CHEMICAL APPLICATIONS OF GROUP THEORY

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2

DEFINITIONS AND THEOREMS OF GROUP THEORY

2.1 THE DEFINING PROPERTIES OF A GROUP

A *group* is a collection of *elements* that are interrelated according to certain rules. We need not specify what the elements are or attribute any physical significance to them in order to discuss the group which they constitute. In this book, of course, we shall be concerned with the groups formed by the sets of symmetry operations that may be carried out on molecules or crystals, but the basic definitions and theorems of group theory are far more general.

In order for any set of elements to form a mathematical group, the following conditions or rules must be satisfied.

1. *The product of any two elements in the group and the square of each element must be an element in the group.* In order for this condition to have meaning, we must, of course, have agreed on what we mean by the terms "multiply" and "product." They need not mean what they do in ordinary algebra and arithmetic. Perhaps we might say "combine" instead of "multiply" and "combination" instead of "product" in order to avoid unnecessary and perhaps incorrect connotations. Let us not yet commit ourselves to any particular law of combination but merely say that, if A and B are two elements of a group, we indicate that we are combining them by simply writing AB or BA. Now immediately the question arises if it makes any difference whether we write AB or BA. In ordinary algebra it does not, and we say that multiplication is commutative, that is $xy = yx$, or $3 \times 6 = 6 \times 3$. In group theory, the commutative law does not in general hold. Thus AB may give C while BA may give D, where C and D are two more elements in the group.

There are some groups, however, in which combination is commutative, and such groups are called *Abelian* groups. Because of the fact that multiplication is not in general commutative, it is sometimes convenient to have a means of stating whether an element B is to be multiplied by A in the sense AB or BA. In the first case we can say that B is *left-multiplied* by A, and in the second case that B is *right-multiplied* by A.

2. *One element in the group must commute with all others and leave them unchanged.* It is customary to designate this element with the letter E, and it is usually called the *identity element.* Symbolically we define it by writing $EX = XE = X$.

3. *The associative law of multiplication must hold.* This is expressed in the following equality:

$$A(BC) = (AB)C$$

In plain words, we may combine B with C in the order BC and then combine this product, S, with A in the order AS, or we may combine A with B in the order AB, obtaining a product, say R, which we then combine with C in the order RC and get the same final product either way. In general, of course, the associative property must hold for the continued product of any number of elements, namely,

$$(AB)(CD)(EF)(GH) = A(BC)(DE)(FG)H = (AB)C(DE)(FG)H \cdots$$

4. *Every element must have a reciprocal, which is also an element of the group.* The element R is the reciprocal of the element S if $RS = SR = E$, where E is the identity. Obviously, if R is the reciprocal of S, then S is the reciprocal of R. Also, E is its own reciprocal.

At this point we shall prove a small theorem concerning reciprocals which will be of use later. The rule is

The reciprocal of a product of two or more elements is equal to the product of the reciprocals, in reverse order.

This means that

$$(ABC \cdots XY)^{-1} = Y^{-1}X^{-1} \cdots C^{-1}B^{-1}A^{-1}$$

PROOF. For simplicity we shall prove this for a ternary product, but it will be obvious that it is true generally. If A, B, and C are group elements, their product, say D, must also be a group element, namely,

$$ABC = D$$

If now we right-multiply each side of this equation by $C^{-1}B^{-1}A^{-1}$, we obtain

$$\begin{aligned} ABCC^{-1}B^{-1}A^{-1} &= DC^{-1}B^{-1}A^{-1} \\ ABEB^{-1}A^{-1} &= DC^{-1}B^{-1}A^{-1} \\ &\vdots \\ E &= DC^{-1}B^{-1}A^{-1} \end{aligned}$$

Since D times $C^{-1}B^{-1}A^{-1} = E$, $C^{-1}B^{-1}A^{-1}$ is the reciprocal of D, and since $D = ABC$, we have

$$D^{-1} = (ABC)^{-1} = C^{-1}B^{-1}A^{-1}$$

which proves the above rule.

2.2 SOME EXAMPLES OF GROUPS

Most of our attention in this book, until we reach Chapter 11, will be concentrated on a type of symmetry group called a point group. The significance of these terms, "symmetry group" and "point group." need not detain us here (see Chapter 3). Most of them contain a finite number of elements, but two (to which linear molecules belong) are infinite. The number of elements in a finite group is called its *order*, and the conventional symbol for the order is h. To illustrate the above defining rules, we may consider an infinite group and then some finite groups.

As an infinite group we may take all of the integers, both positive and negative, and zero. If we take as our law of combination the ordinary algebraic process of addition, then rule 1 is satisfied. Clearly, any integer may be obtained by adding two others. Note that we have an Abelian group since the order of addition is immaterial. The identity of the group is 0, since $0 + n = n + 0 = n$. Also, the associative law of combination holds, since, for example, $[(+3) + (-7)] + (+1043) = (+3) + [(-7) + (+1043)]$. The reciprocal of any element, n, is $(-n)$, since $(+n) + (-n) = 0$.

Group Multiplication Tables

If we have a complete and nonredundant list of the h elements of a finite group and we know what all of the possible products (there are h^2) are, then the group is completely and uniquely defined—at least in an abstract sense. The foregoing information can be presented most conveniently in the form of the group multiplication table. This consists of h rows and h columns. Each column is labeled with a group element, and so is each row. The entry in the table under a given column and along a given row is the product of the elements which head that column and that row. Because multiplication is in general not commutative, we must have an agreed upon and consistent rule for the order of multiplication. Arbitrarily, we shall take the factors in the order: (column element) × (row element). Thus at the intersection of the column labeled by X and the row labeled by Y we find the element, which is the product XY.

We now prove an important theorem about group multiplication tables, called the *rearrangement theorem.*

Each row and each column in the group multiplication table lists each of the group elements once and only once. From this, it follows that no two rows may be identical nor may any two columns be identical. Thus each row and each column is a rearranged list of the group elements.

PROOF. Let the group consist of the h elements $E, A_2, A_3, \ldots, A_h$. The elements in a given row, say the nth row, are

$$EA_n, A_2A_n, \ldots, A_nA_n, \ldots, A_hA_n$$

Since no two group elements, A_i and A_j for instance, are the same, no two products, A_iA_n and A_jA_n, can be the same. The h entries in the nth row are all different. Since there are only h group elements, each of them must be present once and only once. The argument can obviously be adapted to the columns.

