

Molecular Symmetry

12.1 Symmetry Elements and Operations

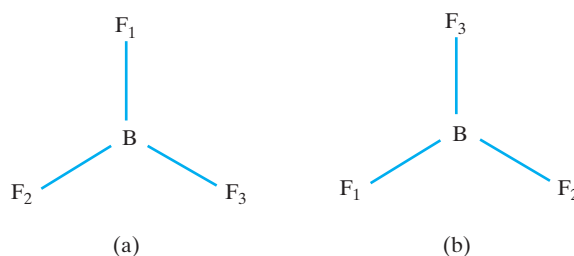
Qualitative information about molecular wave functions and properties can often be obtained from the symmetry of the molecule. By the symmetry of a molecule, we mean the symmetry of the framework formed by the nuclei held fixed in their equilibrium positions. (Our starting point for molecular quantum mechanics will be the Born–Oppenheimer approximation, which regards the nuclei as fixed when solving for the electronic wave function; see Section 13.1.) The symmetry of a molecule can differ in different electronic states. For example, HCN is linear in its ground electronic state, but nonlinear in certain excited states. Unless otherwise specified, we shall be considering the symmetry of the ground electronic state.

Symmetry Elements and Operations

A **symmetry operation** is a transformation of a body such that the final position is physically indistinguishable from the initial position, and the distances between all pairs of points in the body are preserved. For example, consider the trigonal-planar molecule BF_3 (Fig. 12.1a), where for convenience we have numbered the fluorine nuclei. If we rotate the molecule counterclockwise by 120° about an axis through the boron nucleus and perpendicular to the plane of the molecule, the new position will be as in Fig. 12.1b. Since in reality the fluorine nuclei are physically indistinguishable from one another, we have carried out a symmetry operation. The axis about which we rotated the molecule is an example of a symmetry element. Symmetry elements and symmetry operations are related but different things, which are often confused. A **symmetry element** is a geometrical entity (point, line, or plane) with respect to which a symmetry operation is carried out.

We say that a body has an **n -fold axis of symmetry** (also called an *n -fold proper axis* or an *n -fold rotation axis*) if rotation about this axis by $360/n$ degrees (where n is an

FIGURE 12.1 (a) The BF_3 molecule. (b) BF_3 after a 120° rotation about the axis through B and perpendicular to the molecular plane.



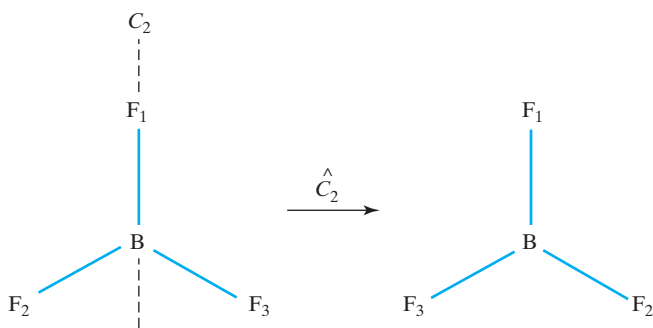


FIGURE 12.2 A C_2 axis in BF_3 .

integer) gives a configuration physically indistinguishable from the original position; n is called the *order* of the axis. For example, BF_3 has a threefold axis of symmetry perpendicular to the molecular plane. The symbol for an n -fold rotation axis is C_n . The threefold axis in BF_3 is a C_3 axis. To denote the operation of counterclockwise rotation by $(360/n)^\circ$, we use the symbol $\hat{C}_n$. The “hat” distinguishes symmetry operations from symmetry elements. BF_3 has three more rotation axes; each B—F bond is a twofold symmetry axis (Fig. 12.2).

A second kind of symmetry element is a plane of symmetry. A molecule has a **plane of symmetry** if reflection of all the nuclei through that plane gives a configuration physically indistinguishable from the original one. The symbol for a symmetry plane is σ (lowercase sigma). (*Spiegel* is the German word for mirror.) The symbol for the operation of reflection is $\hat{\sigma}$. BF_3 has four symmetry planes. The plane of the molecule is a symmetry plane, since nuclei lying in a reflection plane do not move when a reflection is carried out. The plane passing through the B and F_1 nuclei and perpendicular to the plane of the molecule is a symmetry plane, since reflection in this plane merely interchanges F_2 and F_3 . It might be thought that this reflection is the same symmetry operation as rotation by 180° about the C_2 axis passing through B and F_1 , which also interchanges F_2 and F_3 . This is not so. The reflection carries points lying above the plane of the molecule into points that also lie above the molecular plane, whereas the $\hat{C}_2$ rotation carries points lying above the molecular plane into points below the molecular plane. *Two symmetry operations are equal only when they represent the same transformation of three-dimensional space.* The remaining two symmetry planes in BF_3 pass through B— F_2 and B— F_3 and are perpendicular to the molecular plane.

The third kind of symmetry element is a **center of symmetry**, symbolized by i (no connection with $\sqrt{-1}$). A molecule has a center of symmetry if the operation of inverting all the nuclei through the center gives a configuration indistinguishable from the original one. If we set up a Cartesian coordinate system, the operation of **inversion** through the origin (symbolized by $\hat{i}$) carries a nucleus originally at (x, y, z) to $(-x, -y, -z)$. Does BF_3 have a center of symmetry? With the origin at the boron nucleus, inversion gives the result shown in Fig. 12.3. Since we get a configuration that is physically distinguishable from

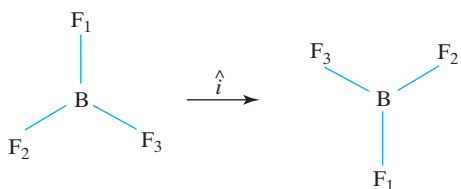
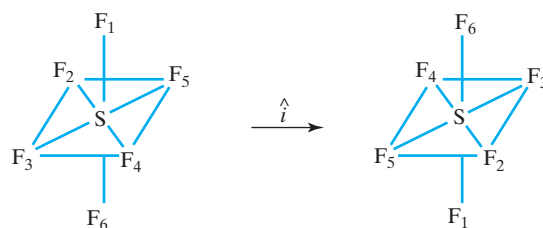


FIGURE 12.3 Effect of inversion in BF_3 .

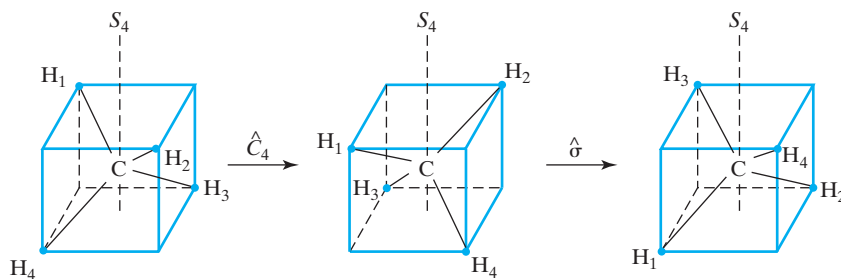
FIGURE 12.4 Effect of inversion in BF_6 .

the original one, BF_3 does not have a center of symmetry. For SF_6 , inversion through the sulfur nucleus is shown in Fig. 12.4, and it is clear that SF_6 has a center of symmetry. (An operation such as $\hat{i}$ or $\hat{C}_n$ may or may not be a symmetry operation. Thus, $\hat{i}$ is a symmetry operation in SF_6 but not in BF_3 .)

