# 1.12: 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 $\sigma_v$ 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 Figure 1.12.1 as {1, 2, 3}, reading in clockwise order from the bottom. A counterclockwise rotation by $120°$, designated
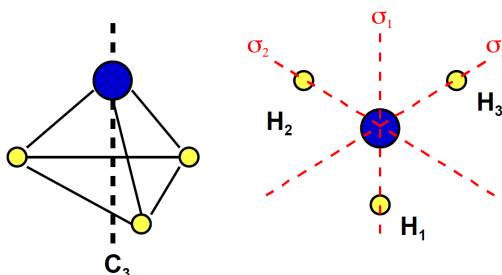


Figure 1.12.1: Two views of the ammonia molecule.

by the operator $C_3$, produces the orientation {2, 3, 1}. A second counterclockwise rotation, designated $C_3^2$, produces {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 $C_{3v}$ can be summarized as follows:

$$E\{1,2,3\} = \{1,2,3\} \quad C_3\{1,2,3\} = \{2,3,1\} \tag{1.12.1}$$

$$C_3^2\{1,2,3\} = \{3,1,2\} \quad \sigma_1\{1,2,3\} = \{1,3,2\} \tag{1.12.2}$$

$$\sigma_2\{1,2,3\} = \{3,2,1\} \quad \sigma_3\{1,2,3\} = \{2,1,3\} \tag{1.12.3}$$

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

$$\sigma_1 C_3\{1,2,3\} = \sigma_1\{2,3,1\} = \{2,1,3\} \tag{1.12.4}$$

But this is equivalent to the single operation $\sigma_3$. This can be represented as an algebraic relation among symmetry operators

$$\sigma_1 C_3 = \sigma_3 \tag{1.12.5}$$

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

$$C_3\sigma_1\{1,2,3\} = C_3\{1,3,2\} = \{3,2,1\} = \sigma_2\{1,2,3\} \tag{1.12.6}$$

Thus symmetry operations do *not*, in general commute

$$AB \not\equiv BA \tag{1.12.7}$$

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.

$$
\begin{array}{c|cccccc}
\text{1}^{st} & E & C_3 & C_3^2 & \sigma_1 & \sigma_2 & \sigma_3 \\
\text{2}^{nd} & & & & & & \\
\hline
E & E & C_3 & C_3^2 & \sigma_1 & \sigma_2 & \sigma_3 \\
C_3 & C_3 & C_3^2 & E & \sigma_3 & \sigma_1 & \sigma_2 \\
C_3^2 & C_3^2 & E & C_3 & \sigma_2 & \sigma_3 & \sigma_1 \\
\sigma_1 & \sigma_1 & \sigma_2 & \sigma_3 & E & C_3 & C_3^2 \\
\sigma_2 & \sigma_2 & \sigma_3 & \sigma_1 & C_3^2 & E & C_3 \\
\sigma_3 & \sigma_3 & \sigma_1 & \sigma_2 & C_3 & C_3^2 & E \\
\end{array}
\tag{1.12.8}
$$

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:

$$
A_1 : E = 1, C_3 = 1, C_3^2 = 1, \sigma_1 = 1, \sigma_2 = 1, \sigma_3 = 1
\tag{1.12.9}
$$

A slightly less trivial representation is $A_2$:

$$
A_2 : E = 1, C_3 = 1, C_3^2 = 1, \sigma_1 = -1, \sigma_2 = -1, \sigma_3 = -1
\tag{1.12.10}
$$

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

$$
E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad C_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}
\tag{1.12.11}
$$

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

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

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:

$$
\chi(M) \equiv \sum_k M_{kk}
\tag{1.12.12}
$$

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

$$\chi(E) = 2, \quad \chi(C_3) = -1, \quad \chi(C_3^2) = -1,$$
$$\chi(\sigma_1) = 0, \quad \chi(\sigma_2) = 0, \quad \chi(\sigma_3) = 0 \tag{1.12.13}$$

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

$$\chi(E) = 2, \quad \chi(C_3) = -1, \quad \chi(\sigma_v) = 0 \tag{1.12.14}$$

For one-dimensional representations, such as $A_1$ and $A_2$, the characters are equal to the matrices themselves, so Equations 1.12.9 and 1.12.10 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 $C_{3v}$

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

$$\tag{1.12.15}$$

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

$$[\hat{G}_i, \hat{H}] = 0 \quad i = 1...h \tag{1.12.16}$$

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 (Equation 1.12.9) imply that, for $i = 1...h$,

$$\hat{G}_i\hat{H}\psi_{nk} = \hat{H}\hat{G}_i\psi_{nk} = E_n\hat{G}_i\psi_{nk} \text{ for } k = 1...d \tag{1.12.17}$$

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

$$\hat{G}_i\psi_{nk} = \sum_{m=1}^{d} D(G_i)_{km}\psi_{nm} \tag{1.12.18}$$

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 labeled A, while those antisymmetric are labeled 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 {H1,H2,H3}, then the six group operations generate the following algebra

$$
E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}
$$
$$
C_3^2 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \quad \sigma_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{1.12.19}
$$
$$
\sigma_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}
$$

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 blockdiagonal 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 (Equation 1.12.19) are

$$
\Gamma : \qquad \chi(E) = 3, \quad \chi(C_3) = 0, \quad \chi_{(\sigma_v)} = 1 \tag{1.12.20}
$$

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

$$
\Gamma = A_1 \oplus E \tag{1.12.21}
$$

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

$$
\psi = \psi_{1s}(1) + \psi_{1s}(2) + \psi_{1s}(3) \tag{1.12.22}
$$

transforms like $A_1$. The two remaining linear combinations which transform like E must be orthogonal to (Equation 1.12.22) and to one another. One possible choice is

$$
\psi' = \psi_{1s}(2) - \psi_{1s}(3), \quad \psi'' = 2\psi_{1s}(1) - \psi_{1s}(2) - \psi_{1s}(3) \tag{1.12.23}
$$

Now, Equation 1.12.22 can be combined with the N 1s, 2s and $2p_z$ to form MO's of $A_1$ symmetry, while Equation 1.12.23 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.

## Contributors and Attributions

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