Groups of Orders 1, 2, and 3

Let us now systematically examine the possible abstract groups of low order, using their multiplication tables to define them. There is, of course, formally a group of order 1, which consists of the identity element alone. There is only one possible group of order 2. It has the following multiplication table and will be designated G_2.

G_2	E	A
E	E	A
A	A	E

For a group of order 3, the multiplication table will have to be, in part, as follows:

	E	A	B
E	E	A	B
A	A		
B	B		

There is then only one way to complete the table. Either $AA = B$ or $AA = E$. If $AA = E$, then $BB = E$ and we would augment the table to give

	E	A	B
E	E	A	B
A	A	E	
B	B		E

But then we can get no further, since we would have to accept $BA = A$ and $AB = A$ in order to complete the last column and the last row, respectively, thus repeating A in both the second column and the second row. The alternative, $AA = B$, leads unambiguously to the following table:

G_3	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

Cyclic Groups

G_3 is the simplest, nontrivial member of an important set of groups, the *cyclic* groups. We note that $AA = B$, while $AB\,(=AAA) = E$. Thus we can consider the entire group to be generated by taking the element A and its powers, $A^2(=B)$ and $A^3(=E)$. In general, the cyclic group of order h is defined as an element X and all of its h powers up to $X^h = E$. We shall presently examine several other cyclic groups. An important property of cyclic groups is that they are *Abelian*, that is, all multiplications are commutative. This must be so, since the various group elements are all of the form X^n, X^m, and so on, and, clearly, $X^nX^m = X^mX^n$ for all m and n.

Groups of Order 4

To continue, we ask how many groups of order 4 there are and what their multiplication table(s) will be. Obviously, there will be a cyclic group of order 4. Let us employ the relations.

$$X = A \qquad X^3 = C$$
$$X^2 = B \qquad X^4 = E$$

From this we find that the multiplication table, in the usual format, is as follows:

$G_4^{(1)}$	E	A	B	C
E	E	A	B	C
A	A	B	C	E
B	B	C	E	A
C	C	E	A	B

That there is a second type of G_4 group, $G_4^{(2)}$, is fairly obvious. We note that for $G_4^{(1)}$ only one element, namely B, is its own inverse. Suppose, instead, we assume that each of two elements, A and B, is its own inverse. We shall then have no choice but to also make C its own inverse, since each of the four E's in the table must lie in a different row and column. Thus, we would obtain

	E	A	B	C
E	E	A	B	C
A	A	E		
B	B		E	
C	C			E

A moment's consideration will show that there is only one way to complete this table:

$G_4^{(2)}$	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	E	A
C	C	B	A	E

It is also clear that there are no other possibilities.* Thus, there are two groups of order 4, namely $G_4^{(1)}$ and $G_4^{(2)}$, which may be considered to be defined by their multiplication tables.

Groups of Orders 5 and 6

It is left as an exercise (Exercise 2.2) to show that there is only one group of order 5. Similarly, a systematic examination of the possibilities for groups of

* If we make up a table in which only one element (other than E) is its own inverse and let that element be A or C instead of B as in the $G_4^{(1)}$ table given, we are *not* inventing a different G_4. We are only permuting the arbitrary symbols for the group elements.

order 6 is also left as an exercise (Exercise 2.9). To provide illustrative material for several topics that we shall take up next, the multiplication table for one of the groups of order 6 is given.

$G_6^{(2)}$	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

2.3 SUBGROUPS

Inspection of the multiplication table for the group $G_6^{(2)}$ will show that within this group of order 6 there are smaller groups. The identity E in itself is a group of order 1. This will, of course, be true in any group and is trivial. Of a nontrivial nature are the groups of order 2, namely, E, A; E, B; E, C; and the group of order 3, namely, E, D, F. The last should be recognized also as the cyclic group G_3, since $D^2 = F$, $D^3 = DF = FD = E$. But to return to the main point, smaller groups that may be found within a larger group are called subgroups. There are, of course, groups that have no subgroups other than the trivial one of E itself.

Let us now consider whether there are any restrictions on the nature of subgroups, restrictions that are logical consequences of the general definition of a group and not of any additional or special characteristics of a particular group. We may note that the orders of the group $C_6^{(2)}$ and its subgroups are 6 and 1, 2, 3; in short, the orders of the subgroups are all factors of the order of the main group. We shall now prove the following theorem:

The order of any subgroup g of a group of order h must be a divisor of h.

In other words, $h/g = k$ where k is an integer.

PROOF. Suppose that the set of g elements, $A_1, A_2, A_3, \ldots, A_g$, forms a subgroup. Now let us take another element B in the group which is not a member of this subgroup and form all of the g products: $BA_1, BA_2, \ldots, BA_g$. No one of these products can be in the subgroup. If, for example,

$$BA_2 = A_4$$

then, if we take the reciprocal of A_2, perhaps A_5, and right-multiply the above equality, we obtain

$$BA_2A_5 = A_4A_5$$

$$BE = A_4A_5$$

$$B = A_4A_5$$

But this contradicts our assumption that B is not a member of the subgroup $A_1, A_2, \ldots, A_g$, since A_4A_5 can only be one of the A_i. Hence, if all the products BA_i are in the large group in addition to the A_i themselves, there are at least $2g$ members of the group. If $h > 2g$, we can choose still another element of the group, namely C, which is neither one of the A_i nor one of the BA_i, and on multiplying the A_i by C we will obtain g more elements, all members of the main group, but none members of the A_i or of the BA_i sets. Thus we now know that h must be at least equal to $3g$. Eventually, however, we must reach the point where there are no more elements by which we can multiply the A_i that are not among the sets A_i, BA_i, CA_i, and so forth, already obtained. Suppose after having found k such elements, we reach the point where there are no more. Then $h = kg$, where k is an integer, and $h/g = k$, which is what we set out to prove.

Although we have shown that the order of any subgroup, g, must be a divisor of h, we have not proved the converse, namely, that there are subgroups of all orders that are divisors of h, and, indeed, this is not in general true. Moreover, as our illustrative group proves, there can be more than one subgroup of a given order.

2.4 CLASSES

We have seen that in a given group it may be possible to select various smaller sets of elements, each such set including E, however, which are in themselves groups. There is another way in which the elements of a group may be separated into smaller sets, and such sets are called *classes*. Before defining a class we must consider an operation known as *similarity transformation*.

If A and X are two elements of a group, then $X^{-1}AX$ will be equal to some element of the group, say B. We have

$$B = X^{-1}AX$$

We express this relation in words by saying that B is the *similarity transform* of A by X. We also say that A and B are *conjugate*. The following properties of conjugate elements are important.