The fourth and final kind of symmetry element is an **n -fold rotation–reflection axis of symmetry** (also called an *improper axis* or an *alternating axis*), symbolized by S_n . A body has an S_n axis if rotation by $(360/n)^\circ$ (n integral) about the axis, followed by reflection in a plane perpendicular to the axis, carries the body into a position physically indistinguishable from the original one. Clearly, if a body has a C_n axis and also has a plane of symmetry perpendicular to this axis, then the C_n axis is also an S_n axis. Thus the C_3 axis in BF_3 is also an S_3 axis. It is possible to have an S_n axis that is not a C_n axis. An example is CH_4 . In Fig. 12.5 we have first carried out a 90° proper rotation ($\hat{C}_4$) about what we assert is an S_4 axis. As can be seen, this operation does not result in an equivalent configuration. When we follow the $\hat{C}_4$ operation by reflection in the plane perpendicular to the axis and passing through the carbon atom, we do get a configuration indistinguishable from the one existing before we performed the rotation and reflection. Hence CH_4 has an S_4 axis. The S_4 axis is not a C_4 axis, although it is a C_2 axis. There are two other S_4 axes in methane, each perpendicular to a pair of faces of the cube in which the tetrahedral molecule is inscribed.

The operation of counterclockwise rotation by $(360/n)^\circ$ about an axis, followed by reflection in a plane perpendicular to the axis, is denoted by $\hat{S}_n$. An $\hat{S}_1$ operation is a 360° rotation about an axis, followed by a reflection in a plane perpendicular to the axis. Since a 360° rotation restores the body to its original position, an $\hat{S}_1$ operation is the same as reflection in a plane; $\hat{S}_1 = \hat{\sigma}$. A plane of symmetry has an S_1 axis perpendicular to it.

Consider now the $\hat{S}_2$ operation. Let the S_2 axis be the z axis (Fig. 12.6). Rotation by 180° about the S_2 axis changes the x and y coordinates of a point to $-x$ and $-y$, respectively, and leaves the z coordinate unaffected. Reflection in the xy plane then converts the z coordinate to $-z$. The net effect of the $\hat{S}_2$ operation is to bring a point originally at (x, y, z) to $(-x, -y, -z)$, which amounts to an inversion through the origin: $\hat{S}_2 = \hat{i}$. Any axis passing through a center of symmetry is an S_2 axis. Reflection in a plane and inversion are special cases of the $\hat{S}_n$ operation.

FIGURE 12.5 An S_4 axis in CH_4 .

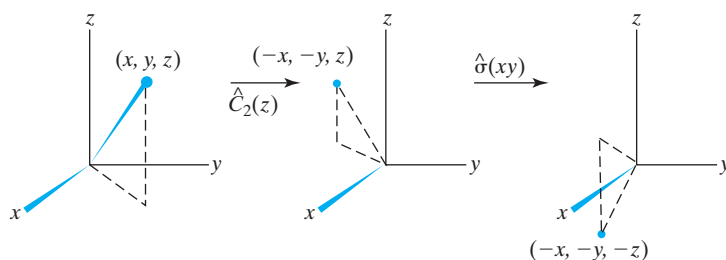


FIGURE 12.6 The $\hat{S}_2$ operation.

The $\hat{S}_n$ operation may seem an arbitrary kind of operation, but it must be included as one of the kinds of symmetry operations. For example, the transformation from the first to the third CH_4 configuration in Fig. 12.5 certainly meets the definition of a symmetry operation, but it is neither a proper rotation nor a reflection nor an inversion.

Performing a symmetry operation on a molecule gives a nuclear configuration that is physically indistinguishable from the original one. Hence the center of mass must have the same position in space before and after a symmetry operation. For the operation $\hat{C}_n$, the only points that do not move are those on the C_n axis. Therefore, a C_n symmetry axis must pass through the molecular center of mass. Similarly, a center of symmetry must coincide with the center of mass; a plane of symmetry and an S_n axis of symmetry must pass through the center of mass. The center of mass is the common intersection of all the molecular symmetry elements.

In discussing the symmetry of a molecule, we often place it in a Cartesian coordinate system with the molecular center of mass at the origin. The rotational axis of highest order is made the z axis. A plane of symmetry containing this axis is designated σ_v (for *vertical*); a plane of symmetry perpendicular to this axis is designated σ_h (for *horizontal*).

Products of Symmetry Operations

Symmetry operations are operators that transform three-dimensional space, and (as with any operators) we define the **product** of two such operators as meaning successive application of the operators, the operator on the right of the product being applied first. Clearly, the product of any two symmetry operations of a molecule must be a symmetry operation.

As an example, consider BF_3 . The product of the $\hat{C}_3$ operator with itself, $\hat{C}_3\hat{C}_3 = \hat{C}_3^2$, rotates the molecule 240° counterclockwise. If we take $\hat{C}_3\hat{C}_3\hat{C}_3 = \hat{C}_3^3$, we have a 360° rotation, which restores the molecule to its original position. We define the **identity operation** $\hat{E}$ as the operation that does nothing to a body. We have $\hat{C}_3^3 = \hat{E}$. (The symbol comes from the German word *Einheit*, meaning unity.)

Now consider a molecule with a sixfold axis of symmetry, for example, C_6H_6 . The operation $\hat{C}_6$ is a 60° rotation, and $\hat{C}_6^2$ is a 120° rotation; hence $\hat{C}_6^2 = \hat{C}_3$. Also $\hat{C}_6^3 = \hat{C}_2$. Therefore, a C_6 symmetry axis is also a C_3 and a C_2 axis.

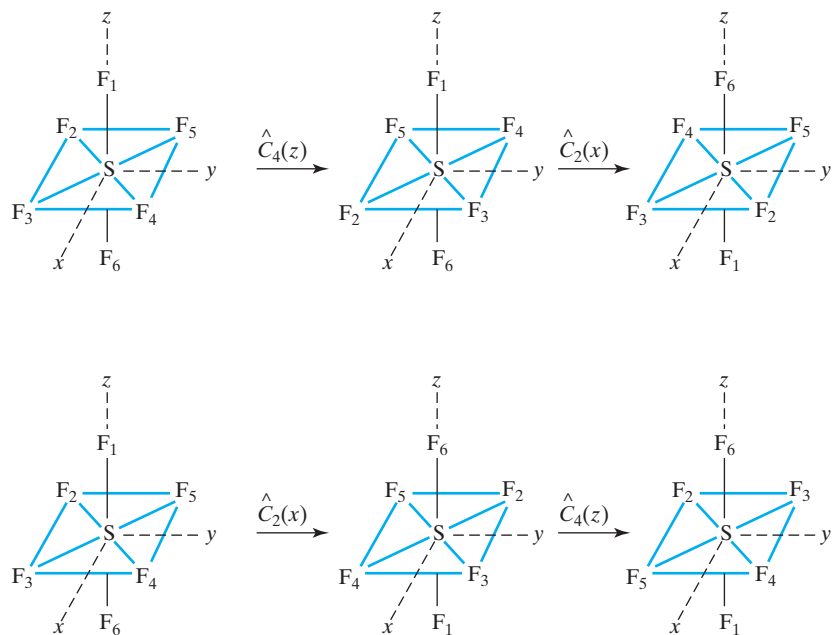
Since two successive reflections in the same plane bring all nuclei back to their original positions, we have $\hat{\sigma}^2 = \hat{E}$. Also, $\hat{i}^2 = \hat{E}$. More generally, $\hat{\sigma}^n = \hat{E}$, $\hat{i}^n = \hat{E}$ for even n , while $\hat{\sigma}^n = \hat{\sigma}$, $\hat{i}^n = \hat{i}$ for odd n .

Do symmetry operators always commute? Consider SF_6 . We examine the products of a $\hat{C}_4$ rotation about the z axis and a $\hat{C}_2$ rotation about the x axis. **Figure 12.7** shows that $\hat{C}_4(z)\hat{C}_2(x) \neq \hat{C}_2(x)\hat{C}_4(z)$. Thus symmetry operations do not always commute. Note that we describe symmetry operations with respect to a fixed coordinate system that does not move with the molecule when we perform a symmetry operation. Thus the $C_2(x)$ axis does not move when we perform the $\hat{C}_4(z)$ operation.

FIGURE 12.7 Products of two symmetry operations in SF_6 .

Top: $\hat{C}_2(x)\hat{C}_4(z)$.

Bottom: $\hat{C}_4(z)\hat{C}_2(x)$.



