $P^E = P^E_{1_4} + P^E_{3_4}$. One says that the E irrep of C_{4v} or D_4 is CORRELATED with the 1_4 and 3_4 irreps of subgroup C_4. Similarly, other irreps in (3.6.3) are correlated with C_4 irreps; though, of course, one-dimensional levels cannot split. For example, comparing the first three columns of the table with C_4 irreps gives

$$\mathscr{D}^{A_1} \downarrow C_4 = \mathscr{D}^{A_2} \downarrow C_4 = D^{0_4} = D^A, \qquad (3.6.15a)$$

$$\mathscr{D}^{B_1} \downarrow C_4 = \mathscr{D}^{B_2} \downarrow C_4 = D^{2_4} = D^B. \qquad (3.6.15b)$$

This means A_1 and A_2 waves which could not combine in C_{4v} or D_4 symmetry can do so under the lower symmetry, since they belong to the same irrep $A \equiv 0_4$ of C_4. The same applies to B_1 and B_2 waves. It means that waves that had to be standing waves before may combine with complex coefficients in the presence of a magnetic field and get moving again. Indeed, one of the effects of magnetic fields it to improve the "circulation" of otherwise quenched orbitals.

B. Hexagonal Symmetry

C_{6v} and D_6 symmetry groups are particularly easy to treat, since they are outer products of groups that we have already solved. Since they are both symmetries of hexagonal objects (see Figure 3.6.4) they contain a 60° rotation (h) around the z axis. This implies the existence of a 180° rotation (h^3) which commutes with the transverse 180° rotations (ρ_j) in D_6 or reflections ($\sigma_j = I\rho_j$) in C_{6v}. Hence it is permissible to write

$$D_3 \times C_2 = \{1, h^2, h^4, \rho_1, \rho_2, \rho_3\} \times \{1, h^3\}$$

$$= \{1, h^2, h^4, \rho_1, \rho_2, \rho_3, h^3, h^5, h, \rho_1 h^3, \rho_2 h^3, \rho_3 h^3\}$$

$$= D_6 \qquad (3.6.16)$$

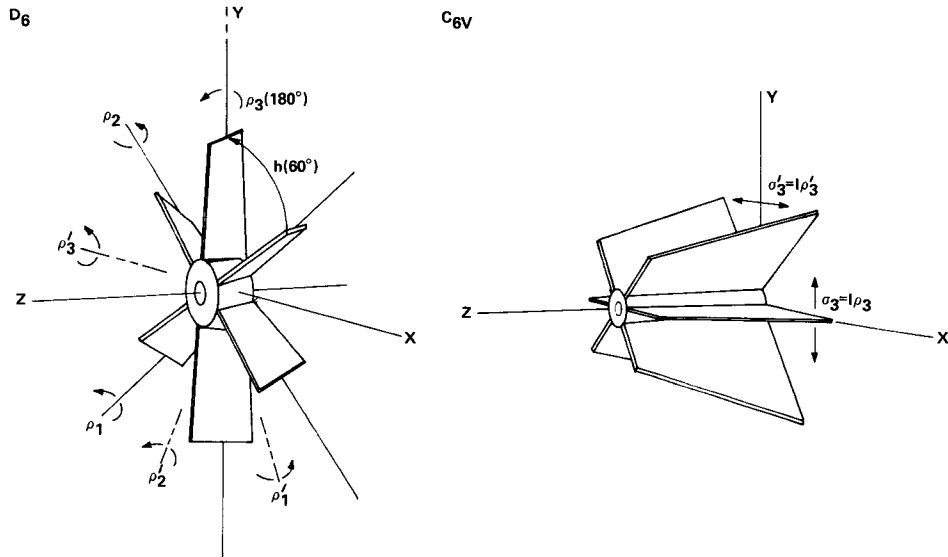according to the definition of the outer product given in Section 2.10. Each

Figure 3.6.4   Pictorial comparison of D_6 and C_{6v} symmetry. Note that the 180° rotations in D_6 which are marked with primes (ρ'_j) have axes of rotation which are orthogonal to those of the corresponding unprimed rotations (ρ_j). The same applies to the C_{6v} reflections.

element in D_6 is a unique product of elements in D_3 and $C_2 = \{1, h^3\}$. The $\pm 60°$ rotations are $h = h^4 h^3$ and $h^5 = h^2 h^3$, respectively. The new 180° rotations are $\rho'_1 \equiv \rho_1 h^3$, $\rho'_2 = \rho_2 h^3$, and $\rho'_3 \equiv \rho_3 h^3$, and their axes are indicated in Figure 3.6.4.

The cross-product definition allows the immediate construction of the D_6 character table from those in D_3 and C_2:

D_3	1	$(h^2 h^4)$	(ρ_i)
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$\times$

C_2	1	h^3
A	1	1
B	1	-1

D_6	1	$(h^2 h^4)$	(ρ_i)	h^3	(hh^5)	(ρ'_i)
A_1	1	1	1	1	1	1
A_2	1	1	-1	1	1	-1
$= E_2$	2	-1	0	2	-1	0
B_1	1	1	1	-1	-1	-1
B_2	1	1	-1	-1	-1	1
E_1	2	-1	0	-2	1	0

$. \quad (3.6.17)$

The process is the same as was used in Section 2.10 for Abelian groups, except now there are two-dimensional irreps involved. The bottom row of the character table is the trace of the irrep $\mathscr{D}^{E_1}$ given by the cross-product relation

$$\mathscr{D}_{ij}^{E_1} \text{ (of } D_6) = \mathscr{D}_{ij}^{E} \text{ (of } D_3) \; \mathscr{D}^{B} \text{ (of } C_2). \tag{3.6.18}$$

For example, using standing-wave irreps of D_3 one has

$$\mathscr{D}^{E_1}(h^4) = \mathscr{D}^{E}(h^4)\mathscr{D}^{B}(1), \qquad \mathscr{D}^{E_1}(h) = \mathscr{D}^{E}(h^4)\mathscr{D}^{B}(h^3)$$

$$= \begin{pmatrix} -\dfrac{1}{2} & \dfrac{\sqrt{3}}{2} \\ -\dfrac{\sqrt{3}}{2} & -\dfrac{1}{2} \end{pmatrix} \qquad = \begin{pmatrix} \dfrac{1}{2} & -\dfrac{\sqrt{3}}{2} \\ \dfrac{\sqrt{3}}{2} & \dfrac{1}{2} \end{pmatrix} \tag{3.6.18}_x$$

for the z rotation by $\omega_z = 240°$ and $\omega_z = 60°$, respectively. Note that either one is given by the rotation matrix formula

$$\mathscr{D}^{E_1}(\omega_z) = \begin{pmatrix} \cos \omega_z & -\sin \omega_z \\ \sin \omega_z & \cos \omega_z \end{pmatrix} \tag{3.6.19}$$

for x and y components for a vector. The other two-dimensional irrep $\mathscr{D}^{E_2}$ is given by the cross-product relation

$$\mathscr{D}_{ij}^{E_2} \text{ (of } D_6) = \mathscr{D}_{ij}^{E} \text{ (of } D_3) \; \mathscr{D}^{A} \text{ (of } C_2). \tag{3.6.20}$$

For the z rotations by $\omega_z = 240°$ (h^4) and $\omega_z = 60°$ (h) one has identical matrices:

$$\mathscr{D}^{E_2}(h^4) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} = \mathscr{D}^{E_2}(h). \tag{3.6.20}_x$$

The matrix formula which gives the $\mathscr{D}^{E_2}$ z rotations is

$$\mathscr{D}^{E_2} = \begin{pmatrix} \cos 2\omega_z & \sin 2\omega_z \\ -\sin 2\omega_z & \cos 2\omega_z \end{pmatrix}, \tag{3.6.21}$$

and it is appropriate for irreducible tensor rotations, as will be explained in Chapter 6.

For now it is easier to appreciate the difference between E_1 and E_2 irreps, and the A and B irreps as well, by appealing to Bloch-wave structure.
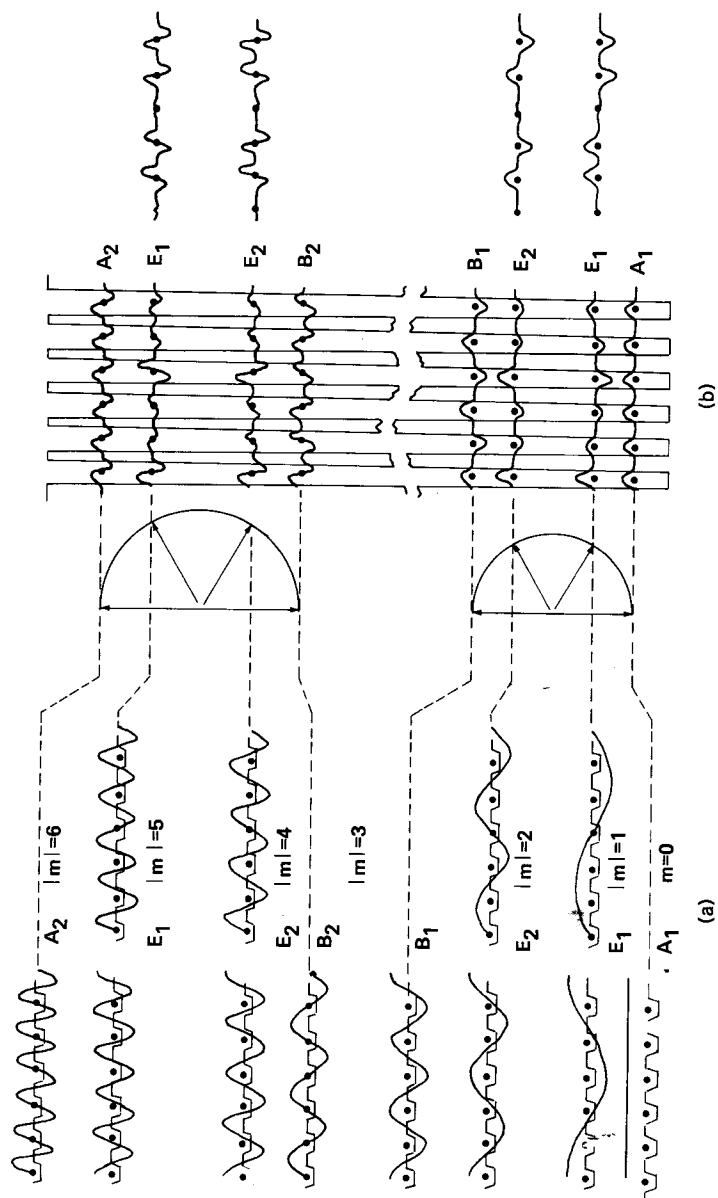
Figure 3.6.5 One-dimensional Bohr and Bloch waves in D_6 symmetry. (a) Weak D_6 potential. (b) Strong D_6 potential.