(i) *Every element is conjugate with itself.* This means that if we choose any particular element A it must be possible to find at least one element X such that

$$A = X^{-1}AX$$

If we left-multiply by A^{-1} we obtain

$$A^{-1}A = E = A^{-1}X^{-1}AX = (XA)^{-1}(AX)$$

which can hold only if A and X commute. Thus the element X may always be E, and it may be any other element that commutes with the chosen element, A.

(ii) If *A is conjugate with B, then B is conjugate with A.* This means that if

$$A = X^{-1}BX$$

then there must be some element Y in the group such that

$$B = Y^{-1}AY$$

That this must be so is easily proved by carrying out appropriate multiplications, namely,

$$XAX^{-1} = XX^{-1}BXX^{-1} = B$$

Thus, if $Y = X^{-1}$ (and thus also $Y^{-1} = X$), we have

$$B = Y^{-1}AY$$

and this must be possible, since any element, say X, must have an inverse, say Y.

(iii) *If A is conjugate with B and C, then B and C are conjugate with each other.* The proof of this should be easy to work out from the foregoing discussion and is left as an exercise.

We may now define a class of elements.

A complete set of elements that are conjugate to one another is called a class of the group.

In order to determine the classes within any particular group we can begin with one element and work out all of its transforms, using all the elements in the group, including itself, then take a second element, which is not one of those found to be conjugate to the first, and determine all its transforms, and so on until all elements in the group have been placed in one class or another.

Let us illustrate this procedure with the group $G_6^{(2)}$. All of the results given below may be verified by using the multiplication table. Let us start with E.

$$E^{-1}EE = EEE = E$$
$$A^{-1}EA = A^{-1}AE = E$$
$$B^{-1}EB = B^{-1}BE = E$$
$$\vdots$$

Thus E must constitute by itself a class, of order 1, since it is not conjugate with any other element. This will, of course, be true in any group. To continue,

$$E^{-1}AE = A$$
$$A^{-1}AA = A$$
$$B^{-1}AB = C$$
$$C^{-1}AC = B$$
$$D^{-1}AD = B$$
$$F^{-1}AF = C$$

Thus the elements A, B, and C are all conjugate and are therefore members of the same class. It is left for the reader to show that all of the transforms of B and C are either A, B, or C. Thus A, B, and C are in fact the only members of the class.

Continuing we have

$$E^{-1}DE = D$$
$$A^{-1}DA = F$$
$$B^{-1}DB = F$$
$$C^{-1}DC = F$$
$$D^{-1}DD = D$$
$$F^{-1}DF = D$$

It will also be found that every transform of F is either D or F. Hence, D and F constitute a class of order 2.

It will be noted that the classes have orders 1, 2, and 3, which are all factors of the group order, 6. It can be proved, by a method similar to that used in connection with the orders of subgroups, that the following theorem is true:

The orders of all classes must be integral factors of the order of the group.

We shall see later (Section 3.13) that in a symmetry group the classes have useful geometrical significance.

EXERCISES

2.1. Prove that in any Abelian group, each element is in a class by itself.

2.2. Show that there can be only one group of order h, when h is a prime number.

2.3. Write down the multiplication table for the cyclic group of order 5. Show by trial and error that no other one is possible.

2.4. Why can we not have a group in which $A^2 = B^2 \neq E$?

2.5. If we start with the multiplication table for group G_3 and add another element, C, which commutes with both A and B, what multiplication table do we end up with?

2.6. Show that for any cyclic group, $X, X^2, X^3, \ldots, X^h (\equiv E)$, there must be one subgroup corresponding to each integral divisor of the order h. Give an example.

2.7. Invent as many different noncyclic groups of order 8 as you can and give the multiplication table for each.

2.8. For each of the groups of order 8, show how it breaks down into subgroups and classes.

2.9. Derive the multiplication table for all other groups of order 6 besides the one shown in the text. This will require you to show that a group of order 6 in which every element is its own inverse is impossible.

2.10. For the groups $G_4^{(1)}$, $G_4^{(2)}$ and the cyclic group of order 6, show what classes and subgroups each one has.

3

MOLECULAR SYMMETRY AND THE SYMMETRY GROUPS

3.1 GENERAL REMARKS

It is perhaps appropriate to begin this chapter by sketching what we intend to do here. It is certainly intuitively obvious what we mean when we say that some molecules are more symmetrical than others, or that some molecules have high symmetry whereas others have low symmetry or no symmetry. But in order to make the idea of molecular symmetry as useful as possible, we must develop some rigid mathematical criteria of symmetry. To do this we shall first consider the kinds of *symmetry elements* that a molecule may have and the *symmetry operations* generated by the symmetry elements. We shall then show that a complete but nonredundant set of symmetry *operations* (not elements) constitutes a mathematical group. Finally, we shall use the general properties of groups, developed in Chapter 2, to aid in correctly and systematically determining the symmetry operations of any molecule we may care to consider. We shall also describe here the system of notation normally used by chemists for the various symmetry groups. An alternative system used primarily in crystallography is explained in Chapter 11.

It may also be worthwhile to offer the following advice to the student of this chapter. The use of three-dimensional models is extremely helpful in learning to recognize and visualize symmetry elements. Indeed, it is most unlikely that any but a person of the most exceptional gifts in this direction can fail to profit significantly from the examination of models. At the same time, it may also be said that anyone with the intelligence to master other aspects of modern chemical knowledge should, by the use of models, surely succeed in acquiring a good working knowledge of molecular symmetry.

3.2 SYMMETRY ELEMENTS AND OPERATIONS

The two things, symmetry elements and symmetry operations, are inextricably related and therefore are easily confused by the beginner. They are, however, different *kinds* of things, and it is important to grasp and retain, from the outset, a clear understanding of the difference between them.

Definition of a Symmetry Operation

A symmetry operation is a movement of a body such that, after the movement has been carried out, every point of the body is coincident with an equivalent point (or perhaps the same point) of the body in its original orientation. In other words, if we note the position and orientation of a body before and after a movement is carried out, that movement is a symmetry operation if these two positions and orientations are indistinguishable. This would mean that, if we were to look at the body, turn away long enough for someone to carry out a symmetry operation, and then look again, we would be completely unable to tell whether or not the operation had actually been performed, because in either case the position and orientation would be indistinguishable from the original. One final way in which we can define a symmetry operation is to say that its effect is to take the body into an *equivalent configuration*—that is, one which is indistinguishable from the original, though not necessarily identical with it.