Symmetry and Dipole Moments

As an application of symmetry, we consider molecular dipole moments. Since a symmetry operation produces a configuration that is physically indistinguishable from the original one, the direction of the dipole-moment vector must remain unchanged after a symmetry operation. (This is a nonrigorous, unsophisticated argument.) Hence, if we have a C_n axis of symmetry, the dipole moment must lie along this axis. If we have two or more noncoincident symmetry axes, the molecule cannot have a dipole moment, since the dipole moment cannot lie on two different axes. CH_4 , which has four noncoincident C_3 axes, has no dipole moment. If there is a plane of symmetry, the dipole moment must lie in this plane. If there are several symmetry planes, the dipole moment must lie along the line of intersection of these planes. In H_2O the dipole moment lies on the C_2 axis, which is also the intersection of the two symmetry planes (Fig. 12.8). A molecule with a center of symmetry cannot have a dipole moment, since inversion reverses the direction of a vector. A monatomic molecule has a center of symmetry. Hence atoms do not have dipole moments. (There is one exception to this statement; see Prob. 14.4.) Thus we can use symmetry to discover whether a molecule has a dipole moment. In many cases symmetry also tells us along what line the dipole moment lies.

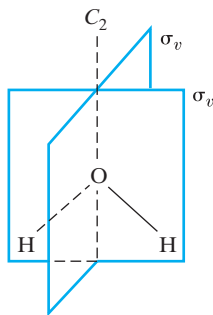


FIGURE 12.8 The symmetry elements of H_2O .

Symmetry and Optical Activity

Certain molecules rotate the plane of polarization of plane-polarized light that is passed through them. Experimental evidence and a quantum-mechanical treatment (*Kauzmann*, pp. 703–713) show that the optical rotary powers of two molecules that are mirror images of each other are equal in magnitude but opposite in sign. Hence, if a molecule is its own mirror image, it is optically inactive: $\alpha = -\alpha$, $2\alpha = 0$, $\alpha = 0$, where α is the optical rotary power. If a molecule is not superimposable on its mirror image, it may be optically active. If the conformation of the mirror image differs from that of the original molecule only by rotation about a bond with a low rotational barrier, then the molecule will not be optically active.

What is the connection between symmetry and optical activity? Consider the $\hat{S}_n$ operation. It consists of a rotation ($\hat{C}_n$) and a reflection ($\hat{\sigma}$). The reflection part of the

$\hat{S}_n$ operation converts the molecule to its mirror image, and if the $\hat{S}_n$ operation is a symmetry operation for the molecule, then the $\hat{C}_n$ rotation will superimpose the molecule and its mirror image:



We conclude that a molecule with an S_n axis is optically inactive. If the molecule has no S_n axis, it may be optically active.

Since $\hat{S}_1 = \hat{\sigma}$ and $\hat{S}_2 = \hat{i}$, a molecule with either a plane or a center of symmetry is optically inactive. However, an S_n axis of any order rules out optical activity.

A molecule can have a symmetry element and still be optically active. If a C_n axis is present and there is no S_n axis, the molecule can be optically active.

Symmetry Operations and Quantum Mechanics

What is the relation between the symmetry operations of a molecule and quantum mechanics? To classify the states of a quantum-mechanical system, we consider those operators that commute with the Hamiltonian operator and with each other. For example, we classified the states of many-electron atoms using the quantum numbers L , S , J , and M_J , which correspond to the operators $\hat{L}^2$, $\hat{S}^2$, $\hat{J}^2$, and $\hat{J}_z$, all of which commute with one other and with the Hamiltonian (omitting spin-orbit interaction). The symmetry operations discussed in this chapter act on *points* in three-dimensional space, transforming each point to a corresponding point. All the quantum-mechanical operators we have discussed act on *functions*, transforming each function to a corresponding function. Corresponding to each symmetry operation $\hat{R}$, we define an operator $\hat{O}_R$ that acts on functions in the following manner. Let $\hat{R}$ bring a point originally at (x, y, z) to the location (x', y', z') :

$$\hat{R}(x, y, z) \rightarrow (x', y', z') \quad (12.1)$$

The operator $\hat{O}_R$ is defined so that the function $\hat{O}_R f$ has the same value at (x', y', z') that the function f has at (x, y, z) :

$$\hat{O}_R f(x', y', z') = f(x, y, z) \quad (12.2)$$

For example, let $\hat{R}$ be a counterclockwise 90° rotation about the z axis: $\hat{R} = \hat{C}_4(z)$; and let f be a $2p_x$ hydrogen orbital: $f = 2p_x = Nxe^{-k(x^2+y^2+z^2)^{1/2}}$. The shape of the $2p_x$ orbital is two distorted ellipsoids of revolution about the x axis (Section 6.7). Let these ellipsoids be “centered” about the points $(a, 0, 0)$ and $(-a, 0, 0)$, where $a > 0$ and $2p_x > 0$ on the right ellipsoid. The operator $\hat{C}_4(z)$ has the following effect (Fig. 12.9):

$$\hat{C}_4(z)(x, y, z) \rightarrow (-y, x, z) \quad (12.3)$$

For example, the point originally at $(a, 0, 0)$ is moved to $(0, a, 0)$, while the point at $(-a, 0, 0)$ is moved to $(0, -a, 0)$. From (12.2), the function $\hat{O}_{C_4(z)} 2p_x$ must have

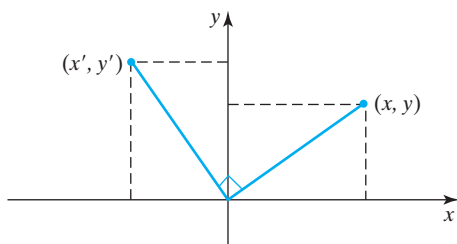
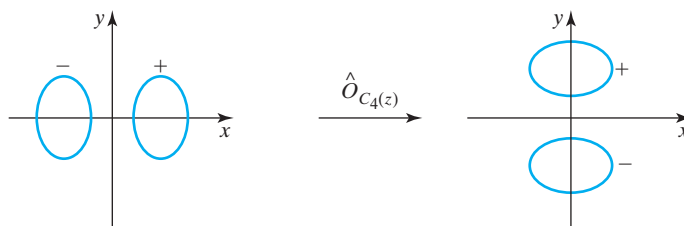


FIGURE 12.9 The effect of a $\hat{C}_4(z)$ rotation is to move the point at (x, y) to (x', y') . Use of trigonometry shows that $x' = -y$ and $y' = x$.

FIGURE 12.10 Effect of $\hat{O}_{C_4(z)}$ on a p_x orbital.

its contours centered about $(0, a, 0)$ and $(0, -a, 0)$, respectively. We conclude that (Fig. 12.10)

$$\hat{O}_{C_4(z)} 2p_x = 2p_y \quad (12.4)$$

For the inversion operation, we have

$$\hat{i}(x, y, z) \rightarrow (-x, -y, -z) \quad (12.5)$$

and (12.2) reads

$$\hat{O}_i f(-x, -y, -z) = f(x, y, z)$$

We now rename the variables as follows: $\bar{x} = -x$, $\bar{y} = -y$, $\bar{z} = -z$. Hence

$$\hat{O}_i f(\bar{x}, \bar{y}, \bar{z}) = f(-\bar{x}, -\bar{y}, -\bar{z})$$

The point $(\bar{x}, \bar{y}, \bar{z})$ is a general point in space, and we can drop the bars to get

$$\hat{O}_i f(x, y, z) = f(-x, -y, -z)$$

We conclude that $\hat{O}_i$ is the parity operator (Section 7.5): $\hat{O}_i = \hat{\Pi}$.

The wave function of an n -particle system is a function of $4n$ variables, and we extend the definition (12.2) of $\hat{O}_R$ to read

$$\hat{O}_R f(x'_1, y'_1, z'_1, m_{s1}, \dots, x'_n, y'_n, z'_n, m_{sn}) = f(x_1, y_1, z_1, m_{s1}, \dots, x_n, y_n, z_n, m_{sn})$$

Note that $\hat{O}_R$ does not affect the spin coordinates. Thus, in looking at the parity of atomic states in Section 11.5, we looked at the spatial factors in each term of the expansion of the Slater determinant and omitted consideration of the spin factors, since these are unaffected by $\hat{\Pi}$.