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The standing-wave solutions ($\sin m\phi$) and ($\cos m\phi$) for weak D_6 symmetric potentials are drawn in Figure 3.6.5(a) for $0 \leq m \leq 6$. Note that E_1 and E_2 label the $m = 1$ and $m = 2$ waves, respectively, and these states are doubly degenerate. E_1 and E_2 also label the $m = 5$ and $m = 4$ waves, since $5 = -1$ mod 6 and $4 = -2$ mod 6, respectively.

The B_1 and B_2 waves each have $m = 3$ waves on the ring, but are not degenerate. A source of possible confusion concerns the question of which has higher energy. Figure 3.6.5(a) shows the B_1 wave with antinodes or maxima in potential valleys. Hence, it has lower energy than the B_2 wave, which sits on the potential hills. This implies that B_1 is symmetric to 180° rotations around axes centered in valleys and antisymmetric to rotations around axes centered in hills. The B_1 characters from Eq. (3.6.17) for transverse 180° rotations are

$$\chi_\rho^{B_1} = 1, \qquad \chi_{\rho'}^{B_1} = -1. \tag{3.6.22}$$

This indicates an implicit assumption about how the ρ_j rotation axes are related to the potential: they lie in *valleys*. Then the local parity in each valley determines A and B indices. (1) labels evenness or symmetry, and (2) labels oddness or antisymmetry. The A_1 and B_1 characters,

$$\chi_\rho^{A_1} = \chi_\rho^{B_1} = 1, \tag{3.6.23}$$

are positive, while the A_2 and B_2 characters,

$$\chi_\rho^{A_2} = \chi_\rho^{B_2} = -1, \tag{3.6.24}$$

are negative. Whenever possible we shall let valley operators label the symmetry. This is particularly important for large potentials, as indicated in Figure 3.6.5(b). Then the rapidly varying parts of the wave function are squeezed into the valleys, and their shapes determine the energy of a whole band. A_1 and B_1 levels are upper or lower energy bounds for a band of waves made of locally even wave functions in valleys. A_2 and B_2 levels are the same for locally odd wave functions.

Finally, remember that A and B levels refer to even or odd behavior under axial or cyclic rotation (h or h^5) from one well to the next. The A waves are identical in each well and have unit characters:

$$\chi_h^{A_1} = \chi_h^{A_2} = 1. \tag{3.6.25}$$

The B waves change sign from well to well and have negative characters:

$$\chi_h^{B_1} = \chi_h^{B_2} = -1. \tag{3.6.26}$$

The correlation of D_6 irreps with those of subgroup $C_6 = \{1, h, h^2, h^3, h^4, h^5\}$ and with those of subgroup $C_2 = \{1, \rho_3\}$ can be deduced by characters. From the preceding equations we deduce that

$$\mathscr{D}^{A_1} \downarrow C_6 = \mathscr{D}^{A_2} \downarrow C_6 = D^A \text{ (of } C_6) = D^{0_6},$$

$$\mathscr{D}^{B_1} \downarrow C_6 = \mathscr{D}^{B_2} \downarrow C_6 = D^B \text{ (of } C_6) = D^{3_6}.$$

this is analogous to Eqs. (3.6.15) for $D_4 \downarrow C_4$ correlation. Similarly, we deduce from Eqs. (3.6.23) and (3.6.24) that

$$\mathscr{D}^{A_1} \downarrow C_2 = \mathscr{D}^{B_1} \downarrow C_2 = D^+ \text{ (of } C_2) = D^{0_2},$$

$$\mathscr{D}^{A_2} \downarrow C_2 = \mathscr{D}^{B_2} \downarrow C_2 = D^- \text{ (of } C_2) = D^{1_2}$$

is the $C_2 = \{1, \rho_3\}$ correlation for A and B irreps of D_6.

It is convenient to summarize all such correlations into CORRELATION TABLES such as the following for $D_6 \downarrow C_6$ and $D_6 \downarrow C_2$:

	D^{0_6}	D^{1_6}	D^{2_6}	D^{3_6}	D^{4_6}	D^{5_6}
$\mathscr{D}^{A_1} \downarrow C_6 =$	1	·	·	·	·	·
$\mathscr{D}^{A_2} =$	1	·	·	·	·	·
$\mathscr{D}^{B_1} =$	·	·	·	1		
$\mathscr{D}^{B_2} =$	·	·	·	1		
$\mathscr{D}^{E_1} =$	·	1	·	·	·	1
$\mathscr{D}^{E_2} =$	·	·	1	·	1	·

$$, \tag{3.6.27a}$$

	D^{0_2}	D^{1_2}
$\mathscr{D}^{A_1} \downarrow C_2 =$	1	·
$\mathscr{D}^{A_2} =$	·	1
$\mathscr{D}^{B_1} =$	1	·
$\mathscr{D}^{B_2} =$	·	1
$\mathscr{D}^{E_1} =$	1	1
$\mathscr{D}^{E_2} =$	1	1

$$. \tag{3.6.27b}$$

The last two rows in either table indicate Zeeman splittings such as

$$\mathscr{D}^{E_1} \downarrow C_6 = D^{1_6} + D^{5_6}.$$

Finally, note that C_n or D_n symmetry with odd n cannot have B waves. Neither can D_n have two classes ρ_j and ρ'_j of valley and hill 180° rotations, since hills are opposite valleys on the odd-n symmetric ring. You should be able to construct diagrams like Figure 3.6.5 for the irreps A_1, A_2, E_1, and E_2 of D_5, and the irreps A_1, A_2, E_1, E_2, and E_3 of D_7.

C. Higher D_n Symmetries: D_{nh} and D_{nd}

Anyone who has resolved D_2, D_3, and D_4 symmetries and their representations can quickly understand all the other dihedral or D-type symmetries. This includes the crystal point symmetries D_{2h}, D_{3h}, D_{4h}, D_{6h}, D_{2d}, and D_{3d}. (D_{2h} is Abelian.) However, the noncrystal or molecular point symmetries D_{5h}, D_{7h}, D_{8h}, ..., etc., or D_{4d}, D_{5d}, D_{6d}, ..., etc., are no more difficult.

The D_{nh} symmetries all contain a horizontal or xy-plane reflection operation:

$$\sigma_h = \sigma_{xy} = IR_z^2 \, (180°).$$

This operation commutes with all R_z rotations and all transverse 180° ρ_j operations. Hence, the group D_{nh} can be written as an outer product,

$$D_{nh} = D_n \times C_h = D_n \times \{1, \sigma_h\}. \qquad (3.6.28)$$

For even n the rotation R_z (180°) and the product $R_z\sigma_h = I$, i.e., inversion, must be in D_{nh}. Then one can write

$$D_{nh} = D_n \times C_i = D_n \times \{1, I\} \qquad (n \text{ even}). \qquad (3.6.29)$$

D_{nh} symmetry can be pictured as two parallel and identical regular n polygons placed one above the other. Some examples are shown in Figure 3.6.6(a). To have D_{nh} symmetry each vertex of the upper polygon must lie directly above a vertex of the lower one. If one polygon is rotated halfway by diagonal angle $\frac{1}{2}(2\pi/n)$ then the symmetry D_{nd} results. As shown in Figure 3.6.6(b) the center of each polygonal face of the upper D_{nd} polygon lies above a diagonal or vertex of the lower one.

From Figure 3.6.6 one can appreciate that two types of D_{nd} groups emerge. For n odd ($n \geq 3$) the symmetry contains inversion and can be
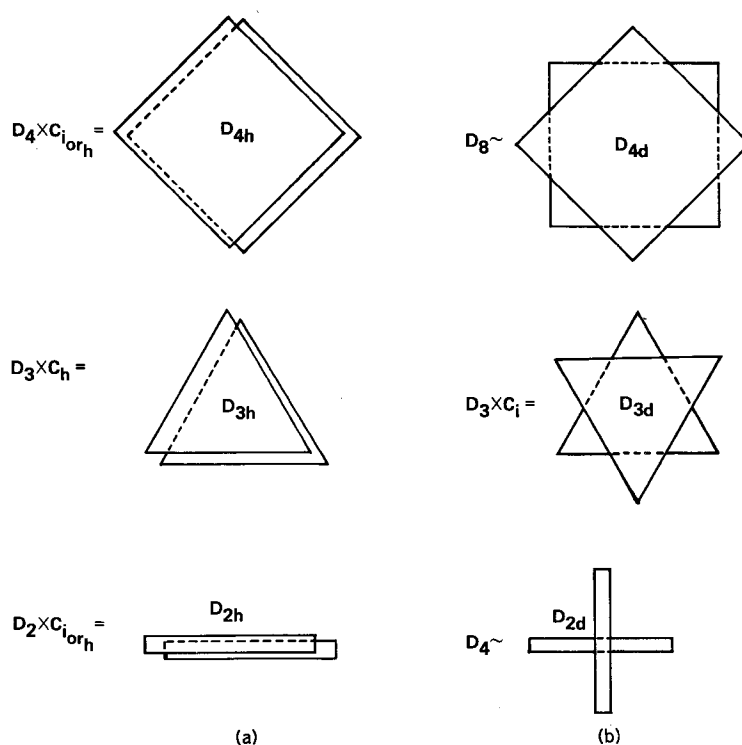
Figure 3.6.6 Comparison of horizontial and diagonal dihedral symmetries. (a) Horizontial D_{nh} symmetries. (b) Diagonal D_{nd} symmetries.

written

$$D_{nd} = D_n \times C_i = D_n \times \{1, I\} \qquad (n \text{ odd}). \qquad (3.6.30)$$

For n even $(n \geq 2)$ D_{nd} is isomorphic ($\sim$) to a higher D_{2n} or C_{2nv} group:

$$D_{nd} \sim D_{2n} \qquad (n \text{ even}). \qquad (3.6.31)$$

For example, D_{2d} contains the operations

$$D_{2d} = \{1, R^2, IR, IR^3, IR_1^2, IR_2^2, i_3, i_4\}. \qquad (3.6.32)$$

D_{2d} is the same as D_4 except for the extra inversion attached to the R and R_1^2 class elements. It is then easy to see that D_{2d} has the same group table as D_4 or C_{4v}. Hence, one set of irreps can be used for all three of these groups.