Definition of a Symmetry Element

A symmetry element is a geometrical entity such as a line, a plane, or a point, with respect to which one or more symmetry operations may be carried out.

Symmetry elements and symmetry operations are so closely interrelated because the operation can be defined only with respect to the element, and at the same time the existence of a symmetry element can be demonstrated only by showing that the appropriate symmetry operations exist. Thus, since the existence of the element is contingent on the existence of the operation(s) and vice versa, we shall discuss related types of elements and operations together.

In treating molecular symmetry, only four types of symmetry elements and operations need be considered. These, in the order in which they will be discussed, are listed in Table 3.1.

3.3 SYMMETRY PLANES AND REFLECTIONS

A symmetry plane must pass through a body, that is, the plane cannot be completely outside of the body. The conditions which must be fulfilled in order that a given plane be a symmetry plane can be stated as follows. Let

TABLE 3.1 The Four Kinds of Symmetry Elements and Operations Required in Specifying Molecular Symmetry

Symmetry Element	Symmetry Operation(s)
1. Plane	Reflection in the plane
2. Center of symmetry or center of inversion	Inversion of all atoms through the center
3. Proper axis	One or more rotations about the axis
4. Improper axis	One or more repetitions of the sequence: rotation followed by reflection in a plane ⊥ to the rotation axis

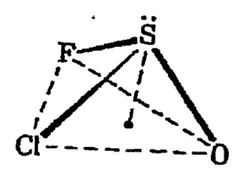
us apply a Cartesian coordinate system to the molecule in such a way that the plane includes two of the axes (say x and y) and is therefore perpendicular to the third (i.e., z). The position of every atom in the molecule may also be specified in this same coordinate system. Suppose now, for each and every atom, we leave the x and y coordinates fixed and change the sign of the z coordinate: thus the ith atom, originally at (x_i, y_i, z_i), is moved to the point $(x_i, y_i, -z_i)$. Another way of expressing the above operation is to say, "Let us drop a perpendicular from each atom to the plane, extend that line an equal distance on the opposite side of the plane, and move the atom to this other end of the line." If, when such an operation is carried out on every atom in a molecule, an equivalent configuration is obtained, the plane used is a symmetry plane.

Clearly, atoms lying in the plane constitute special cases, since the operation of reflecting through the plane does not move them at all. Consequently, any planar molecule is bound to have at least one plane of symmetry, namely, its molecular plane. Another significant and immediate consequence of the definition is a restriction on the numbers of various kinds of atoms in a molecule having a plane of symmetry. All atoms of a given species that do not lie in the plane must occur in even numbers, since each one must have a twin on the other side of the plane. Of course, any number of atoms of a given species may be in the plane. Furthermore, if there is only one atom of a given species in a molecule, it must be in each and every symmetry plane that the molecule may have. This means that it must be on the line of intersection between two or more planes or at the point of intersection of three or more planes (if there is such a point), since this atom must lie in all of the symmetry planes simultaneously.

The standard symbol for a plane of symmetry is σ. The same symbol is also used for the operation of reflecting through the plane.

It should be explicitly noted that the existence of *one* symmetry plane gives rise to, requires, or, as usually stated, *generates one* symmetry operation. We may also note here, for future use, that the effect of applying the same reflection operation twice is to bring all atoms back to their original positions. Thus, while the operation σ produces a configuration *equivalent* to the original, the application of the same σ twice produces a configuration *identical* with the original. Now we can conveniently denote the successive application of the operation σ n times by writing σ^n. We can then also write, $\sigma^2 = E$, where we use the symbol E to represent *any* combination of operations which takes the molecule to a configuration identical with the original one. We call E, or any combination of operations equal to E, the *identity operation*. It should be obvious that $\sigma^n = E$ when n is even and $\sigma^n = \sigma$ when n is odd.

Let us now consider some illustrative examples of symmetry planes in molecules. At one extreme are molecules that have no symmetry planes at all. One such general class consists of those which are not planar and which have odd numbers of all atoms. An example is FClSO, seen below.



At the other extreme are molecules possessing an infinite number of symmetry planes, that is, linear molecules. For these any plane containing the molecular axis is a symmetry plane, and there is obviously an infinite number of these planes. Most small molecules fall between these extremes; that is, they have one or a few symmetry planes. If, instead of FClSO, we take F_2SO or Cl_2SO, we have a molecule with one symmetry plane, which passes through S and O and is perpendicular to the Cl, Cl, O or the F, F, O plane. The H_2O molecule has two symmetry planes. One is, of course, coextensive with the molecular plane. The other includes the oxygen atom (it must, since there is only one such atom) and is perpendicular to the molecular plane. The effect of reflection through this second plane is to leave the oxygen atom fixed but to exchange the hydrogen atoms, while reflection through the first plane leaves all atoms unshifted. A tetrahedral molecule of the type AB_2C_2 (e.g., CH_2Cl_2) also has two mutually perpendicular planes of symmetry. One contains AB_2, and reflection through it leaves these three atoms unshifted while interchanging the C atoms; the other contains AC_2, and reflection through it interchanges only the B atoms.

The molecules NH_3 and $CHCl_3$ are representative of a type containing three planes of symmetry. For NH_3, any plane of symmetry would have to include the nitrogen atom and either one or all three of the hydrogen atoms. Since NH_3 is not planar, there can be no symmetry plane including N and all three H atoms; hence we look for planes including N and one H and bisecting the line between the remaining two H atoms. There are clearly three such planes. For $CHCl_3$, the situation is quite analogous except that the hydrogen atom must also lie in the symmetry planes.

The NH_3 molecule is only one example of the general class of pyramidal AB_3 molecules. Let us see what happens as we begin flattening such a molecule by pushing the A atom down toward the plane of the three B atoms. It should be easily seen that this does not disturb the three symmetry planes, even in the limit of coplanarity. Nor does it introduce any new planes of symmetry *except* in the limit of coplanarity. Once AB_3 becomes planar there is then a fourth symmetry plane, which is the molecular plane. Molecules and ions of the planar AB_3 type possessing four symmetry planes, three perpendicular to the molecular plane, are fairly numerous and important. There are, for example, the boron halides, CO_3^{2-}, NO_3^-, and SO_3.