When a system is characterized by the symmetry operations $\hat{R}_1, \hat{R}_2, \dots$, then the corresponding operators $\hat{O}_{R_1}, \hat{O}_{R_2}, \dots$ commute with the Hamiltonian. (For a proof, see *Schonland*, Sections 7.1–7.3.) For example, if the nuclear framework of a molecule has a center of symmetry, then the parity operator $\hat{\Pi}$ commutes with the Hamiltonian for the electronic motion. We can then choose the electronic states (wave functions) as even or odd, according to the eigenvalue of $\hat{\Pi}$. Of course, not all the symmetry operations may commute among themselves (Fig. 12.7). Hence the wave functions cannot in general be chosen as eigenfunctions of all the symmetry operators $\hat{O}_R$. (Further discussion on the relation between symmetry operators and molecular wave functions is given in Section 15.2.)

There is a close connection between symmetry and the *constants of the motion* (these are properties whose operators commute with the Hamiltonian $\hat{H}$). For a system whose Hamiltonian is invariant (that is, doesn't change) under any translation of spatial coordinates, the linear-momentum operator $\hat{p}$ will commute with $\hat{H}$ and p can be assigned a definite value in a stationary state. An example is the free particle. For a system with $\hat{H}$ invariant under any rotation of coordinates, the operators for the angular-momentum components commute with $\hat{H}$, and the total angular momentum and one of its components are specifiable. An example is an atom. A linear molecule has axial symmetry, rather than the spherical symmetry of an atom; here only the axial component of angular momentum can be specified (Chapter 13).

Matrices and Symmetry Operations

The symmetry operation $\hat{R}$ moves the point originally at x, y, z to the new location x', y', z' , where each of x', y', z' is a linear combination of x, y, z (for proof of this see *Schonland*, pp. 52–53):

$$\begin{aligned} x' &= r_{11}x + r_{12}y + r_{13}z \\ y' &= r_{21}x + r_{22}y + r_{23}z \\ z' &= r_{31}x + r_{32}y + r_{33}z \end{aligned} \quad \text{or} \quad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

where $r_{11}, r_{12}, \dots, r_{33}$ are constants whose values depend on the nature of $\hat{R}$. One says that the symmetry operation $\hat{R}$ is **represented** by the matrix $\mathbf{R}$ whose elements are $r_{11}, r_{12}, \dots, r_{33}$. The set of functions x, y, z , whose transformations are described by $\mathbf{R}$, is said to be the **basis** for this representation.

For example, from (12.3) and (12.5), for the $\hat{C}_4(z)$ operation, we have $x' = -y, y' = x, z' = z$; for $\hat{i}$, we have $x' = -x, y' = -y, z' = -z$. The matrices representing $\hat{C}_4(z)$ and $\hat{i}$ in the x, y, z basis are

$$\mathbf{C}_4(z) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{i} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

If the product $\hat{R}\hat{S}$ of two symmetry operations is $\hat{T}$, then the matrices representing these operations in the x, y, z basis multiply in the same way; that is, if $\hat{R}\hat{S} = \hat{T}$, then $\mathbf{RS} = \mathbf{T}$. (For proof, see *Schonland*, pp. 56–57.)

12.2 Symmetry Point Groups

We now consider the possible combinations of symmetry elements. We cannot have arbitrary combinations of symmetry elements in a molecule. For example, suppose a molecule has one and only one C_3 axis. Any symmetry operation must send this axis into itself. The molecule cannot, therefore, have a plane of symmetry at an arbitrary angle to the C_3 axis; any plane of symmetry must either contain this axis or be perpendicular to it. (In BF_3 there are three σ_v planes and one σ_h plane.) The only possibility for a C_n axis noncoincident with the C_3 axis is a C_2 axis perpendicular to the C_3 axis. The corresponding $\hat{C}_2$ operation will send the C_3 axis into itself. Since $\hat{C}_3$ and $\hat{C}_3^2$ are symmetry operations, if we have one C_2 axis perpendicular to the C_3 axis, we must have a total of three such axes (as in BF_3).

The set of all the symmetry operations of a molecule forms a mathematical group. A **group** is a set of entities (called the **elements** or **members** of the group) and a rule for combining any two members of the group to form the product of these members, such that certain requirements are met. Let $A, B, C, D, \dots$ (assumed to be all different from one another) be the members of the group and let $B * C$ denote the product of B and C . The product $B * C$ need not be the same as $C * B$. The requirements that must be met to have a group are as follows: (1) The product of any two elements (including the product of an element with itself) must be a member of the group (the **closure** requirement). (2) There is a single element I of the group, called the **identity element**, such that $K * I = K$ and $I * K = K$ for every element K of the group. (3) Every element K of the group has an **inverse** (symbolized by K^{-1}) that is a member of the group and that satisfies $K * K^{-1} = I$ and $K^{-1} * K = I$, where I is the identity element. (4) Group multiplication is **associative**, meaning that $(B * D) * G = B * (D * G)$ always holds for elements of the group.

The number of elements in a group is called the **order** of the group. A group for which $B * C = C * B$ for every pair of group elements is **commutative** or **Abelian**.

An example of a group is the set of all integers (positive, negative, and zero) with the rule of combination being ordinary addition. Closure is satisfied since the sum of two integers is an integer. The identity element is 0. The inverse of the integer n is the integer $-n$. Addition is associative. This group is of infinite order and is Abelian.

The set of all symmetry operations of a three-dimensional body, with the rule of combination of $\hat{R}$ and $\hat{S}$ being successive performance of $\hat{R}$ and $\hat{S}$, forms a group. Closure is satisfied because the product of any two symmetry operations must be a symmetry operation. The identity element of the group is the identity operation $\hat{E}$, which does nothing. Associativity is satisfied [Eq. (3.6)]. The inverse of a symmetry operation $\hat{R}$ is the symmetry operation that undoes the effect of $\hat{R}$. For example, the inverse of the inversion operation $\hat{i}$ is $\hat{i}$ itself, since $\hat{i}\hat{i} = \hat{E}$. The inverse of a $\hat{C}_3$ 120° counterclockwise rotation is a 120° clockwise rotation, which is the same as a 240° counterclockwise rotation: $\hat{C}_3\hat{C}_3^2 = \hat{E}$ and $\hat{C}_3^{-1} = \hat{C}_3^2$. *Note that it is the symmetry operations of a molecule (and not the symmetry elements) that are the members (elements) of the group.* We will make some use of group theory in Section 15.2, but a full development of group theory and its applications is omitted (see *Cotton* or *Schonland*).

For any symmetry operation of a molecule, the point that is the center of mass remains fixed. Hence the symmetry groups of isolated molecules are called **point groups**. For a crystal of infinite extent, we can have symmetry operations (for example, translations) that leave no point fixed, giving rise to *space groups*. Consideration of space groups is omitted.

Every molecule belongs to one of the symmetry point groups that we now list. For convenience the point groups have been classified into four divisions. Script letters denote point groups.

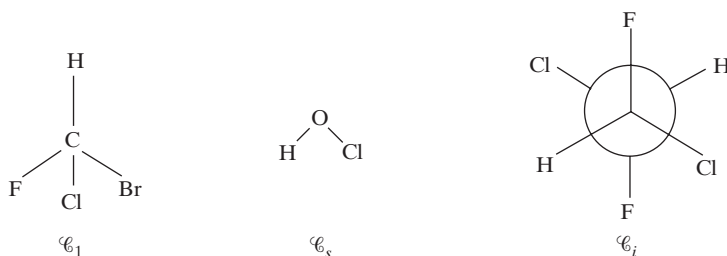
I. Groups with no C_n axis : $\mathcal{C}_1$, $\mathcal{C}_s$, $\mathcal{C}_i$

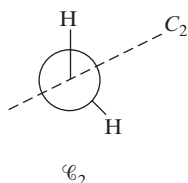
$\mathcal{C}_1$: If a molecule has no symmetry elements at all, it belongs to this group. The only symmetry operation is $\hat{E}$ (which is a $\hat{C}_1$ rotation). CHFCIBr belongs to point group $\mathcal{C}_1$.