The presence of inversion symmetry in even-n D_{nh} and odd-n D_{nd}-symmetries should be emphasized. Whenever possible the irrep labels should indicate inversion parity by subindices X_g for even and X_u for odd, where $X = A_i$, B_i, or E_m labels the rest of the symmetry. For example, the D_{2h}

irreps are obtained quickly for those of D_2 and C_i using Eq. (3.6.29):

$$D_2 = \quad 1 \quad R_z^2 \quad R_y^2 \quad R_x^2$$

	1	R_z^2	R_y^2	R_x^2
A_1	1	1	1	1
B_2	1	-1	1	-1
A_2	1	1	-1	-1
B_2	1	-1	-1	1

$$\times \quad C_i = \quad 1 \quad I$$

	1	I
g	1	1
u	1	-1

$$D_{2h} = \quad 1 \quad R_z^2 \quad R_y^2 \quad R_x^2 \quad I \quad IR_z^2 \quad IR_y^2 \quad IR_x^2$$

	1	R_z^2	R_y^2	R_x^2	I	IR_z^2	IR_y^2	IR_x^2
A_{1g}	1	1	1	1	1	1	1	1
B_{1g}	1	-1	1	-1	1	-1	1	-1
A_{2g}	1	1	-1	-1	1	1	-1	-1
$= B_{2g}$	1	-1	-1	1	1	-1	-1	1
A_{1u}	1	1	1	1	-1	-1	-1	-1
B_{1u}	1	-1	1	-1	-1	1	-1	1
A_{2u}	1	1	-1	-1	-1	-1	1	1
B_{2u}	1	-1	-1	1	-1	1	1	-1

. (3.6.33)

Similarly, the characters of $D_{3d} = D_3 \times C_i$ follow:

$$D_3 = \quad 1 \quad (r, r^2) \quad (\rho_1 \rho_2 \rho_3)$$

	1	(r, r^2)	$(\rho_1 \rho_2 \rho_3)$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$$\times \quad C_i = \quad 1 \quad I$$

	1	I
g	1	1
u	1	-1

$$D_{3d} = \quad 1 \quad r \quad \rho_i \quad I \quad Ir \quad I\rho_i$$

	1	r	ρ_i	I	Ir	$I\rho_i$
A_{1g}	1	1	1	1	1	1
A_{2g}	1	1	-1	1	1	-1
$= E_g$	2	-1	0	2	-1	0
A_{1u}	1	1	1	-1	-1	-1
A_{2u}	1	1	-1	-1	-1	1
E_u	2	-1	0	-2	1	0

. (3.6.34)

Now you should have no trouble producing the character table for the largest crystallographic D group

$$D_{6h} = D_6 \times C_i = D_3 \times C_2 \times C_i. \tag{3.6.35}$$

The odd-n D_{nh} symmetries have horizontal reflection symmetry but no inversion center. This may be shown in a prime (X') and double-prime (X'') notation for even and odd reflection symmetry, respectively. For example, using Eq. (3.6.28) one has D_{3h} characters:

$D_3 =$	1	(r, r^2)	$(\rho_1 \rho_2 \rho_3)$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$\times$

$C_h =$	1	σ_h
A'	1	1
A''	1	-1

$D_{3h} =$	1	r	ρ_i	σ_h	$\sigma_h r$	$\sigma_h \rho_i$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
$= E'$	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

$$(3.6.36)$$

However, the actual irreps and characters of D_{3h} are the same as those of the isomorphic group $D_{3d} \sim D_{3h}$ in the previous equation (3.6.34). Only the notation and physical action of the operations is different.

The economy of symmetry mathematics should be evident by now. Just by learning irreps of C_2, C_3, C_4, D_3, and D_4 one becomes able to treat 27 of the 32 crystal point groups listed in Figure 3.1.1.

3.7 AMMONIA (NH₃) VIBRATIONAL MODES

A detailed C_{3v} projection analysis of ammonia (NH₃) molecular vibrational modes will be presented in this section. A reader who is studying symmetry analysis for the first time may want to skip ahead to Chapter 4. References contained at the end of the chapter should be consulted after studying this section.

This section will be devoted to a comparatively simple spring-mass model of the NH₃ molecule. Only two spring constants j and k will be used for the N—H and H—H bonds, respectively, as shown in Figure 3.7.1. However, all models of NH₃ must take account of 12 coordinates for the four masses and acceleration or energy operators which involve the coordinates in the Hamiltonian. Therefore, it is important to develop procedures which will use symmetry analysis efficiently and find the easiest way to solve *any* model Hamiltonian.

For complex problems that are not nearly perfect or regular representations of the symmetry, one can usually save a lot of algebra by dealing
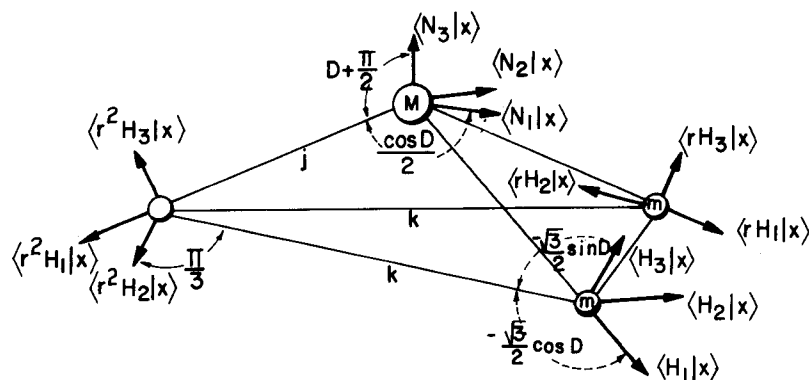
Figure 3.7.1 Spring-mass model for ammonia (NH_3) molecule. Dashed arrows indicate coordinate bond angles by giving the cosine of the angle. Base (H—H) bands have spring constants k, while the pyramidal (N—H) bands have constant j.

separately with the force operator F and the inertia operator m instead of diagonalizing directly the acceleration operator $a = m^{-1}F$. In this way it is possible to keep unpleasant algebraic factors out of the denominators. Also, one does not have to orthogonalize or normalize the basis if so doing would involve still more algebra. The procedures for dealing with F and m operators were introduced in Section 1.4.

In order to construct the reduced forms of the (F) and (m) representations, one needs the irrep bases $P_{ij}^{\alpha}|x_a\rangle$ obtained from C_{3v} irreps $\alpha = 1$ (or A_1), 2 (or A_2), and 3 (or E). Twelve base vectors $P_{ij}^{\alpha}|x_a\rangle$ are shown on the left-hand side of Figure 3.7.2 with their representative vibrational displacements. To make these vectors it is convenient to first collect coordinates or state vectors into SYMMETRY ORBITS. Orbits are sets of vectors which can be transformed directly into one another by symmetry operations. For example, the three downward radially pointing hydrogen bases $\{|H_1\rangle, |rH_1\rangle = r|H_1\rangle, |r^2H_1\rangle = r^2|H_1\rangle$ form an orbit. Operating on this orbit with the C_{3v} projectors P^1, P_{11}^E, and P_{21}^E gives three states which, when norma'- ized, are the following:

$$P^1|H_1\rangle\rangle\sqrt{3} = \left(|H_1\rangle + |rH_1\rangle + |r^2H_1\rangle\right)/\sqrt{3},$$

$$P_{11}^3|H_1\rangle\sqrt{3/2} = \left(2|H_1\rangle - |rH_1\rangle - |r^2H_1\rangle\right)/\sqrt{6},$$

$$P_{21}^3|H_1\rangle\sqrt{3/2} = \left(|rH_1\rangle - |r^2H_1\rangle\right)/\sqrt{2}. \tag{3.7.1}$$

Note that operators P^2, P_{12}^E, and P_{22}^E will annihilate the state $|H_1\rangle$ since it is symmetric to local plane reflection:

$$|H_1\rangle = \sigma_3|H_1\rangle = P_1|H_1\rangle, \tag{3.7.2}$$

where

$$P_1 = (1 + \sigma_3)/2.$$

Exactly the same holds for the three upward radially pointing hydrogen bases $\{|H_3\rangle, |rH_3\rangle, |r^2H_3\rangle\}$. The states $P_{i1}^\alpha|H_{1 \text{ or } 3}\rangle$ are shown in Figure 3.7.2, along with the remaining states projected from the orbits $\{|H_2\rangle, |rH_2\rangle, |r^2H_2\rangle, \{|N_1\rangle, r|N_1\rangle\}$, and $\{|N_3\rangle\}$. The angular hydrogen base $|H_2\rangle$ is locally antisymmetric; i.e.,

$$|H_2\rangle = -\sigma_3|H_2\rangle = P_2|H_2\rangle, \tag{3.7.3}$$

where

$$P_2 = (1 - \sigma_3)/2. \tag{3.7.4}$$

Hence, only operators P^2, P_{12}^3, and P_{22}^3 give nonzero states:

$$P^2|H_2\rangle\sqrt{3} = (|H_2\rangle + |rH_2\rangle + |r^2H_2\rangle)/\sqrt{3},$$

$$P_{12}^3|H_2\rangle\sqrt{3/2} = (-|rH_1\rangle + |r^2H_2\rangle)/\sqrt{2},$$

$$P_{22}^3|H_2\rangle\sqrt{3/2} = (2|H_2\rangle - |rH_2\rangle - |r^2H_2\rangle)/\sqrt{6}. \tag{3.7.5}$$

