CHAPTER 12

MOLECULAR SYMMETRY

In many cases, the symmetry of a molecule provides a great deal of information about its quantum states, even without a detailed solution of the Schrödinger equation. A geometrical transformation which turns a molecule into an indistinguishable copy of itself is called a *symmetry operation.* A symmetry operation can consist of a rotation about an axis, a reflection in a plane, an inversion through a point, or some combination of these.

The Ammonia Molecule

We shall introduce the concepts of symmetry and group theory by considering a concrete example–the ammonia molecule NH_3. In any symmetry operation on NH_3, the nitrogen atom remains fixed but the hydrogen atoms can be permuted in 3!=6 different ways. The axis of the molecule is called a C_3 axis, since the molecule can be rotated about it into 3 equivalent orientations, 120° apart. More generally, a C_n axis has n equivalent orientations, separated by $2\pi/n$ radians. The axis of highest symmetry in a molecule is called the *principal axis.* Three mirror planes, designated $\sigma_1, \sigma_2, \sigma_3$, run through the principal axis in ammonia. These are designated as σ_v or *vertical* planes of symmetry. Ammonia belongs to the symmetry group designated C_{3v}, characterized by a three-fold axis with three vertical planes of symmetry.

Let us designate the orientation of the three hydrogen atoms in Fig. 1 as $\{1, 2, 3\}$, reading in clockwise order from the bottom. A counterclockwise rotation by 120°, designated

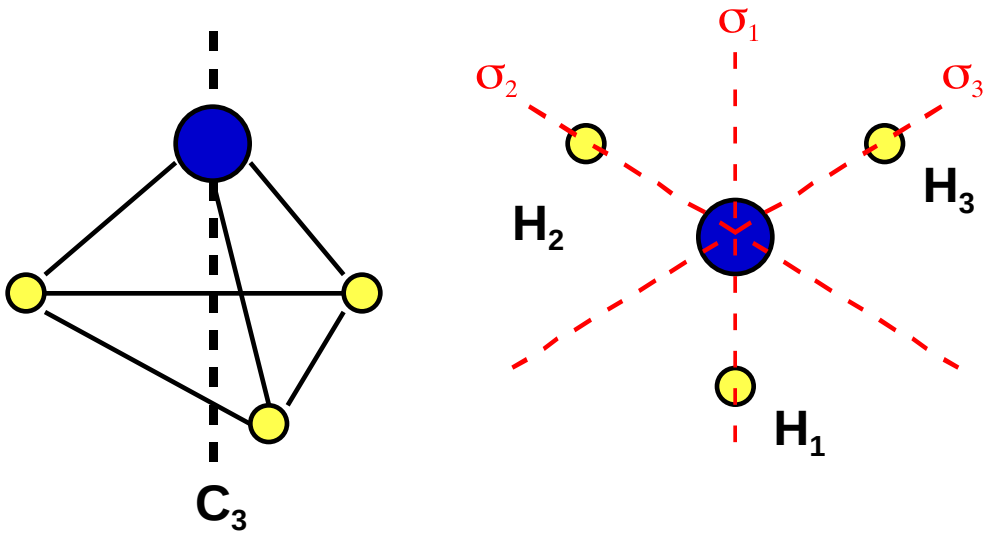

Figure 1. Two views of the ammonia molecule.

by the operator C_3, produces the orientation $\{2,3,1\}$. A second counterclockwise rotation, designated C_3^2, produces gives $\{3,1,2\}$. Note that two successive counterclockwise rotations by 120° is equivalent to one clockwise rotation by 120°, so the last operation could also be designated C_3^{-1}. The three reflection operations $\sigma_1, \sigma_2, \sigma_3$ applied to the original configuration $\{1,2,3\}$ produces $\{1,3,2\}$, $\{3,2,1\}$ and $\{2,1,3\}$, respectively. Finally, we must include the identity operation, designated E, which leaves an orientation unchanged. The effects of the six possible operations of the symmetry group $\mathrm{C_{3v}}$ can be summarized as follows:

$$E\{1,2,3\} = \{1,2,3\} \qquad C_3\{1,2,3\} = \{2,3,1\}$$

$$C_3^2\{1,2,3\} = \{3,1,2\} \qquad \sigma_1\{1,2,3\} = \{1,3,2\}$$

$$\sigma_2\{1,2,3\} = \{3,2,1\} \qquad \sigma_3\{1,2,3\} = \{2,1,3\}$$

We have thus accounted for all 6 posssible permutations of the three hydrogen atoms.