$\mathcal{C}_s$: A molecule whose only symmetry element is a plane of symmetry belongs to this group. The symmetry operations are $\hat{E}$ and $\hat{\sigma}$. An example is HOCl (**Fig. 12.11**).

$\mathcal{C}_i$: A molecule whose only symmetry element is a center of symmetry belongs to this group. The symmetry operations are $\hat{i}$ and $\hat{E}$.

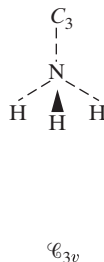
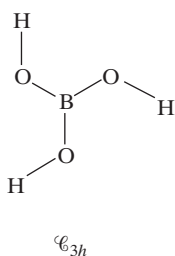
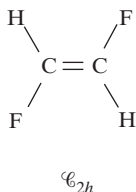
FIGURE 12.11 Molecules with no C_n axis.





H_2O_2 ; the O—O bond is perpendicular to the plane of the paper

FIGURE 12.12 Molecules with a single C_n axis.



II. Groups with a single C_n axis: $\mathcal{C}_n$, $\mathcal{C}_{nh}$, $\mathcal{C}_{nv}$, $\mathcal{I}_{2n}$

$\mathcal{C}_n$, $n = 2, 3, 4, \dots$: A molecule whose only symmetry element is a C_n axis belongs to this group. The symmetry operations are $\hat{C}_n, \hat{C}_n^2, \dots, \hat{C}_n^{n-1}, \hat{E}$. A molecule belonging to $\mathcal{C}_2$ is shown in Fig. 12.12.

$\mathcal{C}_{nh}$, $n = 2, 3, 4, \dots$: If we add a plane of symmetry perpendicular to the C_n axis, we have a molecule belonging to this group. Since $\hat{\sigma}_h \hat{C}_n = \hat{S}_n$, the C_n axis is also an S_n axis. If n is even, the C_n axis is also a C_2 axis, and the molecule has the symmetry operation $\hat{\sigma}_h \hat{C}_2 = \hat{S}_2 = \hat{i}$. Thus, for n even, a molecule belonging to $\mathcal{C}_{nh}$ has a center of symmetry. (The group $\mathcal{C}_{1h}$ is the group $\mathcal{C}_s$ discussed previously.) Examples of molecules belonging to groups $\mathcal{C}_{2h}$ and $\mathcal{C}_{3h}$ are shown in Fig. 12.12.

$\mathcal{C}_{nv}$, $n = 2, 3, 4, \dots$: A molecule in this group has a C_n axis and n vertical symmetry planes passing through the C_n axis. (Group $\mathcal{C}_{1v}$ is the group $\mathcal{C}_s$.) H_2O with a C_2 axis and two vertical symmetry planes belongs to $\mathcal{C}_{2v}$. NH_3 belongs to $\mathcal{C}_{3v}$. (See Fig. 12.12.)

$\mathcal{I}_n$, $n = 4, 6, 8, \dots$: $\mathcal{I}_n$ is the group of symmetry operations associated with an S_n axis. First consider the case of odd n . We have $\hat{S}_n = \hat{\sigma}_h \hat{C}_n$. The operation $\hat{C}_n$ affects the x and y coordinates only, while the $\hat{\sigma}_h$ operation affects the z coordinate only. Hence these operations commute, and we have

$$\hat{S}_n^n = (\hat{\sigma}_h \hat{C}_n)^n = \hat{\sigma}_h \hat{C}_n \hat{\sigma}_h \hat{C}_n \cdots \hat{\sigma}_h \hat{C}_n = \hat{\sigma}_h^n \hat{C}_n^n$$

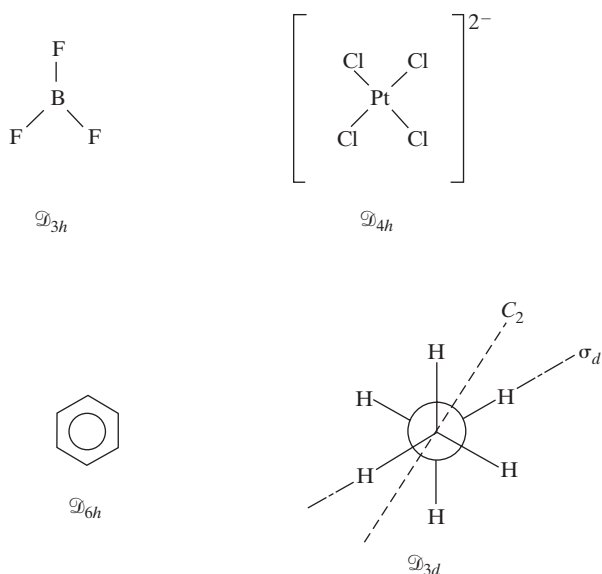
Now $\hat{C}_n^n = \hat{E}$, and, for odd n , $\hat{\sigma}_h^n = \hat{\sigma}_h$. Hence the symmetry operation $\hat{S}_n^n$ equals $\hat{\sigma}_h$ for odd n , and the group $\mathcal{I}_n$ has a horizontal symmetry plane if n is odd. Also,

$$\hat{S}_n^{n+1} = \hat{S}_n^n \hat{S}_n = \hat{\sigma}_h \hat{S}_n = \hat{\sigma}_h \hat{\sigma}_h \hat{C}_n = \hat{C}_n, \quad n \text{ odd}$$

so the molecule has a C_n axis if n is odd. We conclude that $\mathcal{I}_n$ is identical to the group $\mathcal{C}_{nh}$ if n is odd. Now consider even values of n . Since $\hat{S}_2 = \hat{i}$, the group $\mathcal{I}_2$ is identical to $\mathcal{C}_i$. Thus it is only for $n = 4, 6, 8, \dots$ that we get new groups. The S_{2n} axis is also a C_n axis: $\hat{S}_{2n}^2 = \hat{\sigma}_h^2 \hat{C}_{2n}^2 = \hat{E} \hat{C}_n = \hat{C}_n$.

III. Groups with one C_n axis and n C_2 axes: $\mathcal{D}_n$, $\mathcal{D}_{nh}$, $\mathcal{D}_{nd}$

$\mathcal{D}_n$, $n = 2, 3, 4, \dots$: A molecule with a C_n axis and n C_2 axes perpendicular to the C_n axis (and no symmetry planes) belongs to $\mathcal{D}_n$. The angle between adjacent C_2 axes is π/n radians. The group $\mathcal{D}_2$ has three mutually perpendicular C_2 axes, and the symmetry operations are $\hat{E}, \hat{C}_2(x), \hat{C}_2(y), \hat{C}_2(z)$.

FIGURE 12.13 Molecules with a C_n axis and n C_2 axes.

$\mathcal{D}_{nh}$, $n = 2, 3, 4, \dots$: This is the group of a molecule with a C_n axis, n C_2 axes, and a σ_h symmetry plane perpendicular to the C_n axis. As in $\mathcal{C}_{nh}$, the C_n axis is also an S_n axis. If n is even, the C_n axis is a C_2 and an S_2 axis, and the molecule has a center of symmetry. Molecules in $\mathcal{D}_{nh}$ also have n vertical planes of symmetry, each such plane passing through the C_n axis and a C_2 axis. (For the proof, see Prob. 12.29.) BF_3 belongs to $\mathcal{D}_{3h}$; PtCl_4^{2-} belongs to $\mathcal{D}_{4h}$; benzene belongs to $\mathcal{D}_{6h}$ (Fig. 12.13).

$\mathcal{D}_{nd}$, $n = 2, 3, 4, \dots$: A molecule with a C_n axis, n C_2 axes, and n vertical planes of symmetry, which pass through the C_n axis and bisect the angles between adjacent C_2 axes, belongs to this group. The n vertical planes are called **diagonal** planes and are symbolized by σ_d . The C_n axis can be shown to be an S_{2n} axis. The staggered conformation of ethane is an example of group $\mathcal{D}_{3d}$ (Fig. 12.13). [The symmetry of molecules with internal rotation (for example, ethane) actually requires special consideration; see H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).]