The in-σ_3-plane nitrogen base $|N_1\rangle$ is ready-made as a type-3 base along with partner $|N_2\rangle$:

$$P_{11}^3|N_1\rangle = |N_1\rangle, \qquad P_{21}^3|N_1\rangle = |N_2\rangle; \tag{3.7.6}$$

the same is true for the scalar (1)-type base

$$P^1|N_3\rangle = |N_3\rangle. \tag{3.7.7}$$

The states on the left-hand side of Figure 3.7.2 are not genuine vibration states since they all have either translational moment or momentum, rotational momentum, or both. Here we measure rotational momentun around the N atom so that it is easy to calculate. Seven of the states have zero rotation, and so it is easy to combine these into genuine or constrained states or zero linear momentum. From the three type-1 states it is possible to make one state of pure translational motion of the rigid molecule. We are only interested in the two remaining genuine or constrained states:

$$|c^1\rangle = MP^1|H_1\rangle\sqrt{3} + \sqrt{3}\,m \sin D \; P^1|N_3\rangle, \tag{3.7.8}$$

$$|c^1\rangle = MP^1|H_3\rangle\sqrt{3} - \sqrt{3}\,m \cos D \; P^1|N_3\rangle, \tag{3.7.9}$$

shown on the right-hand side of Figure 3.7.2. Similarly, the zero-rotation
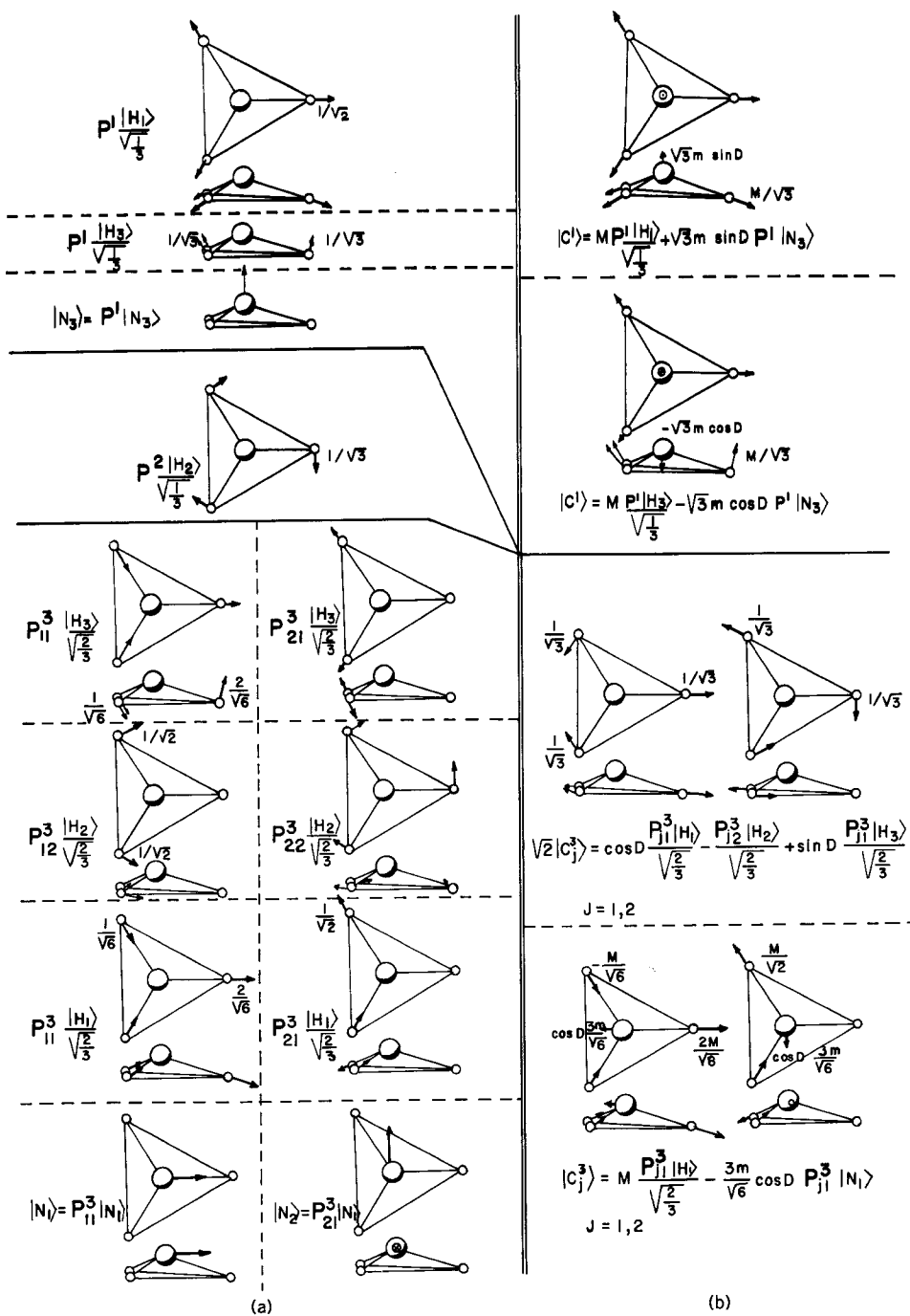
Figure 3.7.2 Symmetry defined motions of NH_3. (a). Primitive projected states obtained in Eqs. (3.7.1)–(3.7.6) are shown. (b) Genuine vibrational states are constrained to have zero translation and rotation.

type-3 states combine to give zero-translation constrained partner states $|c_i^3\rangle$:

$$|c_1^3\rangle = MP_{11}^3|H_1\rangle\sqrt{3/2} - 3m\cos D|N_1\rangle/\sqrt{6}, \qquad (3.7.10\text{a})$$

$$|c_2^3\rangle = MP_{21}^3|H_1\rangle\sqrt{3/2} - 3m\cos D|N_2\rangle/\sqrt{6}. \qquad (3.7.10\text{b})$$

Lastly, one can make type-3 states of rigid rotation around x and y axes. We shall ignore this motion until Chapter 5, and consider only genuine vibrational motion which includes the preceding $|c\rangle$ states and the following ones:

$$|c_1^3\rangle = \left(\cos D\ P_{11}^3|H_1\rangle - P_{12}^3|H_2\rangle + \sin D\ P_{11}^3|H_3\rangle\right)\sqrt{3/2}, \qquad (3.7.11\text{a})$$

$$|c_2^3\rangle = \left(\cos D\ P_{21}^3|H_1\rangle - P_{22}^3|H_2\rangle + \sin D\ P_{21}^3|H_3\rangle\right)\sqrt{3/2}. \qquad (3.7.11\text{b})$$

All the $|c\rangle$ states satisfy the constraint equations

$$\mathbf{T} = m\sum_{i=1}^{3} \mathbf{c}_{H_i} + M\mathbf{c}_N = 0, \qquad (3.7.12\text{a})$$

$$\mathbf{A} = m\sum_{i=1}^{3} \mathbf{r}_{H_i} \times \mathbf{c}_{H_i} + M\mathbf{r}_N \times \mathbf{c}_N = 0, \qquad (3.7.12\text{b})$$

when $\mathbf{c}_p$ is the displacement from equilibrium of atom p. Note that the translational constraint ($\mathbf{T} = 0$) guarantees that any new choice of origin for the angular constraint would still give zero $\mathbf{A}$. If $\mathbf{A} = 0$, then

$$\mathbf{T} \times \mathbf{d} = m\sum_{i=1}^{3} \mathbf{c}_{H_i} \times \mathbf{d} + M\mathbf{c}_N \times \mathbf{d} = 0$$

implies that

$$\mathbf{A'} = m\sum_{i=1}^{3} \left(\mathbf{r}_{H_i} + \mathbf{d}\right) \times \mathbf{c}_{H_i} + M(\mathbf{r}_N + \mathbf{d}) \times \mathbf{c}_N = 0$$

is zero also.

The preceding constraints and C_{3v} symmetry analysis reduce the genuine vibration problem from NH₃ to the calculation and solution of two 2×2 matrices:

$$\langle Q\rangle^1 = \begin{pmatrix} \langle c^1|Q|c^1\rangle & \langle c^1|Q|c^{1'}\rangle \\ \langle c^{1'}|Q|c^1\rangle & \langle c'|Q|c^{1'}\rangle \end{pmatrix}, \qquad \langle Q\rangle^3 = \begin{pmatrix} \langle c_1^3|Q|c_1^3\rangle & \langle c_1^3|Q|c_1^{3'}\rangle \\ \langle c_1^{3'}|Q|c_1^3\rangle & \langle c_1^{3'}|Q|c_1^{3'}\rangle \end{pmatrix},$$

representing $Q = F$ and $Q = m$ operators. Note that vectors $|c^\alpha\rangle$ and $|c^{\alpha'}\rangle$ are not orthogonal, and so we are committed to a separate treatment of the F and m operators. One needs only the rows of these matrices that correspond to the first vector of each orbit, namely, $\langle H_1|$, $\langle H_2|$, $\langle H_3|$, $\langle N_1|$, and $\langle N_3|$, as given in Eqs. (3.7.13) below:

$$\langle F \rangle =$$

	$|H_1\rangle$	$r|H_1\rangle$	$r^2|H_1\rangle$	$|H_2\rangle$	$r|H_2\rangle$	$r^2|H_2\rangle$	$|H_3\rangle$	$r|H_3\rangle$	$r^2|H_3\rangle$	$|N_1\rangle$	$|N_2\rangle$	$|N_3\rangle$
$\langle H_1|$	$\frac{3k}{2}\cos^2 D + j$	$\frac{3k}{4}\cos^2 D$	$\frac{3k}{4}\cos^2 D$	0	$\frac{\sqrt{3}k}{4}\cos D$	$-\frac{\sqrt{3}k}{4}\cos D$	$\frac{3k}{2}\sin D\cos D$	$\frac{3k}{4}\sin D\cos D$	$\frac{3k}{4}\sin D\cos D$	$-j\cos D$	0	$j\sin D$
$\langle H_2|$	0	$-\frac{\sqrt{3}k}{4}\cos D$	$\frac{\sqrt{3}k}{4}\cos D$	$\frac{k}{2}$	$-\frac{k}{4}$	$-\frac{k}{4}$	0	$-\frac{\sqrt{3}k}{4}\sin D$	$\frac{\sqrt{3}k}{4}\sin D$	0	0	0
$\langle H_3|$	$\frac{3k}{4}\sin D\cos D$		$\frac{3k}{4}\sin D\cos D$	0	$\frac{\sqrt{3}k}{4}\sin D$	$-\frac{\sqrt{3}k}{4}\sin D$	$\frac{3k}{2}\sin^2 D$	$\frac{3k}{4}\sin^2 D$	$\frac{3k}{4}\sin^2 D$	0	0	0
$\langle N_1|$										$\frac{3j}{2}\cos^2 D$	0	0
$\langle N_3|$										0	0	$3j\sin^2 D$

$$(3.7.13a)$$

$$\langle m \rangle =$$

	$|H_1\rangle$	$r|H_1\rangle$	$r^2|H_1\rangle$	$|H_2\rangle$	$r|H_2\rangle$	$r^2|H_2\rangle$	$|H_3\rangle$	$r|H_3\rangle$	$r^2|H_3\rangle$	$|N_1\rangle$	$|N_2\rangle$	$|N_3\rangle$
$\langle H_1|$	m	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$
$\langle H_2|$	$\cdot$	$\cdot$	$\cdot$	m	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$
$\langle H_3|$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	m	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$
$\langle N_1|$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	M	$\cdot$	$\cdot$
$\langle N_3|$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	$\cdot$	M

$$(3.7.13b)$$

The calculation of the representations of operators $Q = F$ or $Q = m$ in the $|c_j^\alpha\rangle$ basis can be made easier by using the properties of the elementary operators. Let us begin with the vector $|c_1^{3'}\rangle$ from Eq. (3.7.10):

$$\langle c_1^{3'}|Q|c_1^{3'}\rangle$$

$$= M(3/2)^{1/2}\langle H_1|P_{11}^3 Q\left[M(3/2)^{1/2}P_{11}^3|H_1\rangle - 3m\cos D|N_1\rangle/\sqrt{6}\right]$$

$$- (3m/\sqrt{6})\cos D\langle N_1|Q\left[M(3/2)^{1/2}P_{11}^3|H_1\rangle - 3m\cos D|N_1\rangle/\sqrt{6}\right].$$