The successive application of two symmetry operations is equivalent to some single symmetry operation. For example, applying C_3, then σ_1 to our starting orientation, we have

$$\sigma_1\, C_3\, \{1,2,3\} = \sigma_1\, \{2,3,1\} = \{2,1,3\}$$

But this is eqivalent to the single operation σ_3. This can be represented as an algebraic relation among symmetry operators

$$\sigma_1\, C_3 = \sigma_3$$

Note that successive operations are applied in the order *right to left* when represented algebraically. For the same two operations in reversed order, we find

$$C_3\, \sigma_1\, \{1,2,3\} = C_3\, \{1,3,2\} = \{3,2,1\} = \sigma_2\, \{1,2,3\}$$

Thus symmetry operations do *not*, in general commute

$$A\, B \not\equiv B\, A \tag{1}$$

although they *may* commute, for example, C_3 and C_3^2.

The algebra of the group $\mathrm{C_{3v}}$ can be summarized by the following multiplication table.

2^{nd} \ 1^{st}	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^2	E

Notice that each operation occurs once and only once in each row and each column.

Group Theory

In mathematics, a *group* is defined as a set of g elements $\mathcal{G} \equiv \{G_1, G_2 \ldots G_h\}$ together with a rule for combination of elements, which we usually refer to as a *product*. The elements must fulfill the following four conditions.

(*i*) The product of any two elements of the group is another element of the group. That is $G_i G_j = G_k$ with $G_k \in \mathcal{G}$

(*ii*) Group multiplication obeys an associative law, $G_i(G_j G_k) = (G_i G_j)G_k \equiv G_i G_j G_k$.

(*iii*) There exists an *identity element* E such that $EG_i = G_i E = G_i$ for all i.

(*iv*) Every element G_i has a unique inverse G_i^{-1}, such that $G_i G_i^{-1} = G_i^{-1} G_i = E$ with $G_i^{-1} \in \mathcal{G}$.

The number of elements h is called the *order* of the group. Thus C_{3v} is a group of order 6.

a set of quantities which obeys the group multiplication table is called a *representation* of the group. Because of the possible noncommutativity of group elements [cf. Eq (1)], simple numbers are not always adequate to represent groups; we must often use matrices. The group C_{3v} has three *irreducible representations*, or IR's, which cannot be broken down into simpler representations. A trivial, but nonetheless important, representation of any group is the *totally symmetric representation*, in which each group element is represented by 1. The multiplication table then simply reiterates that $1 \times 1 = 1$. For C_{3v} this is called the A_1 representation:

$$A_1 : E = 1,\ C_3 = 1,\ C_3^2 = 1,\ \sigma_1 = 1,\ \sigma_2 = 1,\ \sigma_3 = 1 \qquad (2)$$

A slightly less trivial representation is A_2:

$$A_2 : E = 1,\ C_3 = 1,\ C_3^2 = 1,\ \sigma_1 = -1,\ \sigma_2 = -1,\ \sigma_3 = -1 \qquad (3)$$

Much more exciting is the E representation, which requires 2×2 matrices :

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad C_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

$$C_3^2 = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \qquad \sigma_1 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\sigma_2 = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \tag{4}$$

The operations C_3 and C_3^2 are said to belong to the same *class* since they perform the same geometric function, but for different orientations in space. Analogously, σ_1, σ_2 and σ_3 are obviously in the same class. E is in a class by itself. The class structure of the group is designated by $\{E, 2C_3, 3\sigma_v\}$. We state without proof that the number of irreducible representations of a group is equal to the number of classes. Another important theorem states that the sum of the squares of the dimensionalities of the irreducible representations of a group adds up to the order of the group. Thus, for C_{3v}, we find $1^2 + 1^2 + 2^2 = 6$.

The *trace* or *character* of a matrix is defined as the sum of the elements along the main diagonal:

$$\chi(M) \equiv \sum_k M_{kk} \tag{5}$$

For many purposes, it suffices to know just the characters of a matrix representation of a group, rather than the complete

matrices. For example, the characters for the E representation of C_{3v} in Eq (4) are given by

$$\chi(E) = 2, \quad \chi(C_3) = -1, \quad \chi(C_3^2) = -1,$$
$$\chi(\sigma_1) = 0, \quad \chi(\sigma_2) = 0, \quad \chi(\,\sigma_3) = 0 \qquad (6)$$

It is true in general that the characters for all operations in the same class are equal. Thus Eq (6) can be abbreviated to

$$\chi(E) = 2, \quad \chi(C_3) = -1, \quad \chi(\sigma_v) = 0 \qquad (7)$$

For one-dimensional representations, such as A_1 and A_2, the characters are equal to the matrices themselves, so Eqs (2) and (3) can be read as a table of characters.

The essential information about a symmetry group is summarized in its *character table*. We display here the character table for C_{3v}

$\mathbf{C_{3v}}$	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	z^2, x^2+y^2
A_2	1	1	-1		
E	2	-1	0	(x,y)	$(xy, x^2-y^2), (xz, yz)$

The last two columns show how the cartesian coordinates x, y, z and their products transform under the operations of the group.