IV. Groups with more than one C_n axis, $n > 2$: $\mathcal{T}_d$, $\mathcal{T}$, $\mathcal{T}_h$, $\mathcal{O}_h$, $\mathcal{O}$, $\mathcal{I}_h$, $\mathcal{I}$, $\mathcal{H}_h$

These groups are related to the symmetries of the Platonic solids, solids bounded by congruent regular polygons and having congruent polyhedral angles. There are five such solids: The tetrahedron has four triangular faces, the cube has six square faces, the octahedron has eight triangular faces, the pentagonal dodecahedron has twelve pentagonal faces, and the icosahedron has twenty triangular faces.

$\mathcal{T}_d$: The symmetry operations of a regular tetrahedron constitute this group. The prime example is CH_4 . The symmetry elements of methane are four C_3 axes (each C—H bond), three S_4 axes, which are also C_2 axes (Fig. 12.5), and six symmetry planes, each such plane containing two C—H bonds. (The number of combinations of 4 things taken 2 at a time is $4!/2!2! = 6$.)

$\mathcal{O}_h$: The symmetry operations of a cube or a regular octahedron constitute this group. The cube and octahedron are said to be *dual* to each other; if we connect the mid-points of adjacent faces of a cube, we get an octahedron, and vice versa. Hence the

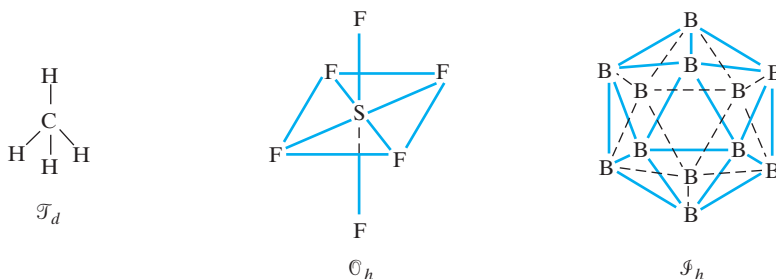


FIGURE 12.14 Molecules with more than one C_n axis, $n > 2$. (For $B_{12}H_{12}^{2-}$, the hydrogen atoms have been omitted for clarity.)

cube and octahedron have the same symmetry elements and operations. A cube has six faces, eight vertices, and twelve edges. Its symmetry elements are as follows: a center of symmetry, three C_4 axes passing through the centers of opposite faces of the cube (these are also S_4 and C_2 axes), four C_3 axes passing through opposite corners of the cube (these are also S_6 axes), six C_2 axes connecting the midpoints of pairs of opposite edges, three planes of symmetry parallel to pairs of opposite faces, and six planes of symmetry passing through pairs of opposite edges. Octahedral molecules such as SF_6 belong to $\mathcal{O}_h$.

$\mathcal{I}_h$: The symmetry operations of a regular pentagonal dodecahedron or icosahedron (which are dual to each other) constitute this group. The $B_{12}H_{12}^{2-}$ ion belongs to group $\mathcal{I}_h$. The twelve boron atoms lie at the vertices of a regular icosahedron (Fig. 12.14). The soccer-ball-shaped molecule C_{60} (buckminsterfullerene) belongs to $\mathcal{I}_h$. Its shape is a truncated icosahedron formed by slicing off each of the 12 vertices of a regular icosahedron (Fig. 12.14), thereby generating a figure with 12 pentagonal faces (5 faces meet at each vertex of the original icosahedron), 20 hexagonal faces (formed from the 20 triangular faces of the original icosahedron), and $12 \times 5 = 60$ vertices (5 new vertices are formed when one of the original vertices is sliced off).

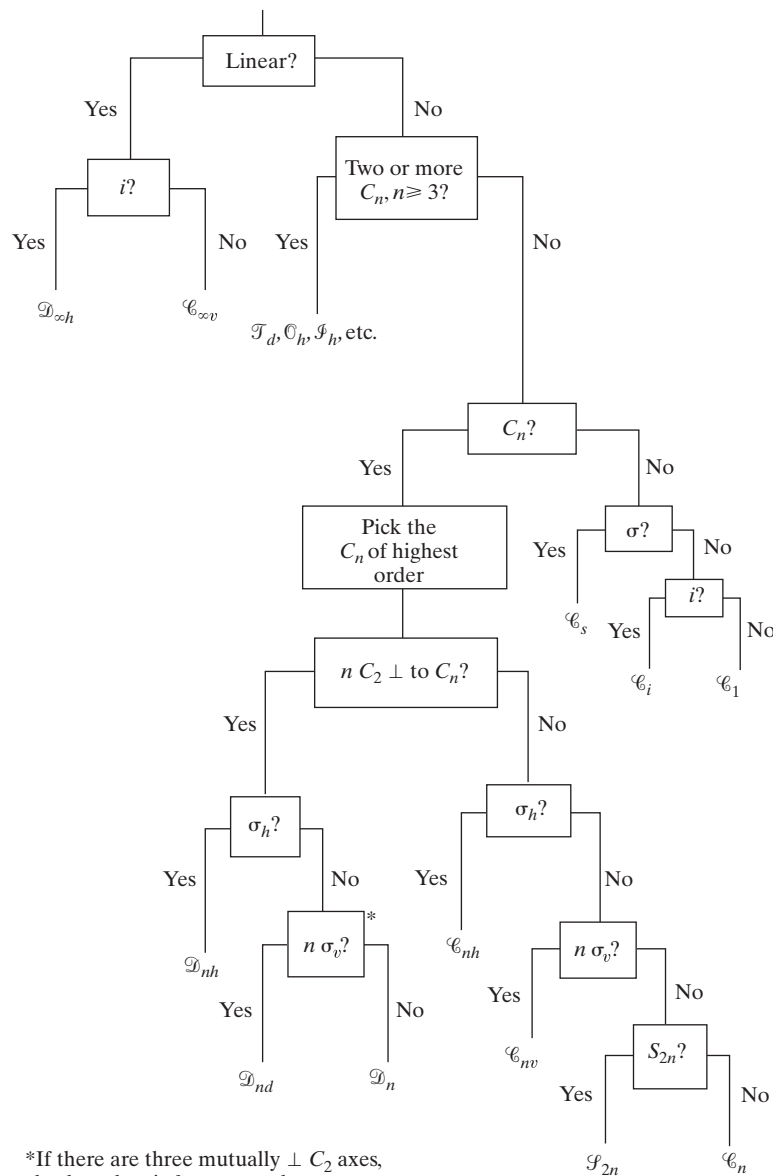
$\mathcal{K}_h$: This is the group of symmetry operations of a sphere. (*Kugel* is the German word for sphere.) An atom belongs to this group.

For completeness, we mention the remaining groups related to the Platonic solids; these groups are chemically unimportant. The groups $\mathcal{T}$, $\mathcal{O}$, and $\mathcal{I}$ are the groups of symmetry proper rotations of a tetrahedron, cube, and icosahedron, respectively. These groups do not have the symmetry reflections and improper rotations of these solids or the inversion operation of the cube and icosahedron. The group $\mathcal{T}_h$ contains the symmetry rotations of a tetrahedron, the inversion operation, and certain reflections and improper rotations.

What groups do linear molecules belong to? A rotation by any angle about the internuclear axis of a linear molecule is a symmetry operation. A regular polygon of n sides has a C_n axis, and taking the limit as $n \rightarrow \infty$ we get a circle, which has a C_∞ axis. The internuclear axis of a linear molecule is a C_∞ axis. Any plane containing this axis is a symmetry plane. If the linear molecule does not have a center of symmetry (for example, CO, HCN), it belongs to the group $\mathcal{C}_{\infty v}$. If the linear molecule has a center of symmetry (for example, H_2 , C_2H_2), then it also has a σ_h symmetry plane and an infinite number of C_2 axes perpendicular to the molecular axis. Hence it belongs to $\mathcal{D}_{\infty h}$.