A planar species of the type $[PtCl_4]^{2-}$ or $[AuCl_4]^-$ possesses five symmetry planes. One is the molecular plane. There are also two, perpendicular to the molecular plane and perpendicular to each other, which pass through three atoms. Finally, there are two more, also perpendicular to the molecular plane and perpendicular to each other, which bisect Cl—Pt—Cl or Cl—Au—Cl angles.

A regular tetrahedral molecule possesses six planes of symmetry. Using the numbering system illustrated in Figure 3.1, we may specify these symmetry planes by stating the atoms they contain:

$$AB_1B_2,\ AB_1B_3,\ AB_1B_4,\ AB_2B_3,\ AB_2B_4,\ AB_3B_4$$

A regular octahedron possesses, in all, nine symmetry planes. Reference will be made to the numbered figure on page 22 in specifying these. There are first three of the same type, namely, those including the following sets of atoms: $AB_1B_2B_3B_4$, $AB_2B_4B_5B_6$, and $AB_1B_3B_5B_6$. There are then six more of a second type, one of which includes AB_5B_6 and bisects the B_1—B_2 and

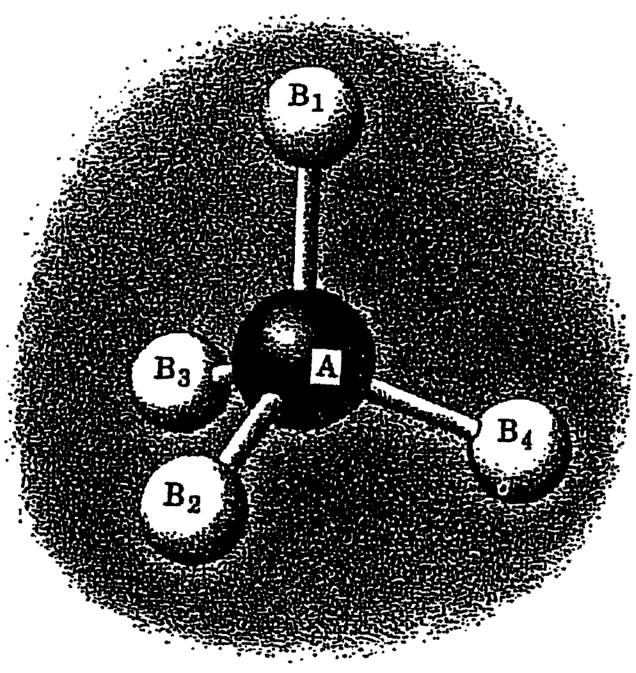
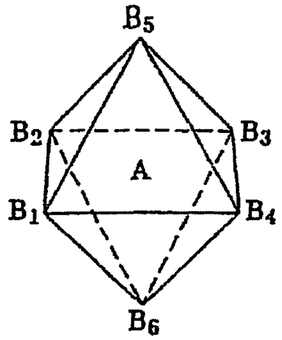


Figure 3.1 A tetrahedral AB_4 molecule.

B_3—B_4 lines, a second which includes AB_1B_3 and bisects the B_2—B_5 and B_4—B_6 lines, and so forth.



3.4 THE INVERSION CENTER

If a molecule can be brought into an equivalent configuration by changing the coordinates (x, y, z) of every atom, where the origin of coordinates lies at a point within the molecule, into $(-x, -y, -z)$, then the point at which the origin lies is said to be a center of symmetry or center of inversion. The symbol for the inversion center and for the operation of inversion is an italic *i*. Like a plane, the center is an element that generates only one operation.

It may be noted that, when a center of inversion exists, restrictions are placed on the numbers of all atoms, or all but one atom, in the molecule. Since the center is a point, only one atom may be at the center. If there is an atom at the center, that atom is unique, since it is the only one in the molecule that is not shifted when the inversion is performed. All other atoms must occur in pairs, since each must have a twin with which it is exchanged when the inversion is performed. From this it follows that we need not bother to look for a center of symmetry in molecules that contain an odd number of more than one species of atom.

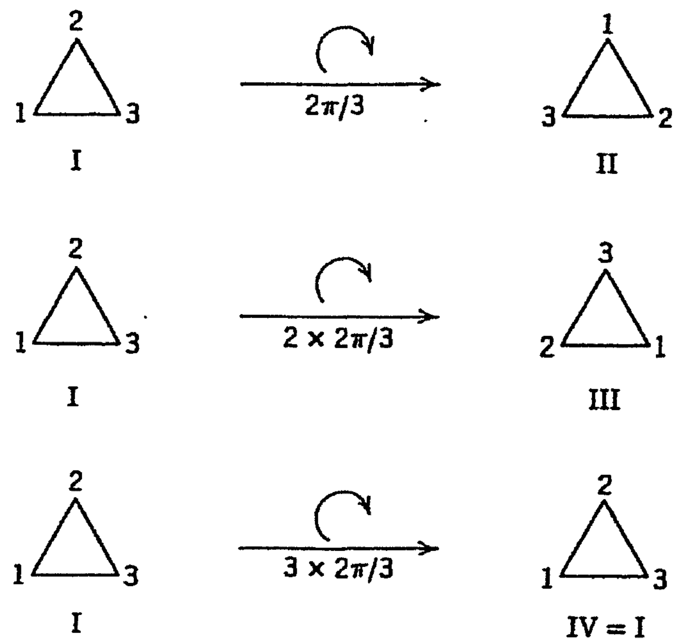
The effect of carrying out the inversion operation n times may be expressed as i^n. It should be easily seen that $i^n = E$ when n is even, and $i^n = i$ when n is odd.

Some examples of molecules having inversion centers are octahedral AB_6, planar AB_4, planar and *trans* AB_2C_2, linear ABA, ethylene, and benzene. Two examples of otherwise fairly symmetrical molecules that do not have centers of inversion are $C_5H_5^-$ (plane pentagon) and tetrahedral AB_4 (even though A is at the "center" and B's come in even numbers).

3.5 PROPER AXES AND PROPER ROTATIONS

Before discussing proper axes and rotations in a general way, let us take a specific case. A line drawn perpendicular to the plane of an equilateral triangle and intersecting it at its geometric center is a proper axis of rotation for that triangle. Upon rotating the triangle by 120° ($2\pi/3$) about this axis, the triangle is brought into an equivalent configuration. It may be noted that a rotation by 240 ($2 \times 2\pi/3$) also produces an equivalent configuration.

