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, $120^\circ$ 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 $\sigma_v$ 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 $120^\circ$, 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 $120^\circ$ is equivalent to one clockwise rotation by $120^\circ$, 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 $C_{3v}$ can be summarized as follows:

\[
E \{1, 2, 3\} = \{1, 2, 3\} \quad C_3 \{1, 2, 3\} = \{2, 3, 1\} \\
C_3^2 \{1, 2, 3\} = \{3, 1, 2\} \quad \sigma_1 \{1, 2, 3\} = \{1, 3, 2\} \\
\sigma_2 \{1, 2, 3\} = \{3, 2, 1\} \quad \sigma_3 \{1, 2, 3\} = \{2, 1, 3\}
\]

We have thus accounted for all 6 possible 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 $\sigma_1$ to our starting orientation, we have

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

But this is equivalent to the single operation $\sigma_3$. 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

$$AB \not\equiv BA$$

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

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

<table>
<thead>
<tr>
<th>2nd</th>
<th>1st</th>
<th>$E$</th>
<th>$C_3$</th>
<th>$C_3^2$</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
<td>$\sigma_3$</td>
<td></td>
</tr>
<tr>
<td>$C_3$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$\sigma_3$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
<td></td>
</tr>
<tr>
<td>$C_3^2$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$\sigma_2$</td>
<td>$\sigma_3$</td>
<td>$\sigma_1$</td>
<td></td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
<td>$\sigma_3$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td></td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>$\sigma_2$</td>
<td>$\sigma_3$</td>
<td>$\sigma_1$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$C_3$</td>
<td></td>
</tr>
<tr>
<td>$\sigma_3$</td>
<td>$\sigma_3$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td></td>
</tr>
</tbody>
</table>

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 \( E G_i = G_i E = G_i \) 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:

\[
A_1 : E = 1, \ C_3 = 1, \ C_3^2 = 1, \ \sigma_1 = 1, \ \sigma_2 = 1, \ \sigma_3 = 1
\]  

(2)

A slightly less trivial representation is \( A_2 \):

\[
A_2 : E = 1, \ C_3 = 1, \ C_3^2 = 1, \ \sigma_1 = -1, \ \sigma_2 = -1, \ \sigma_3 = -1
\]  

(3)
Much more exciting is the $E$ representation, which requires $2 \times 2$ matrices:

\[
E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \\
C_3^2 = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad \sigma_1 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \\
\sigma_2 = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}
\]

(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, $\sigma_1$, $\sigma_2$ and $\sigma_3$ 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:

\[
\chi(M) \equiv \sum_k M_{kk}
\]

(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

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

(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

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

(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 $C_{3v}$

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>E</th>
<th>$2C_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>z</td>
<td>$z^2, x^2 + y^2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(x, y)</td>
<td>$(xy, x^2 - y^2), (xz, yz)$</td>
</tr>
</tbody>
</table>

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

$$
[\hat{G}_i, \hat{H}] = 0 \quad i = 1 \ldots h
$$

(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 $i = 1 \ldots h$,

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

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 $\psi_{nk}$. More precisely, the eigenfunctions transform among themselves according to

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

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 \( \sigma_v \) plane.

(v) Primes and double primes indicate symmetry and antisymmetry to a \( \sigma_h \) 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 \( 3 \times 3 \) 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

\[ E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \]

\[ C_3^2 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \]

\[ \sigma_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (11) \]

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

\[ \Gamma : \quad \chi(E) = 3, \quad \chi(C_3) = 0, \quad \chi(\sigma_v) = 1 \quad (12) \]

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 \( \Gamma \) are seen to equal the sum of the characters of \( A_1 \) plus \( E \). This reducibility relation is expressed by writing

\[ \Gamma = A_1 \oplus E \quad (13) \]

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

\[ \psi = \psi_{1s}(1) + \psi_{1s}(2) + \psi_{1s}(3) \quad (14) \]
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.