Using the idempotent properties $(P_{11}^3 P_{11}^3 = P_{11}^3)$, commutivity $(P_{11}^3 Q = QP_{11}^3)$, and Eq. (3.7.5), the following expression results:

$$\langle c_1^{3'}|Q|c_1^{3'}\rangle = M^2\sum_{n=0}^{1}\mathscr{D}_{11}^{3*}(r^n)\langle H_1|Q|r^n H_1\rangle - 3Mm\cos D\langle H_1|Q|N_1\rangle$$

$$+ \frac{9m^2}{6}\cos^2 D\langle N_1|Q|N_1\rangle. \tag{3.7.15}$$

Here the formula (3.4.19) for P_{11}^3 is used again. Now substituting the required F-matrix components for Eq. (3.7.13a) gives the desired component:

$$\langle c_1^{3'}|F|c_1^{3'}\rangle = M^2(j + (3k/4)\cos^2 D) + 3jM\cos^2 D + jm^2(9/4)\cos^4 D$$

$$= M^2\left[(3k/4)\cos^2 D + j\left[(3m/2M)\cos^2 D + 1\right]^2\right]. \tag{3.7.16}$$

Similarly, the m-matrix component is

$$\langle c_1^{3'}|m|c_1^{3'}\rangle = Mm^2\left[1 + (3m/2M)\cos^2 D\right]. \tag{3.7.17}$$

The off-diagonal $\langle c_1^3|Q|c_1^{3'}\rangle$ is produced in the same way:

$$\langle c_1^3|Q|c_1^{3'}\rangle = (M/\sqrt{8})\cos D\sum_{n=0}^{2}\langle H_1|Q|r^n H_1\rangle\mathscr{D}_{11}^{3*}(r^n)$$

$$- (3m/\sqrt{8})\cos^2 D\langle H_1|Q|N_2\rangle$$

$$- (M/\sqrt{8})\sum_{n=0}^{2}\langle H_2|Q|r^n H_1\rangle\mathscr{D}_{21}^{3*}(r^n)$$

$$+ (3m/\sqrt{8})\cos D\langle H_2|Q|N_2\rangle$$

$$+ (M/\sqrt{8})\sin D\sum\langle H_3|Q|r^n H_1\rangle\mathscr{D}_{11}^{3*}(r^n)$$

$$- (3m/\sqrt{8})\sin D\cos D\langle H_3|Q|N_1\rangle.$$

The off-diagonal F component

$$\langle c_1^3|F|c_1^{3'}\rangle = (M/\sqrt{2})\cos D\left[(3k/2) + j(1 + (3m/2M)\cos^2 D)\right] \quad (3.7.18)$$

is the coupling between the two vibration coordinates. The off-diagonal m component,

$$\langle c_1^3|m|c_1^{3'}\rangle = (Mm/\sqrt{2})\cos D, \quad\quad\quad (3.7.19)$$

indicates that $|c_1^3\rangle$ and $|c_1^{3'}\rangle$ are not orthogonal. The type-3 calculation is completed with the $\langle c_1^3|Q|c_1^3\rangle$ components since $Q^\dagger = Q$ for $Q = F$ and $Q = m$. The resulting F matrix is

$$\langle F\rangle^3 = \begin{pmatrix} 3k/2 + (j/2)\cos^2 D & M\cos D(3k/2 + jH) \\ M\cos D(3k/2 + jH) & M^2[(3k/4)\cos^2 D + jH^2] \end{pmatrix}, \quad (3.7.20)$$

where

$$H \equiv 1 + (3m/2M)\cos^2 D,$$

while the m matrix takes the form

$$\langle m\rangle^3 = \begin{pmatrix} m & (mM/\sqrt{2})\cos D \\ (mM/\sqrt{2})\cos D & mM^2H \end{pmatrix}. \quad (3.7.21)$$

The calculation for the type-1 or A_1 modes proceeds in the same way but without the duplicity of the two-dimensional type-3 modes. The force operator is represented in the $\{|c^1\rangle, |c^{1'}\rangle\}$ basis by the following matrix:

$$\langle F\rangle^1 = \begin{pmatrix} M^2(3k\cos^2 D + jJ) & 3JM^2(k - jm/M)\sin D\cos D \\ 3JM^2(k - jm/M)\sin D\cos D & M^2(3k + j(2m/M)^2\cos^2 D)\sin^2 D \end{pmatrix}, \quad (3.7.22)$$

where

$$J = 1 + (3m/M)\cos^2 D.$$

The mass operator is represented in the same basis by the following matrix

$$\langle m \rangle^1 = \begin{pmatrix} mM^2K & -3(m/M)\sin D \cos D \\ -3(m/M)\sin D \cos D & J \end{pmatrix}, \quad (3.7.23)$$

where

$$K \equiv 1 + (3m/M)\sin^2 D.$$

Combining Eqs. (3.7.20) and (3.7.21) gives the acceleration matrix for type-3 modes:

$$\langle a \rangle^3 = \langle m^{-1}F \rangle^3 = \begin{pmatrix} 3k/m & (3k/m\sqrt{8})M \cos D \\ (j/mM\sqrt{8})\cos D & Hj/m \end{pmatrix}. \quad (3.7.24)$$

The solutions to the secular equation,

$$\lambda_3^2 - S_3\lambda_3 + P_3 = 0,$$

where

$$S_3 = (3k/2 + Hj)/m, \quad (3.7.25a)$$

$$P_3 = (3kj/2m^2)(H - (1/2)\cos^2 D) \quad (3.7.25b)$$

are squared eigenfrequencies of type-3 vibrations:

$$\lambda_{3\pm} = (\omega_{3\pm})^2 = \left(S_3 \pm \sqrt{S_3^2 - 4P_3} \right)\Big/2. \quad (3.7.26)$$

Similarly, the type-1 acceleration matrix is

$$\langle a \rangle^1 = \langle m^{-1}F \rangle^1 = \begin{pmatrix} (3k/m)\cos^2 D + Kj/m & 3(k/m - j/M)\sin D \cos D \\ 3(k/m)\sin D \cos D & 3(k/m)\sin^2 D \end{pmatrix}.$$

$$(3.7.27)$$

Its eigenfrequencies are given by

$$(\omega_{1\pm})^2 = \left(S_1 \pm \sqrt{S_1^2 - 4P_1} \right)\Big/2, \quad (3.7.28)$$

where

$$S_1 = (3k + Kj)/m \qquad\qquad (3.7.29\text{a})$$

$$P_1 = 3kj(1/m^2 + 3/mM)\sin^2 D. \qquad\qquad (3.7.29\text{b})$$

Now the physics begins as one decides what to do with these equations. One of the most interesting applications involves determining the angle D by "listening" to the vibrations of NH_3 and comparing this with what has been found by other methods such as "looking" with x rays. To do this first note that the last term in the secular equations are the products of the roots $P_1 = (\omega_{1+}\omega_{1-})^2$ and $P_3 = (\omega_{3+}\omega_{3-})^2$, respectively. The ratio R in the following is a function only of the angle D and masses $m = 1$ amu and $M = 14$ amu of hydrogen and nitrogen, respectively,

$$R = (\omega_{1+}\omega_{1-}/\omega_{3+}\omega_{3-})^2$$

$$R = P_1/P_3 = 2(1 + 3m/M)\sin^2 D/\left[1 + (3m/2M - 1/2)\cos^2 D\right] \qquad (3.7.30)$$

Solving for angle D gives

$$D = \sin^{-1}\left[R(1 + 3m/M)/[4(1 + 3m/M) - R(1 - 3m/M)]\right]^{1/2}. \qquad (3.7.31)$$

The frequencies $\omega_{\alpha\pm}$ needed to calculate R and D are obtained from spectra such as the infrared adsorption data shown in Figure 3.7.3. The numbers which are quoted in Herzberg's text are as follows:

$$\nu_{1+} = 3337 \text{ cm}^{-1}, \qquad\qquad \nu_{3+} = 3414 \text{ cm}^{-1},$$

$$\omega_{1+} = 6.290 \times 10^{14} \text{ rad/sec}, \qquad \omega_{3+} = 6.435 \times 10^{14} \text{ rad/sec},$$

$$\nu_{1-} = 908 \text{ cm}^{-1}, \qquad\qquad \nu_{3-} = 1628 \text{ cm}^{-1},$$

$$\omega_{1-} = 1.712 \times 10^{14} \text{ rad/sec}, \qquad \omega_{3-} = 3.069 \times 10^{14} \text{ rad/sec}.$$