The general symbol for a proper axis of rotation is C_n, where the subscript n denotes the *order* of the axis. By order is meant the largest value of n such that rotation through $2\pi/n$ gives an equivalent configuration. In the above example, the axis is a C_3 axis. Another way of defining the meaning of the order n of an axis is to say that it is the number of times that the smallest rotation capable of giving an equivalent configuration must be repeated in order to give a configuration not merely equivalent to the original but also identical to it. The meaning of "identical" can be amplified if we attach numbers to each apex of the triangle in our example. Then the effects of rotating by $2\pi/3$, $2 \times 2\pi/3$, and $3 \times 2\pi/3$ are seen to be



Configurations II and III are equivalent to I because without the labels (which are not real, but represent only our mental constructions) they are indistinguishable from I, although with the labels they are distinguishable. However, IV is indistinguishable from I not only without labels but also with them. Hence, it is not merely equivalent; it is *identical*.

The C_3 axis is also called a threefold axis. Moreover, we use the symbol C_3 to represent the *operation* of rotation by $2\pi/3$ around the C_3 axis. For the rotation by $2 \times 2\pi/3$ we use the symbol C_3^2, and for the rotation by $3 \times 2\pi/3$ the symbol C_3^3. Symbolically we can write $C_3^4 = C_3$, and hence only C_3, C_3^2, and C_3^3 are separate and distinct operations. However, C_3^3 produces an identical configuration, and hence we may write $C_3^3 = E$.

After consideration of this example, it is easy to accept some more general statements about proper axes and proper rotations. In general, an n-fold axis is denoted by C_n and a rotation by $2\pi/n$ is also represented by the symbol

C_n. Rotation by $2\pi/n$ carried out successively m times is represented by the symbol C_n^m. Also, in any case, $C_n^n = E$, $C_n^{n+1} = C_n$, $C_n^{n+2} = C_n^2$, and so on.

In discussing planes of symmetry and inversion centers, attention was directed to the fact that only *one* operation, reflection, is generated by a symmetry plane, and only *one* operation, inversion, by an inversion center. A proper axis of order n, however, generates n operations, namely C_n, C_n^2, C_n^3, . . . , C_n^{n+1}, $C_n^n(=E)$.

One last general consequence of the existence of a C_n axis concerns the requirement that there be certain numbers of each species of atom in a molecule containing the axis. Naturally, any atom that lies on a proper axis of symmetry is unshifted by any rotation about that axis. Thus there may be any number, even or odd, of each species of atom lying on an axis (unless other symmetry elements impose restrictions). However, if one atom of a certain species lies off a C_n axis, there must automatically be $n - 1$ more, or a total of n such atoms, since on applying C_n successively n times, the first atom is moved to a total of n different points. Had there not been identical atoms at all the other $n - 1$ points to begin with, the new configurations would not be equivalent configurations; this would mean that the axis would not be a C_n symmetry axis, contrary to the original assumption.

The symbol C_n^m represents a rotation by $m \times 2\pi/n$. Let us consider the operation C_4^2, which is one of those generated by a C_4 axis. This is a rotation by $2 \times 2\pi/4 = 2\pi/2$, and can therefore be written just as well as C_2. Similarly, among the operations generated by a C_6 axis, we find C_6^2, C_6^3, and C_6^4, which may be written, respectively, as C_3, C_2, and C_3^2. It is frequent though not invariable practice to write an operation C_n^m in what, by considering the fraction (m/n) in $(m/n)2\pi$, can be called lowest terms, and the reader should be familiar with this practice so that he immediately recognizes, for example, that the sequence C_6, C_3, C_2, C_3^2, C_6^5, E is identical in meaning with C_6, C_6^2, C_6^3, C_6^4, C_6^5, C_6^6.

Let us now consider some further illustrative examples chosen from commonly encountered types of molecules. Again we may begin by considering extremes. Many molecules possess no axes of proper rotation; FClSO, for example, does not. (Actually, FClSO is a gratuitous example, since as we saw earlier, it possesses no symmetry elements whatsoever.) Neither Cl_2SO nor F_2SO possess an axis of proper rotation. At the other extreme are linear molecules which possess ∞-fold axes of proper rotation, colinear with the molecular axes. Since all atoms in a linear molecule lie on this axis, rotation by any angle whatever, and hence by all (∞ number) angles, leaves a configuration indistinguishable from the original. Again, as with planes of symmetry, most small molecules possess one axis or a few axes, generally of low orders.

Among examples of molecules with a single axis of order 2 are H_2O and CH_2Cl_2. No molecules possess just two twofold axes; this will be shown later to be mathematically impossible. There are many examples of molecules possessing three twofold axes, for example, ethylene (C_2H_4). One C_2 is colinear with the C—C axis. A second is perpendicular to the plane of the

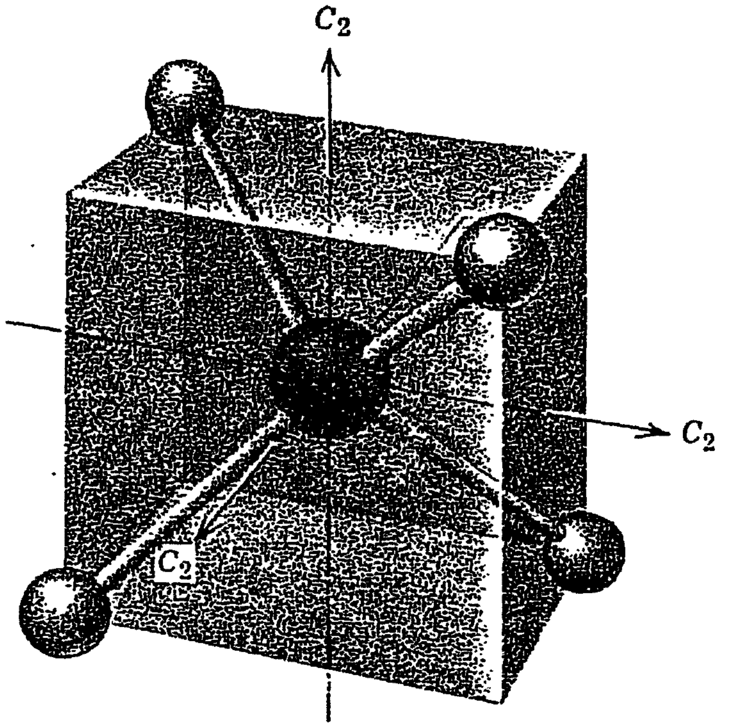
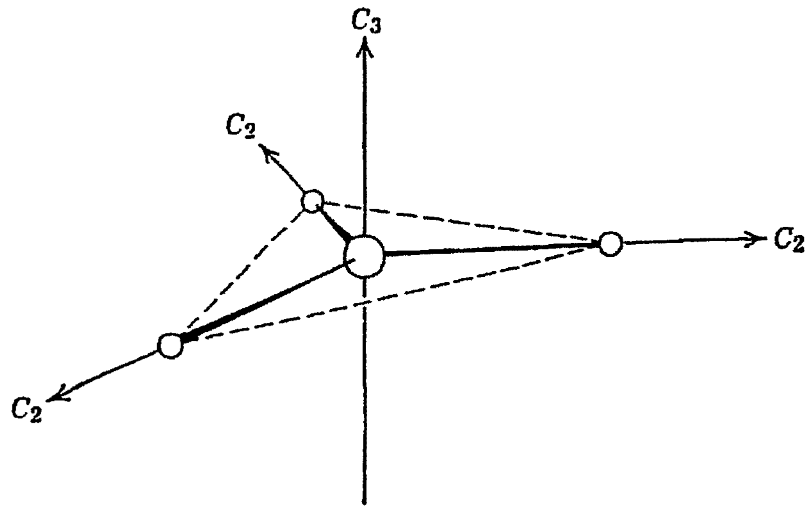