How do we find what point group a molecule belongs to? One way is to find all the symmetry elements and then compare with the above list of groups. A more systematic procedure is given in Fig. 12.15 [J. B. Calvert, *Am. J. Phys.*, **31**, 659 (1963)]. This procedure is based on the four divisions of point groups.

FIGURE 12.15 How to determine the point group of a molecule.



We begin by checking whether or not the molecule is linear. Linear molecules are classified in $D_{\infty h}$ or $C_{\infty v}$ according to whether or not there is a center of symmetry. If the molecule is nonlinear, we look for two or more rotational axes of threefold or higher order. If these are present, the molecule is classified in one of the groups related to the symmetry of the regular polyhedra (division IV). If these axes are not present, we look for any C_n axis at all. If there is no C_n axis, the molecule belongs to one of the groups C_s , C_i , C_1 (division I). If there is at least one C_n axis, we pick the C_n axis of highest order as the main symmetry axis before proceeding to the next step. (If there are three mutually perpendicular C_2 axes, we may pick any one of these axes as the main axis.) We next check for n C_2 axes at right angles to the main C_n axis. If these are present, we have one of the division III groups. If these are absent, we have one of the division II groups. If we find the n C_2 axes,

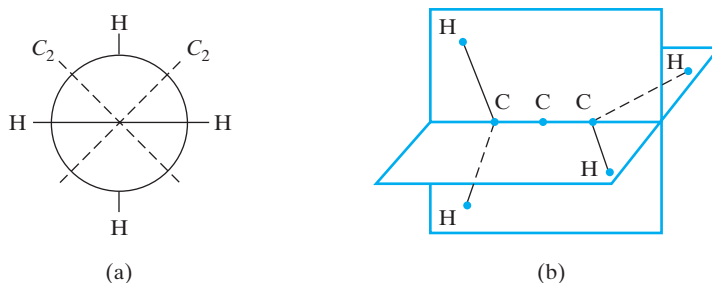


FIGURE 12.16 Two views of allene. The $\text{C}=\text{C}=\text{C}$ axis is perpendicular to the plane of the paper in (a).

we look for a symmetry plane perpendicular to the main C_n axis. If it is present, the group is $\mathcal{D}_{nh}$. If it is absent, we check for n planes of symmetry containing the main C_n axis (if the molecule has three mutually perpendicular C_2 axes, we must try each axis as the main axis in looking for the two σ_v planes; the three C_2 axes are equivalent in the groups $\mathcal{D}_{nh}$ and $\mathcal{D}_n$, but not in $\mathcal{D}_{nd}$). If we find n σ_v planes, the group is $\mathcal{D}_{nd}$; otherwise it is $\mathcal{D}_n$. If the molecule does not have n C_2 axes perpendicular to the main C_n axis, we classify it in one of the groups $\mathcal{C}_{nh}$, $\mathcal{C}_{nv}$, $\mathcal{I}_{2n}$, or $\mathcal{C}_n$, by looking first for a σ_h plane, then for n σ_v planes, and, finally, if these are absent, checking whether or not the C_n axis is an S_{2n} axis. The procedure of Fig. 12.15 does not locate all symmetry elements. After classifying a molecule, check that all the required symmetry elements are indeed present. Although the above procedure might seem involved, it is really quite simple and is easily memorized.

The most common error students make in classifying a molecule is to miss the n C_2 axes perpendicular to the C_n axis of a molecule belonging to $\mathcal{D}_{nd}$. For example, it is easy to see that the $\text{C}=\text{C}=\text{C}$ axis of allene is a C_2 axis, but the other two C_2 axes (Fig. 12.16) are often overlooked. Molecules with two equal halves “staggered” with respect to each other generally belong to $\mathcal{D}_{nd}$. Models may be helpful for those with visualization difficulties.

Summary

A symmetry operation transforms an object into a position that is physically indistinguishable from the original position and preserves the distances between all pairs of points in the object. A symmetry element is a geometrical entity with respect to which a symmetry operation is performed. For molecules, the four kinds of symmetry elements are an n -fold axis of symmetry (C_n), a plane of symmetry (σ), a center of symmetry (i), and an n -fold rotation–reflection axis of symmetry (S_n). The product of symmetry operations means successive performance of them. We have $\hat{C}_n^n = \hat{E}$, where $\hat{E}$ is the identity operation; also, $\hat{S}_1 = \hat{\sigma}$, and $\hat{S}_2 = \hat{i}$, where the inversion operation moves a point at x, y, z to $-x, -y, -z$. Two symmetry operations may or may not commute.

For the symmetry operation $\hat{R}$ that brings a point at x, y, z to x', y', z' , the operator $\hat{O}_R$ is defined by the equation $\hat{O}_R f(x', y', z') = f(x, y, z)$. If a molecule has the symmetry operations $\hat{R}_1, \hat{R}_2, \dots$, then the operators $\hat{O}_{R_1}, \hat{O}_{R_2}, \dots$, commute with the molecular Hamiltonian $\hat{H}$. If $\hat{R}_1, \hat{R}_2, \dots$ all commute with one another, then the molecular wave functions can be taken as eigenfunctions of $\hat{O}_{R_1}, \hat{O}_{R_2}, \dots$.

The set of all symmetry operations of a molecule constitutes a mathematical point group. The possible point groups of molecules are as follows. I. Groups with no C_n axis: $\mathcal{C}_1, \mathcal{C}_s, \mathcal{C}_i$. II. Groups with a single C_n axis: $\mathcal{C}_n, \mathcal{C}_{nh}, \mathcal{C}_{nv}, \mathcal{I}_{2n}$. III. Groups with one C_n axis and n C_2 axes: $\mathcal{D}_n, \mathcal{D}_{nh}, \mathcal{D}_{nd}$. IV. Groups with more than one C_n axis, $n > 2$: $\mathcal{T}_d, \mathcal{O}_h, \mathcal{I}_h$, and others.

Problems

Sec.	12.1	12.2	general
Probs.	12.1–12.15	12.16–12.34	12.35

- 12.1** True or false? (a) Symmetry operations always commute. (b) Symmetry operations never commute. (c) The product of two symmetry operations of a molecule must be a symmetry operation for that molecule.
- 12.2** Give all the symmetry elements of each of the following molecules: (a) H_2S ; (b) NH_3 ; (c) CHF_3 ; (d) HOCl ; (e) 1,3,5-trichlorobenzene; (f) CH_2F_2 ; (g) CHFCIBr .
- 12.3** List all the symmetry operations of each of the molecules in Prob. 12.2.
- 12.4** Consider the square-planar ion PtCl_4^{2-} . Suppose we interchange two Cl atoms that are cis to each other. Does this interchange meet the definition of a symmetry operation (Section 12.1)? If so, express it in terms of some combination of the four kinds of symmetry operations discussed.
- 12.5** What symmetry operation is each of the following products of operations equal to? (a) $\hat{\sigma}^4$; (b) $\hat{\sigma}^7$; (c) $\hat{C}_4^2$; (d) $\hat{C}_6^6$; (e) $\hat{S}_4^2$; (f) $\hat{S}_6^3$; (g) $\hat{C}_{12}^3$; (h) $\hat{i}^3$.
- 12.6** Use Fig. 12.7 to state what symmetry operation in SF_6 each of the following products of symmetry operations is equal to. (a) $\hat{C}_2(x)\hat{C}_4(z)$; (b) $\hat{C}_4(z)\hat{C}_2(x)$.
- 12.7** For SF_6 , which of the following pairs of operations commute? (a) $\hat{C}_4(z), \hat{\sigma}(xy)$; (b) $\hat{C}_4(z), \hat{\sigma}(yz)$; (c) $\hat{C}_2(z), \hat{C}_2(x)$; (d) $\hat{\sigma}(xy), \hat{\sigma}(yz)$; (e) $\hat{i}, \hat{\sigma}(xy)$.
- 12.8** What information does symmetry give about the dipole moment of each of the molecules in Prob. 12.2?
- 12.9** (a) Does H_2O_2 (Fig. 12.12) have an S_n axis? (b) Is it optically active? Explain.
- 12.10** For each of the following symmetry operations, find the matrix representative in the x, y, z basis. (a) $\hat{E}$; (b) $\hat{\sigma}(xy)$; (c) $\hat{\sigma}(yz)$; (d) $\hat{C}_2(x)$; (e) $\hat{S}_4(z)$; (f) $\hat{C}_3(z)$.
- 12.11** (a) Use SF_6 (Fig. 12.7) to verify that $\hat{C}_2(x)\hat{\sigma}(xy) = \hat{\sigma}(xz)$. (b) Write down the matrix representatives in the x, y, z basis of the three operations in part (a). Verify that these matrices multiply the same way the symmetry operations multiply.
- 12.12** (a) What are the eigenvalues of $\hat{O}_{C_4}$? (b) Is this operator Hermitian?
- 12.13** Do the same as in Prob. 12.12 for $\hat{O}_{C_2}$.
- 12.14** To what function is a $2p_z$ hydrogenlike orbital converted by (a) $\hat{O}_{C_4(z)}$; (b) $\hat{O}_{C_4(y)}$?
- 12.15** It is common to use rotation–inversion axes (rather than rotation–reflection axes) to classify the symmetry of crystals. Any S_n axis is equivalent to a rotation–inversion axis (symbolized by $\bar{p}$) whose order p may differ from n . A rotation–inversion operation consists of rotation by $2\pi/p$ radians followed by inversion. Show that