Determination of the frequencies required careful analysis of many such spectra and an understanding of the rotational structure which surrounds each "line" in Figure 3.7.3. The development of laser devices has given a more clear picture of rotational structure and led to better understanding of it, as will be explained later in the book.
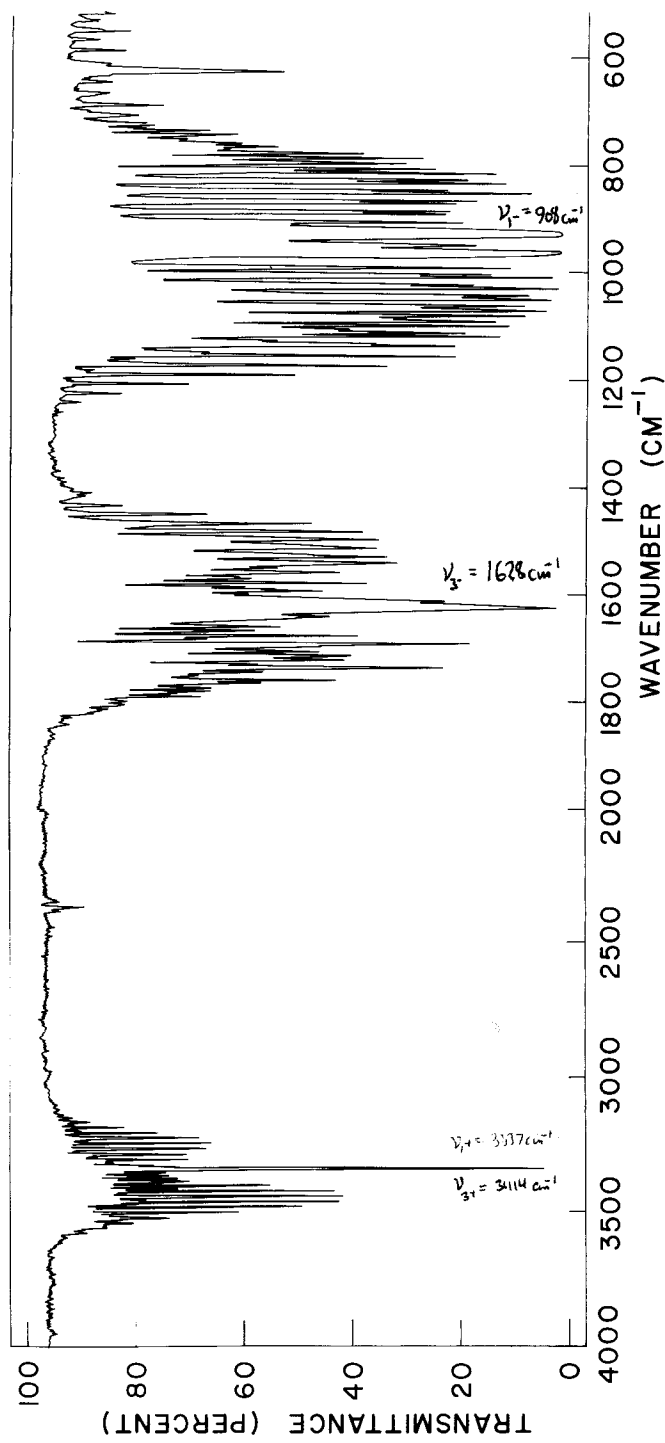
Figure 3.7.3 Infrared spectra of ammonia (NH_3). Tabulated values given by Herzberg are listed beside each line. It appears that the $(3 +)$ line is lost in the rotational sidebands of the $(1 +)$ line.

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Substituting the observed frequencies into Eqs. (3.7.30) and (3.7.31), one obtains $D = 17°$, which agrees fairly well with the angle $20°$ found by other means. ($D = 20°$ corresponds to an H—N—H angle of $109°$.)

One may try to deduce the spring constants k and j from the spectra just given. One procedure is to use the sums $S_\alpha = (\omega_{\alpha+})^2 + (\omega_{\alpha-})^2$, which are the second factors in the secular equations (3.7.25a) and (3.7.29a).

Solving these gives the following:

$$j/m = (2S_3 - S_1)/1 + 3(m/M)\cos 2D),$$

$$3k/2m = S_1(1 + (3m/2M)\cos^2 D) - S_3(1 + (3m/M)\sin^2 D)$$

Substitution of the experimental $\omega^{(\alpha)}$, $D = 20°$, and the H mass ($m = 1.67 \times 10^{-27}$ kg) gives numerical results ($j = 850$ nt/m) and ($k = -62$ nt/m), which indicates some inaccuracy in the $k - j$ spring model. The negative value for k is physically impossible.

However, this model can still be used to estimate and visualize some things if it is approached more carefully than in the foregoing. Instead let us plot in Figure 3.7.4 the eigenvalues ω_α as functions of the ratio k/j for $D = 20°$. Near $k/j = 0.3$ we find that the ratio of the two lowest functions becomes equal to the observed ratio ω_{3-}/ω_{1-}. From this point one may compare the theory to the experiment for the higher levels. Notice that the ω_{1+} prediction is 20% too high but ω_{3-} is pretty close.
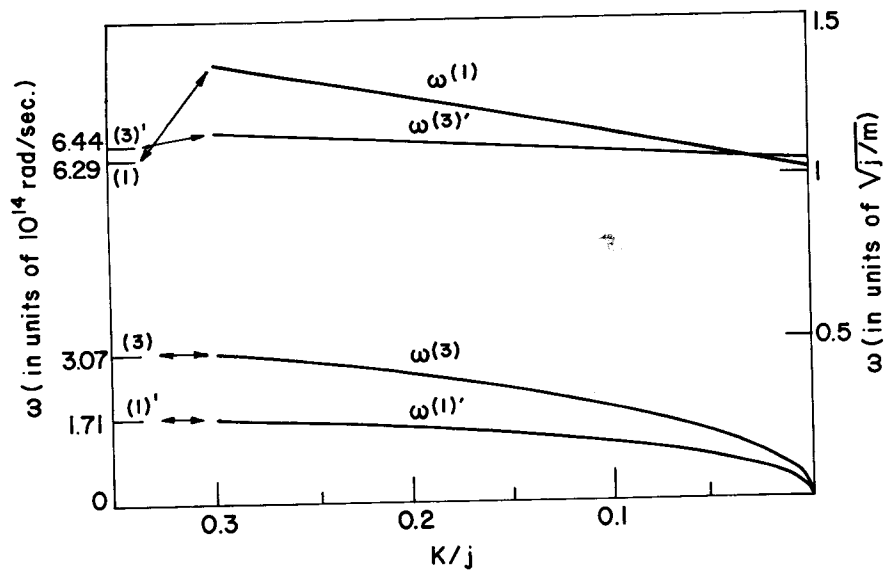

Figure 3.7.4 Plots of k-j model eigenvalues. Experimental values are shown on the left-hand side.

It is possible to make a better theory by including bond-bending constants, i.e., so-called "covalence forces," or other parameters. Indeed, we shall prove by symmetry product analysis in Chapter 6 that the number of parameters at your disposal in any problem of this sort will be exactly enough to make any eigenvalue $(\omega^{(\alpha)}, \omega^{(\alpha)'}, \ldots)$ and eigenvector combination $(a|_i^{(\alpha)}\rangle + b|_i^{(\alpha)'}\rangle + \cdots)$ that is possible. However, the use of too many parameters would give one a rather empty victory unless one goes on to use the parameters for analyzing spectra of other molecules having similar H—H bonds. This approach has been carried out successfully for many cases.

Note in Figure 3.7.4 that ω_{1+} and ω_{3+} are fairly constant and close to $(j/m)^{1/2}$. This is mainly because M is larger than m, so the high modes just amount to hydrogens vibrating more or less independently on j springs. This gives a rough estimate for j: $j = m(6.3 \times 10^{14})^2 = 660$ nt/m. Incidentally, the degeneracy at $k/j = 0.035$ does not, as far as we now, have anything to do with symmetry. Such crossings are called ACCIDENTAL DEGENERACIES.

APPENDIX D. MATHEMATICAL PROPERTIES OF $P_i^\alpha g P_j^\alpha$

This appendix is devoted to closing mathematical loopholes in order to assure that the techniques developed in Chapter 3 are applicable to any finite group $G = \{ \cdots g \cdots \}$ of unitary operators. Sections D.1 and D.2 contain proofs that the operators $\{P_i^\alpha g P_j^\alpha, P_i^\alpha g' P_j^\alpha, \ldots\}$ for all elements $\{g, g', \ldots\}$ in G are simply proportional to each other if the idempotents P_i^α and P_j^α cannot be split. Section D.3 contains a proof that each $P_i^\alpha g P_j^\alpha \neq 0$ exists for some g if the $P^\alpha = P_1^\alpha + P_2^\alpha + \cdots$ are complete sets of all-commuting idempotents.

D.1 LINEAR DEPENDENCE OF $P_i^\alpha g P_i^\alpha, P_i^\alpha g' P_i^\alpha, \ldots$

Consider the set $\{p_g \equiv P_i^\alpha g P_i^\alpha, p_{g'} \equiv P_i^\alpha g' P_i^\alpha, \cdots\}$ of all group elements "guarded" by a Hermitian irreducible idempotent $P_i^\alpha = P_i^\alpha P_i^\alpha = P_i^{\alpha\dagger}$. The assumption that P^α is an idempotent implies that this set is a closed subalgebra. since any product $p_g p_{g'}$ must be a linear combination of some p_g. Furthermore. P^α acts as the identity or unit element ($p_g P_i^\alpha = p_g$) for all p_g. The assumption that P_i^α is Hermitian implies that the algebra contains a conjugate,

$$p_g^\dagger = P_i^{\alpha\dagger} g^\dagger P_i^{\alpha\dagger} = P_i^\alpha g^\dagger P_i^\alpha, \tag{D.1}$$

for each p_g. Hence, the p_g basis can be replaced by a Hermitian basis of

operators

$$h_{g^+} \equiv \left(p_g + p_g^\dagger \right)/2, \qquad h_{g^-} \equiv \left(p_g - p_g^\dagger \right)/2i.$$

$$= h_{g^+}^\dagger \qquad\qquad\qquad = h_{g^-}^\dagger. \qquad\qquad (D.2)$$

Each h satisfies some minimal equation

$$\left(h - \eta_1 P_i^\alpha \right)\left(h - \eta_2 P_i^\alpha \right) \cdots \left(h - \eta_n P_i^\alpha \right) = 0, \qquad (D.3)$$

which contains no repeated eigenvalues ($\eta_i \neq \eta_j$ if $i \neq j$). Note that P_i^α is serving here as the unit element.

Finally, the assumption that P_i^α is irreducible implies that a minimal equation (D.3) must have just one factor

$$\left(h - \eta_1 P_i^\alpha \right) = 0, \qquad\qquad (D.4)$$

or that

$$h = \eta_1 P_i^\alpha.$$

If two or more factors were present in Eq. (D.3) then P_i^α could be split into two or more orthogonal idempotents ($P_i^\alpha = P + P' + \cdots$), contrary to the assumption. Equation (D.4) holds for all h, all p_g, and all combinations of p_g, as well. One has

$$p_g = P_i^\alpha g P_i^\alpha = \rho P_i^\alpha, \qquad\qquad (D.5)$$

where the eigenvalue ρ is given the notation

$$\rho = \mathscr{D}_{ii}^\alpha(g) \qquad\qquad (D.6)$$

in Section 2.3.