Figure 3.2 A tetrahedral molecule inscribed in a cube.

molecule and bisects the C—C line. The third is perpendicular to the first two and intersects both at the midpoint of the C—C line. A regular tetrahedral molecule also possesses three twofold axes, as shown in Figure 3.2.

Threefold axes are quite common. Both pyramidal and planar AB_3 molecules possess threefold proper axes passing through the atom A and perpendicular to the plane of the three B atoms. A tetrahedral molecule, AB_4, possesses four threefold axes, each passing through the atom A and one of the B atoms. An octahedral molecule, AB_6, also possesses four threefold axes, each passing through the centers of two opposite triangular faces and the A atom.

The planar AB_3 molecule possesses three twofold axes perpendicular to the threefold axis as shown in the diagram. The existence of the C_3 axis and



one C_2 axis perpendicular to the C_3 axis means that the other two C_2 axes, at angles of $2\pi/3$ and $4\pi/3$ to the first, *must* exist. For, on carrying out the rotation C_3, we generate the second C_2 axis from the first, and on carrying out the rotation C_3^2, we generate the third C_2 axis from the first.

The effect of the operations $C_n, C_n^2, \ldots, C_n^{n-1}$ in replicating other symmetry elements may profitably be discussed more fully at this point. The other symmetry elements of interest are planes and axes. It will also be sufficient to limit the discussion to axes perpendicular to the axis of the replicating rotations and to planes that contain the axis of the replicating rotations. A plane perpendicular to the axis of the replicating rotations is obviously not replicated, since all rotations carry it into itself. Although a completely general discussion might be given, it seems more instructive to consider separately each of the replicating axes that can be encountered in practice (C_n, $1 < n \leqslant 8$).

An axis perpendicular to a C_2 axis or a plane containing a C_2 goes into itself on carrying out the operation C_2; hence no further axes or planes *of the same type* are required to exist in this case. We have just seen that from one axis perpendicular to a C_3 axis two similar ones are generated. The same is true for a plane of symmetry containing a C_3 axis. We may also deal with the C_5 and C_7 cases (and, indeed, any C_n where n is odd) for they all behave in the same way. One axis perpendicular to a C_5 or C_7 axis or one plane containing a C_5 or C_7 will be made to generate four or six more separate and distinct axes or planes by the operations that the C_5 or C_7 axis makes possible.

For cases where n in C_n is even, the results are less straightforward. Suppose that we have one axis $C_2(1)$ perpendicular to a C_4 axis. On carrying out the rotation C_4, $C_2(1)$ is rotated by $2\pi/4$ and a second C_2 axis, $C_2(2)$, is thus produced. On carrying out the rotation $C_4^2 (= C_2)$ about the C_4 axis, however, $C_2(1)$ merely goes into itself, and $C_2(2)$ also goes into itself. The operation C_4^3 takes $C_2(1)$ into $C_2(2)$ and $C_2(2)$ into $C_2(1)$. Hence, because C_4^2 is really only C_2 and C_4^3 is only C_4 followed by C_2, the C_4 axis requires only that the axis $C_2(1)$ be accompanied by one other such axis and not three others.

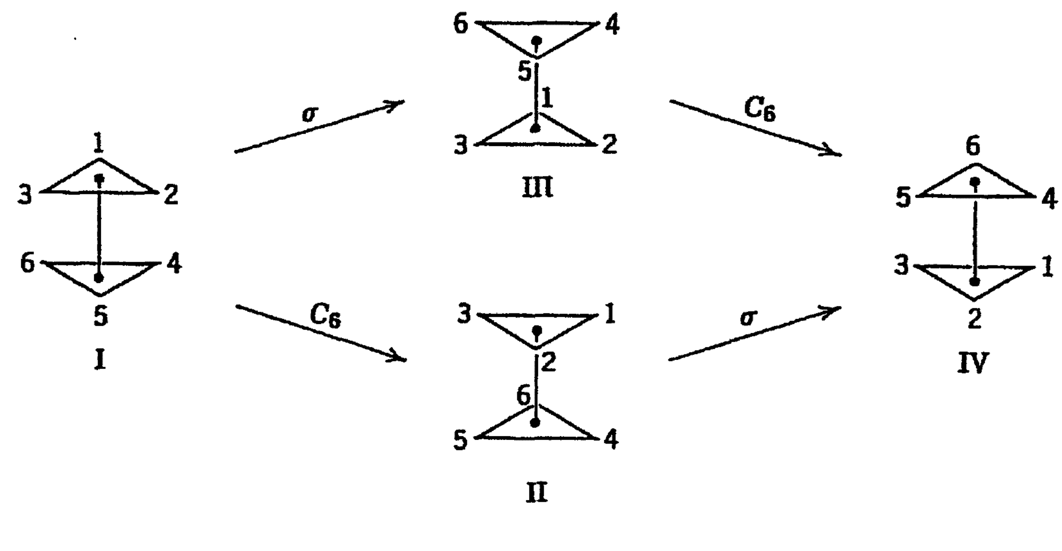
A completely analogous argument holds regarding planes. In the C_6 case, using the same line of argument, it will easily be seen that, if one axis perpendicular to a C_6 or one plane containing a C_6 exists, it must be accompanied by two more of the same type. Similarly, a C_8 axis will replicate a C_2 axis perpendicular to it so as to produce a set of four such C_2 axes.