Group Theory and Quantum Mechanics

When a molecule has the symmetry of a group $\mathcal{G}$, this means that each member of the group commutes with the molecular Hamiltonian

$$[\hat{G}_i, \hat{H}] = 0 \qquad i = 1 \ldots h \qquad (8)$$

where we now explicitly designate the group elements G_i as operators on wavefunctions. As was shown in Chap. 4, commuting operators can have simultaneous eigenfunctions. A representation of the group of dimension d means that there must exist a set of d degenerate eigenfunctions of $\hat{H}$ that transform among themselves in accord with the corresponding matrix representation. For example, if the eigenvalue E_n is d-fold degenerate, the commutation conditions (2) imply that, for $i = 1 \ldots h$,

$$\hat{G}_i \, \hat{H} \, \psi_{nk} = \hat{H} \, \hat{G}_i \, \psi_{nk} = E_n \, \hat{G}_i \, \psi_{nk} \quad \text{for} \quad k = 1 \ldots d \tag{9}$$

Thus each $\hat{G}_i \, \psi_{nk}$ is also an eigenfunction of $\hat{H}$ with the same eigenvalue E_n, and must therefore be represented as a linear combination of the eigenfunctions ψ_{nk}. More precisely, the eigenfunctions transform among themselves according to

$$\hat{G}_i \, \psi_{nk} = \sum_{m=1}^{d} D(G_i)_{km} \psi_{nm} \tag{10}$$

where $D(G_i)_{km}$ means the $\{k, m\}$ element of the matrix representing the operator $\hat{G}_i$.

The character of the identity operation E immediately shows the degeneracy of the eigenvalues of that symmetry. The C_{3v} character table reveals that NH_3, and other molecules of the same symmetry, can have only nondegenerate and two-fold degenerate energy levels. The following notation for symmetry species was introduced by Mulliken:

(i) One dimensional representations are designated either A or B. Those symmetric wrt rotation by $2\pi/n$ about the C_n

principal axis are labelled A, while those antisymmetric are labelled B.

(*ii*) Two dimensional representations are designated E; 3, 4 and 5 dimensional representations are designated T, F and G, respectively. These latter cases occur only in groups of high symmetry: cubic, octahedral and icosohedral.

(*iii*) In groups with a center of inversion, the subscripts g and u indicate even and odd parity, respectively.

(*iv*) Subscripts 1 and 2 indicate symmetry and antisymmetry, respectively, wrt a C_2 axis perpendicular to C_n, or to a σ_v plane.

(*v*) Primes and double primes indicate symmetry and antisymmetry to a σ_h plane.

For individual orbitals, the lower case analogs of the symmetry designations are used. For example, MO's in ammonia are classified a_1, a_2 or e.

For ammonia and other C_{3v} molecules, there exist three species of eigenfunctions. Those belonging to the classification A_1 are transformed into themselves by all symmetry operations of the group. The $1s$, $2s$ and $2p_z$ AO's on nitrogen are in this category. The z-axis is taken as the 3-fold axis. There are no low-lying orbitals belonging to A_2. The nitrogen $2p_x$ and $2p_y$ AO's form a two-dimensional representation of the group C_{3v}. That is to say, any of the six operations of the group transforms either one of these AO's into a linear combination of the two, with coefficients given by the matrices (4). The three hydrogen $1s$ orbitals transform like a 3×3 representation of the group. If we represent the hydrogens by a column vector $\{H_1, H_2, H_3\}$,

then the six group operations generate the following algebra

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad C_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$C_3^2 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad \sigma_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\sigma_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{11}$$

Let us denote this representation by Γ. It can be shown that Γ is a *reducible* representation, meaning that by some unitary transformation the 3×3 matrices can be factorized into block-diagonal form with 2×2 plus 1×1 submatrices. The reducibility of Γ can be deduced from the character table. The characters of the matrices (11) are

$$\Gamma: \qquad \chi(E) = 3, \qquad \chi(C_3) = 0, \qquad \chi(\sigma_v) = 1 \tag{12}$$

The character of each of these permutation operations is equal to the number of H atoms left untouched: 3 for the identity, 1 for a reflection and 0 for a rotation. The characters of Γ are seen to equal the sum of the characters of A_1 plus E. This reducibility relation is expressed by writing

$$\Gamma = A_1 \oplus E \tag{13}$$

The three H atom $1s$ functions can be combined into LCAO functions which transform according to the IR's of the group. Clearly the sum

$$\psi = \psi_{1s}(1) + \psi_{1s}(2) + \psi_{1s}(3) \tag{14}$$

transforms like A_1. The two remaining linear combinations which transform like E must be orthogonal to (14) and to one another. One possible choice is

$$\psi' = \psi_{1s}(2) - \psi_{1s}(3), \quad \psi'' = 2\psi_{1s}(1) - \psi_{1s}(2) - \psi_{1s}(3) \quad (15)$$

Now (14) can be combined with the N $1s$, $2s$ and $2p_z$ to form MO's of A_1 symmetry, while (15) can be combined with the N $2p_x$and $2p_y$ to form MO's of E symmetry. Note that no hybridization of AO's is predetermined, it emerges automatically in the results of computation.