D.2   LINEAR DEPENDENCE OF $\{P_i^\alpha g P_j^\alpha, P_i^\alpha g' P_j^\alpha, \dots\}$

Suppose a "guarded" operator $N = P_i^\alpha g P_j^\alpha$ is nonzero. Then so is its conjugate $N^\dagger = P_j^\alpha g P_i$ and their products:

$$NN^\dagger = P_i^\alpha g P_j^\alpha g^\dagger P_i^\alpha = \lambda P_i^\alpha, \qquad\qquad (D.7a)$$

$$N^\dagger N = P_j g^\dagger P_i^\alpha g P_j^\alpha = \lambda' P_j^\alpha. \qquad\qquad (D.7b)$$

The λP_i^α form of each product follows from Eq. (D.5), where λ and λ' must be real and positive definite. For any other group operators g' one has

$$P_i^\alpha g' P_j^\alpha g^\dagger P_i^\alpha = \nu P_i^\alpha, \tag{D.8}$$

according to Eq. (D.5). Combining the preceding two equations gives

$$0 = \lambda \nu P_i^\alpha - \nu \lambda P_i^\alpha$$

$$= \lambda P_i^\alpha g' P_j^\alpha g^\dagger P_i^\alpha - \nu P_i^\alpha g P_j^\alpha g^\dagger P_i^\alpha,$$

$$0 = \left(\lambda P_i^\alpha g' P_j^\alpha - \nu P_i^\alpha g P_j^\alpha \right) P_j^\alpha g^\dagger P_i^\alpha. \tag{D.9}$$

Attaching $g P_j$ on the right and using Eq. (D.7b) gives

$$0 = \left(\lambda P_i^\alpha g' P_j^\alpha - \nu P_i^\alpha g P_j^\alpha \right) P_j^\alpha g^\dagger P_i^\alpha g P_j^\alpha,$$

$$0 = \left(\lambda P_i^\alpha g' P_j^\alpha - \nu P_i^\alpha g P_j^\alpha \right) \lambda'. \tag{D.10}$$

Assuming λ and λ' are nonzero gives

$$P_i^\alpha g' P_j^\alpha = \nu / \lambda P_i^\alpha g P_j^\alpha, \tag{D.11}$$

Therefore, the irreducible "guards" convert all $\{ g, g', \ldots \}$ to the same operator to within a proportionality factor ν/λ. Next we prove that $P_i^\alpha g P_j^\alpha$ is nonzero for some g; i.e., $\lambda \neq 0$. Of course, if all $\{ P_i^\alpha g P_j^\alpha, P_i^\alpha g' P_j^\alpha, \ldots \}$ were zero one would not have needed to prove that they are proportional.

D.3 EXISTENCE PROOF OF $P_i^\alpha g P_j^\alpha$

Suppose $P_1^\alpha g P_2^\alpha = 0$ for all group operators g. Then we have

$$P_1^\alpha G P_2^\alpha = 0, \tag{D.12}$$

where

$$G = \sum_g \gamma_g g$$

is any combination of operators. In other words we suppose that P_1^α and P_2^α cannot serve together as bodyguards for any operator g without annihilation.

Let the set $\{P_1^\alpha, P_i^\alpha, P_{i'}^\alpha, \ldots\}$ of irreducible idempotents contain those which still may serve as bodyguards with P_1^α, i.e., let

$$P_i^\alpha = \lambda P_i^\alpha h P_1^\alpha h^\dagger P_i^\alpha \tag{D.13}$$

for some h. Let the second set $\{P_2^\alpha, P_j^\alpha, P_{j'}^\alpha, \cdots\}$ contain those which may serve with P_2^α; i.e., let

$$P_j^\alpha = \mu P_j^\alpha k P_2^\alpha k^\dagger P_j^\alpha \tag{D.14}$$

for some k. Combining Eqs. (D.12)–(D.14) implies annihilation,

$$P_i^\alpha g P_j^\alpha = \lambda \mu P_i^\alpha h P_1^\alpha h^\dagger P_i^\alpha g P_j^\alpha k P_2^\alpha k^\dagger P_j^\alpha = 0, \tag{D.15}$$

for all g, due to the factor $P_1^\alpha G P_2^\alpha$. In other words, any idempotent P_i^α in the P_1^α subset annihilates any operator containing a member of the P_2^α subset, and vice versa. This implies that the (α) part of the decomposition

$$g = \mathbf{1}g\mathbf{1} = \sum_\alpha \sum_{m,n} P_m^\alpha g P_n^\alpha$$

splits into (at least) two separate parts

$$g = \sum_\alpha \left(\sum_{i,i'} P_i^\alpha g P_{i'}^\alpha + \sum_{j,j'} P_j^\alpha g P_{j'}^\alpha + \cdots \right)$$

$$= \sum_\alpha \left(P_{(1)}^\alpha g P_{(1)}^\alpha + P_{(2)}^\alpha g P_{(2)}^\alpha + \cdots \right),$$

involving idempotents

$$P_{(1)}^\alpha = P_1^\alpha + P_i^\alpha + P_{i'}^\alpha + \cdots,$$

$$P_{(2)}^\alpha = P_2^\alpha + P_j^\alpha + P_{j'}^\alpha + \cdots,$$

which are sums of the separate sets. These new idempotents satisfy commutation relations

$$P_{(a)}^\alpha g = P_{(a)}^\alpha g P_{(a)}^\alpha = g P_{(a)}^\alpha$$

with all group elements g.

However, this leads to a contradiction. The original all-commuting idempotent

$$P^\alpha = P_1^\alpha + P_2^\alpha + \cdots P_{l^\alpha}^\alpha$$

$$= P_{(1)}^\alpha + P_{(2)}^\alpha + \cdots$$

should not produce any new all-commuting $P_{(a)}^\alpha$ when splitting into irreducible idempotents. (The dimension of the class algebra is fixed.) Hence, any two irreducible idempotents P_1^α and P_2^α from the same family must give some nonzero $P_1^\alpha g P_2^\alpha$.

ADDITIONAL READING

An introduction to Hamilton's turns is given by Biedenharn and Louck.

L. C. Biedenharn and J. D. Louck, in G. C. Rota, Ed., *Angular Momentum in Quantum Mechanics*, Encyclopedia of Mathematics and Its Applications, (Addison-Wesley, Reading, MA, 1981).

The original text by Hamilton (not readily available) is a little difficult for most modern readers.

W. R. Hamilton, *Lectures on Quaternions*, (Dublin, 1853).

The slide rule based upon the turns is described in the author's *American Journal of Physics* article

W. G Harter and N. dos Santos, "Double group theory on the half shell and the two-level systems," *am. J. Phys.*, **46**, 251 (1978).

A complete description of group algebra is found in a mathematics text by Curtis and Reiner.

C. W. Curtis and I. Reiner, *Representation Theory of finite Groups and Associative Algebras*, (Wiley, New York, 1965).

The discussion and bibliography for the NH_3 vibrational spectra found in Herzberg's classic texts is still probably the most complete discussion of molecular spectroscopy.

G. Herzberg, *Molecular Spectra and Molecular Structure:* I. Spectra of Diatomic Molecules, II. Infrared and Raman Spectra of Polyatomic Molecules, III. Electronic Structure of Polyatomic Molecules (Van Nostrand-Reinhold, New York, 1950).

The XY_3 analysis starts on p. 155 of Vol. II.

The standard reference for molecular normal coordinate analysis is

F. B. Wilson, V. C. Decius, and P. C. Cross; *Molecular Vibrations* (McGraw-Hill, New York, 1955).

Two more modern references are

S. Califano *Vibrational States* (Wiley, New York, 1976).

D. Papousek and M. R. Alier, *Molecular Vibrational-Rotational Spectra*, 1982 *Studies in Physical and Theoretical Chemistry*, Vol. 17 (Elsevier Amsterdam, New York, 1982).

PROBLEMS

Section 3.1

3.1.1 The subsets $(\mathcal{H}, \mathcal{H}g_1, \mathcal{H}g_2, \dots)$ or $(\mathcal{H}, g_1\mathcal{H}, g_2\mathcal{H}, \dots)$ of group $\mathcal{G} = \{1, g, g_2, \dots\}$ are called RIGHT or LEFT COSETS, respectively, of subgroup $\mathcal{H} = \{1, h, \dots\} \subset \mathcal{G}$. The subsets $(\mathcal{H}, \mathcal{H}', \mathcal{H}g_1\mathcal{H}', \mathcal{H}g_2\mathcal{H}', \dots)$ are called DOUBLE COSETS of subgroups $\mathcal{H}$ and $\mathcal{H}'$.

    (a) Construct right cosets for subgroup $C_v = \{1, \sigma_3\}$ of C_{3v}.

    (b) Construct left cosets for subgroup $C_v = \{1, \sigma_3\}$ of C_{3v}.

    (c) Construct right cosets for subgroup $C_3 = \{1, r, r^2\}$ of C_{3v}.

    (d) Construct left cosets for subgroup $C_3 = \{1, r, r^2\}$ of C_{3v}.

    (e) Construct double cosets for subgroup $C_v = \{1, \sigma_1\}$ and $C' = \{1, \sigma_2\}$ of C_{3v}.

    (f) Construct double cosets for subgroup $C_v = \{1, \sigma_1\}$ and $C_3 = \{1, r, r^2\}$ of C_{3v}.

3.1.2 A subgroup $\mathcal{N}$ of $\mathcal{G}$ is called a NORMAL or INVARIANT subgroup of group $\mathcal{G}$ if $g\mathcal{N}g^{-1} = \mathcal{N}$ for any g in $\mathcal{G}$.

    (a) Is $C_v = \{1, \sigma_3\}$ a normal subgroup of C_{3v}?

    (b) Is $C_3 = \{1, r, r^2\}$ a normal subgroup of C_{3v}?

    (c) Prove that if the left and right cosets of a subgroup $\mathcal{H}$ are equal, then $\mathcal{H}$ is a normal subgroup. Check this using the results of Problem 3.1.1.

Section 3.2

3.2.1 Use Hamilton's turns or nomograms to derive a multiplication table for each of the following symmetries which includes the $\pm$ signs that would be needed to describe rotations of electrons. Do any of the resulting tables give mutually commuting operators?

    (a) D_2.

    (b) D_3.

    (c) D_4.

3.2.2 Let $^{\circ}\mathcal{N}(g)$ be the number of elements of a group that commute with element g. Let $^{\circ}C_g$ be the order of the class of g in group $\mathcal{G}$. What is the product of these two numbers?