$$\hat{S}_n(z) = \hat{i}[\hat{C}_n(z)\hat{C}_2(z)]$$

Thus we have the following correspondence:

S_n	1	2	3	4
$\bar{p}$	$\bar{2}$	$\bar{1}$	$\bar{6}$	$\bar{4}$

Give the next three pairs of entries in this table.

- 12.16** State whether each of the following is a group. (a) All the real numbers with the rule of combination for forming the product of two elements being addition. (b) All positive integers with the rule of combination being multiplication. (c) All real numbers except zero, with the rule of combination being multiplication.
- 12.17** Does the set of all square matrices of order four form a group if the rule for forming the “product” of two elements is matrix addition?
- 12.18** Does the set of the n th roots of unity [Eq. (1.36)] with the rule of combination being ordinary multiplication form a group? Justify your answer.
- 12.19** Give the point group of each of the following molecules. (a) CH_4 ; (b) CH_3F ; (c) CH_2F_2 ; (d) CHF_3 ; (e) SF_6 ; (f) SF_5Br ; (g) *trans*- SF_4Br_2 ; (h) CDH_3 .

- 12.20 Give the point group of (a) $\text{CH}_2=\text{CH}_2$; (b) $\text{CH}_2=\text{CHF}$; (c) $\text{CH}_2=\text{CF}_2$; (d) *cis*- $\text{CHF}=\text{CHF}$; (e) *trans*- $\text{CHF}=\text{CHF}$.
- 12.21 Give the point group of (a) benzene; (b) fluorobenzene; (c) *o*-difluorobenzene; (d) *m*-difluorobenzene; (e) *p*-difluorobenzene; (f) 1,3,5-trifluorobenzene; (g) 1,4-difluoro-2,5-dibromobenzene; (h) naphthalene; (i) 2-chloronaphthalene.
- 12.22 Give the point group of (a) HCN ; (b) H_2S ; (c) CO_2 ; (d) CO ; (e) C_2H_2 ; (f) CH_3OH ; (g) ND_3 ; (h) OCS ; (i) P_4 ; (j) PCl_3 ; (k) PCl_5 ; (l) $\text{B}_{12}\text{Cl}_{12}^{2-}$; (m) UF_6 ; (n) Ar.
- 12.23 Give the point group of (a) FeF_6^{3-} ; (b) IF_5 ; (c) $\text{CH}_2=\text{C}=\text{CH}_2$; (d) C_8H_8 , cubane; (e) $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$; (f) B_2H_6 ; (g) XeF_4 ; (h) F_2O ; (i) spiropentane.
- 12.24 Give the order of each of the following groups: (a) $\mathcal{C}_{3v}$; (b) $\mathcal{C}_s$; (c) $\mathcal{C}_{\infty v}$; (d) $\mathcal{D}_{3h}$.
- 12.25 The product of two members of a group must be a member of that group. (a) List the members (the symmetry operations) of the group $\mathcal{C}_{2v}$, using the x , y , and z axes to specify the axis or plane with respect to which each symmetry operation is performed. (b) For every possible product of two members of this group, state which symmetry operation it is equal to. Note that symmetry operations do not necessarily commute. (c) The **multiplication table** of a group shows all possible products of two members of the group. Write down the multiplication table for $\mathcal{C}_{2v}$ with each member of the group shown at the top and at the left of the table, and each entry in the table being the product of the member at the left of the row and the member at the top of the column of that entry.
- 12.26 State whether each of these groups is Abelian. (a) $\mathcal{C}_3$; (b) $\mathcal{C}_{3v}$.
- 12.27 The structure of ferrocene, $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_5$, is an iron atom sandwiched midway between two parallel regular pentagons. For the eclipsed conformation, the vertices of the two pentagons are aligned; for the staggered conformation, one pentagon is rotated $2\pi/10$ radians with respect to the other. Electron diffraction results show that the gas-phase equilibrium conformation is the eclipsed one, with a quite low barrier to internal rotation of the rings. [See S. Coriani et al., *ChemPhysChem*, **7**, 245 (2006).] What is the point group of (a) eclipsed ferrocene; (b) staggered ferrocene?
- 12.28 What is the point group of the tris(ethylenediamine)cobalt(III) complex ion? (Each $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ group occupies two adjacent positions of the octahedral coordination sphere.)
- 12.29 Consider a $\mathcal{D}_{nh}$ molecule with the z axis coinciding with the C_n axis and the x axis coinciding with one of the C_2 axes. Show that the product $\sigma(xy)\hat{C}_2(x)$ moves a point originally at (x, y, z) to $(x, -y, z)$. Therefore, $\hat{\sigma}(xy)\hat{C}_2(x) = \hat{\sigma}(xz)$. Since $\hat{C}_2(x)$ and $\hat{\sigma}(xy)$ are symmetry operations, their product must be a symmetry operation. Hence the xz plane is a symmetry plane. The same argument holds for any C_2 axis, so the molecule has n σ_v planes.
- 12.30 Give the point group of (a) a square-based pyramid; (b) a right circular cone; (c) a square lamina; (d) a square lamina with the top and bottom sides painted different colors; (e) a right circular cylinder; (f) a right circular cylinder with the two ends painted different colors; (g) a right circular cylinder with a stripe painted parallel to the axis; (h) a snowflake; (i) a doughnut; (j) a baseball (Fig. 12.17); (k) a $2p_z$ orbital; (l) a human being (ignore internal organs and slight external left–right asymmetries).
- 12.31 (a) What Platonic solid is dual to the regular tetrahedron? (b) How many vertices does a pentagonal dodecahedron have?
- 12.32 (a) For what values of n does the presence of an S_n axis imply the presence of a plane of symmetry? (b) For what values of n does the presence of an S_n axis imply the presence of a center of symmetry? (c) The group $\mathcal{D}_{nd}$ has an S_{2n} axis. For what values of n does it have a center of symmetry?
- 12.33 For which point groups can a molecule have a dipole moment?
- 12.34 For which point groups can a molecule be optically active?
- 12.35 Two people play the following game. Each in turn places a penny on the surface of a large chessboard. The pennies can be put anywhere on the board, as long as they do not overlap previously placed pennies. A penny may overlap more than one square. Once placed, a penny cannot be moved. When one of the players finds there is no room to place another penny on the board, she loses. With best play, will the person placing the first penny or her opponent win? Give the winning strategy.

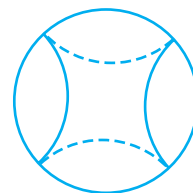


FIGURE 12.17 A baseball. The dashed and solid parts of the seam are in different hemispheres.