Evaluate these numbers for the groups D_2, D_3, and D_4.

Section 3.3

3.3.1 The four flat-bladed fan of arbitrary pitch has D_4 symmetry.

   (a) Name or label all the rotations in D_4 and tell what they do.

   (b) Draw a sketch of something with C_{4v} symmetry and relate C_{4v} symmetry to D_4.

   (c) Construct a Hamilton-turn nomogram for D_4. Could it be used for C_{4v} as well?

   (d) Construct a group multiplication table for D_4. Arrange it according to *classes*.

   (e) Construct a class algebra table using part (d).

   (f) Spectrally decompose the class algebra. Find $\mathbf{P}^{\alpha} = \Sigma\, d_j^{\alpha} c_j$ and $c_j = \Sigma c_j^{\alpha} \mathbf{P}^{\alpha}$.

   (g) Split the all-commuting idempotents found in part (f) into irreducible idempotents of the D_4 algebra with the help of the idempotents from the subgroup $D_2 = \{1, \mathbf{R}_x(180°),\ \mathbf{R}_y(180°),\ \mathbf{R}_z(180°)\}$.

   (h) Split the all-commuting idempotents found in part (f) into irreducible idempotents of the D_4 algebra with the help of the idempotents from the subgroup $C_4 = \{1,\ \mathbf{R}_z(90°), \mathbf{R}_z(180°),\ \mathbf{R}_z(270°)\}$.

3.3.2 The quaternion group $Q = \{1, \underline{1}, \mathbf{i}, \underline{\mathbf{i}}, \mathbf{j}, \underline{\mathbf{j}}, \mathbf{k}, \underline{\mathbf{k}}\}$ is defined by Hamilton's hypercomplex relations: $\mathbf{i}\mathbf{j} = \mathbf{k}$, $\mathbf{j}\mathbf{i} = \underline{\mathbf{k}}$ (and cyclically); $\mathbf{i}\mathbf{i} = \mathbf{j}\mathbf{j} = \mathbf{k}\mathbf{k}$ $= \underline{\mathbf{i}}\underline{\mathbf{i}} = \underline{\mathbf{j}}\underline{\mathbf{j}} = \underline{\mathbf{k}}\underline{\mathbf{k}} = \underline{1}$; $\mathbf{i}\underline{1} = \underline{\mathbf{i}} = \underline{1}\mathbf{i}$ (and cyclically); $\underline{1}\underline{1} = 1$; and 1 is identity.

   (a) Using Hamilton's turns show that this corresponds to the spin-$\frac{1}{2}$ version of the D_2 group with $\mathbf{i} = \mathbf{R}_x$, $\underline{\mathbf{i}} = -\mathbf{R}_x$, $\mathbf{j} = \mathbf{R}_y,\ldots$, etc.

   (b) Redo parts (d), (e), and (f) in Problem 3.3.1 for the quaternion group.

   (c) Use the subgroup $\{1, \mathbf{k}, \underline{1}, \underline{\mathbf{k}}\}$ in Q to split any all-commuting idempotents in the Q algebra that might still need splitting.

Section 3.4

3.4.1 The D_4 symmetric spring-mass model consists of four mass-m particles held by diagonal, external, and side springs of constants d, e, and s, respectively, as shown in the diagram.
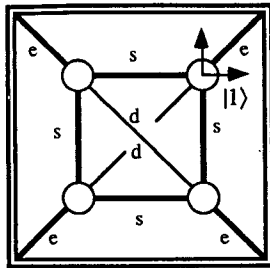
(a) Label the eight x-y-plane coordinates using group operators "named" in Problem 3.3.1.

(b) Write the first row $(\langle 1|\mathbf{a}|1\rangle \cdots \langle 1|\mathbf{a}|8\rangle \cdots)$ of the acceleration matrix in terms of the mass and spring constants.

(c) Use the irreducible $D_2 \subset D_4$ defined idempotents of Problem 3.3.1 to obtain the irreducible operators $\mathbf{P}_i^\alpha \mathbf{g} \mathbf{P}_j^\alpha$. Find all the linearly independent vectors $\mathbf{P}_i^\alpha |1\rangle$ and $\mathbf{P}_i^\alpha \mathbf{g} \mathbf{P}_j^\alpha |1\rangle$ for the system. Draw pictures of the normalized displacements or distortions which they represent. Use these results to find a complete set of irreducible projection operators $\mathbf{P}_{ij}^\alpha$.

(d) Write a table of all the $D_2 \subset D_4$ defined irreducible representations D^α. [Use part (c) of this problem if necessary.]

(e) Derive a table of all the $C_4 \subset D_4$ defined irreducible representations D^α.

(f) Obtain the block-diagram reduced forms of the acceleration matrix $\langle a \rangle$ using symmetry projectors from parts (c) or (d).

(g) Solve any residual block matrices obtained in part (f). Sketch the vibrational normal mode distortions and corresponding frequency levels for constants $e = 0$, $s = 5$, $d = 3$, $m = 1$.

(h) Draw pictures which differ from part (g) of the normal modes for $e = 1$, $s = 5$, $d = 3$, $m = 1$.

3.4.2 Obtain a set of irreducible representations for the quaternion group, following results you obtained in Problem 3.3.2. Is Q isomorphic to D_4?

Section 3.5

3.5.1 Given an n-dimensional class algebra $(\mathbf{c}_i \mathbf{c}_j = \mathbf{c}_j \mathbf{c}_i = \sum_{k=1}^{n} C_{ij}^k \mathbf{c}_k)$ one may construct a "regular" representation; $R(\mathbf{c}_1)R(\mathbf{c}_j) = R(\mathbf{c}_i \mathbf{c}_j)$ of the *algebra* using the structure constants C_{ij}^k. (This is *not* to be confused with *group* regular representation.)

(a) Show how to do this. Make and test such a 3 × 3 representation for C_{3v} classes.

(b) The eigenvalues $(c_j^\alpha, c_j^\beta, c_j^\gamma, \ldots)$ of each matrix $R(c_j)$ can be used to derive characters $(\chi_j^\alpha, \chi_j^\beta, \ldots)$. Give formulas for χ_j^α in terms of c_j^α (and other quantities) and test them using C_{3v}.

3.5.2 The irreducible representation-orthogonality relation is

$$\sum_{\text{all } g \in \mathscr{G}} \mathscr{D}_{ij}^\alpha(g)\, \mathscr{D}_{kl}^\beta(g) = {}^\circ\!\mathscr{G}/l^\alpha \delta^{\alpha\beta} \delta_{ik} \delta_{jl}.$$

(a) Prove this by considering $\mathscr{D}_{ij}^\alpha(P_{kl}^\beta) = ?$

(b) Discuss the form of the completeness relation that would compliment this orthogonality relation, and derive it, too.

(c) Derive an irreducible character completeness relation. $\sum_\alpha \chi_j^{\alpha*} \chi_k^\alpha = ?$

(d) Derive an irreducible character orthogonality relation. $\sum_j {}^\circ\!C_j \chi_j^{\alpha*} \chi_k^\beta = ?$ Here ${}^\circ\!C_j$ is the order of the (j)th class.

3.5.3 (Schur's lemmas)
Suppose an $l^\alpha \times l^\alpha$ matrix $\mathscr{L}$ commutes with all matrices $\{\mathscr{D}^\alpha(g) \cdots \mathscr{D}^\alpha(g') \cdots \}$, where $\mathscr{D}^\alpha$ is an irreducible representation; i.e., $\mathscr{L}\mathscr{D}^\alpha(g) = \mathscr{D}^\alpha(g)\mathscr{L}$ for all **g**.

(a) What special properties must $\mathscr{L}$ have? [Hint: Consider $\mathscr{D}^\alpha(P_{ij}^\alpha)$.]

(b) What special properties should an $l^\alpha \times l^\beta$ matrix $\mathscr{M}$ have in order to satisfy $\mathscr{M}\mathscr{D}^\beta(g) = \mathscr{D}^\alpha(g)\mathscr{M}$ for all g, where α and β label inequivalent irreducible representations. [Consider $D^\alpha(\mathbf{P}^\beta)$.]

3.5.4 An element g is called a COMMUTATOR element of a group $\mathscr{G}$ if it can be written $\mathbf{g} = \mathbf{a}^{-1}\mathbf{b}^{-1}\mathbf{ab}$ for some **a** and **b** in $\mathscr{G}$. The COMMUTATOR SUBGROUP $(\mathscr{H}_c)$ of $\mathscr{G}$ is the smallest subgroup which contains all the commutator elements of $\mathscr{G}$.

(a) If **g** is a commutator, is $\mathbf{g}^{-1}$ also one? Is **1** one?

(b) If **g** is a commutator, is every member of its class one, too?

(c) prove that class sum $\mathbf{c}_j$ contains commutator elements if and only if there is at least one other class sum $\mathbf{c}_k$ such that $\mathbf{c}_j \mathbf{c}_k = \cdots + n\mathbf{c}_k + \cdots$, where $n \neq 0$.

(d) Find the commutator subgroup of C_{3v}.

3.5.5 A representation R is said to be FAITHFUL to a group if $R(\mathbf{g}) = R(\mathbf{g}')$ for all **g** and **g**' that are group elements. A representation R is said to be FAITHFUL to a GROUP ALGEBRA if $R(\mathbf{x}) = R(\mathbf{y})$ implies $\mathbf{x} = \mathbf{y}$ for all possible linear combinations x and y of group elements.

Note: In the second case we are talking about the whole group algebra and require that $R(a) = \mathbf{0}$ if and only if $\mathbf{a} = \mathbf{0}$.

(a) What is the lowest possible dimension of a representation that is faithful to the group C_{3v}? To the group C_{4v}?

(b) What is the lowest possible dimension of a representation that is faithful to the algebra of group C_{3v}? To the algebra of group C_{4v}?

(c) What is the maximum number of mutually commuting group elements in C_{3v}? In group C_{4v}?

(d) What is the maximum number of mutually commuting operators in the group algebra of C_{3v}? In the group algebra of C_{4v}?

(e) Are either of the answers to (c) or (d) related to those of either (a) or (b)? Which and why?

3.5.6 Prove the order $^{\circ}\mathscr{G}$ of a group must be evenly divisible by each of the following numbers. [Part (c) is the hardest to prove.]

(a) The order $^{\circ}\mathscr{H}$ of any of its subgroups.

(b) The order $^{\circ}C_g$ of any of its classes.

(c) The dimension l^{α} of any of its irreducible representations.