Continuing with examples of proper axes in typical molecules, we may cite the planar $PtCl_4^{2-}$ ion, which has a C_4 axis perpendicular to the plane of the ion and four C_2 axes in the plane of the ion. The cyclopentadienyl anion, $C_5H_5^-$, possesses a C_5 axis perpendicular to the molecular plane and five C_2 axes in the molecular plane. Benzene possesses a C_6 axis and two sets of three C_2 axes. Probably the only known example of a molecule with a C_7 axis is the planar $[C_7H_7]^+$, the tropylium ion. An example of a molecule with a C_8 axis is $(C_8H_8)_2U$ (uranocene).

3.6 IMPROPER AXES AND IMPROPER ROTATIONS

An improper rotation may be thought of as taking place in two steps: first a proper rotation and then a reflection through a plane perpendicular to the rotation axis. The axis about which this occurs is called an axis of improper rotation or, more briefly, an *improper axis*, and is denoted by the symbol S_n, where again n indicates the order. The operation of improper rotation by $2\pi/n$ is also denoted by the symbol S_n. Obviously, if an axis C_n and a perpendicular plane exist independently, then S_n exists. More important, however, is that an S_n may exist when neither the C_n nor the perpendicular σ exist separately.

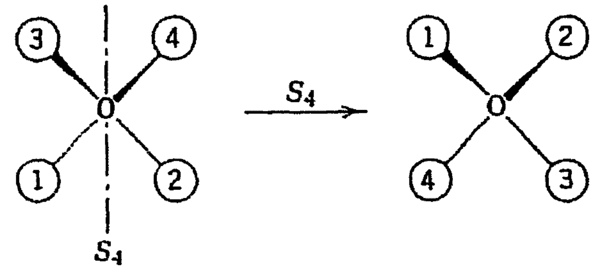
Perhaps this can best be emphasized by taking an example. Let us consider ethane in its staggered configuration. The C—C line defines a C_3 axis, but certainly not a C_6 axis. Yet there is an S_6, as the diagram shows. Observe that II and III are equivalent to each other but that neither is equivalent to I; that is, neither σ nor C_6 is by itself a symmetry operation. But the combination of both, in either order, which we call S_6, is a symmetry operation since it produces IV, which is equivalent to I.



It will be shown later that the operations of rotation and reflection in a plane perpendicular to the rotation axis always give the same result regardless of the order in which they are performed. Thus the definition of improper rotation need not specify the order.

As another important example of the occurrence of improper axes and rotations, let us consider a regular tetrahedral molecule. We have already noted in Section 3.5 that the tetrahedron possesses three C_2 axes. Now each of these C_2 axes is simultaneously an S_4 axis, as can be seen in the diagram on page 28.

The element S_n in general generates a set of operations S_n, S_n^2, S_n^3, ... However, some important features of these operations should be noted. There are differences in the sets generated for even and odd n, so these two cases



will be considered separately. Let us assume that the S_n axis is colinear with the z axis of a coordinate system and that the plane to which the reflection part of the operation S_n is referred is the xy plane.

An improper axis, S_n, of even order generates a set of operations S_n, S_n^2, S_n^3, . . . , S_n^n. Let us first show that (for n even) $S_n^n = E$. S_n^n means that we carry out the operations C_n, σ, C_n, σ, . . . until, in all, C_n and σ have each been carried out n times. Since n is an even number, n repetitions of σ is an identity operation, so that $S_n^n = C_n^n$; but C_n^n is also just E. Therefore, $S_n^n = E$, and $S_n^{n+1} = S_n$; $S_n^{n+2} = S_n^2$, and so on. Now by the same argument S_n^m will be equal to C_n^m whenever m is even. Thus, in any set of operations generated by an even-order S_n, certain of the S_n^m may be written in other ways. Consider, for example, the set S_6, S_6^2, S_6^3, S_6^4, S_6^5, S_6^6. The operation S_6 can be written in no other way. $S_6^2 = C_6^2 = C_3$. $S_6^3 = S_2 = i$. $S_6^4 = C_3^2$. The operation S_6^5 can be written in no other way. $S_6^6 = E$. Hence, the complete set of operations generated by the element S_6 can, and normally would, be written: S_6, C_3, i, C_3^2, S_6^5, E. Having written the set in this way, however, we can readily make another useful observation. The set contains C_3, C_3^2, and E, which are just the operations generated by a C_3 axis. Hence the existence of the S_6 axis automatically requires that the C_3 axis exist. It should not be difficult to see that, in general, the existence of an S_n axis of even order always requires the existence of a $C_{n/2}$ axis.

Let us now turn to improper axes of odd order. Their most important property is that an odd-order S_n requires that C_n and a σ perpendicular to it must exist independently. This is easily proved. The element S_n generates operations S_n, S_n^2, S_n^3, S_n^4, ... Let us examine the operation S_n^n when n is odd. It must have the same effect as will application of C_n^n followed by $\sigma^n = \sigma$. But since $C_n^n = E$, we see that $S_n^n = \sigma$. In other words, the element S_n generates a symmetry operation σ. But if the symmetry operation σ exists, the plane to which it is referred must be a symmetry element in its own right. Now, the operation S_n requires us to reflect in the plane σ, thus carrying a configuration I into another configuration, II, and then to rotate by $2\pi/n$, thus carrying II into III. Because S_n is a symmetry operation, I and III must be equivalent configurations. However, when n is odd, σ is itself a symmetry operation, so that II is also equivalent to I. Then II is also equivalent to III, and we see that rotation by $2\pi/n$ has carried II into an equivalent configuration, III. Thus the operation C_n is also a symmetry operation in its own right.

To gain further familiarity with odd-order improper axes, let us consider how many distinct operations are generated by some such axis, say S_5. The sequence begins $S_5, S_5^2, S_5^3, S_5^4, \ldots$. Using relations and conventions previously developed, we can write certain of these operations in alternative ways, as follows:

$$
\begin{aligned}
S_5 &= C_5 \text{ then } \sigma \text{ (or } \sigma \text{ then } C_5) \\
S_5^2 &= C_5^2 \\
S_5^3 &= C_5^3 \text{ then } \sigma \\
S_5^4 &= C_5^4 \\
S_5^5 &= \sigma \\
S_5^6 &= C_5 \\
S_5^7 &= C_5^2 \text{ then } \sigma \\
S_5^8 &= C_5^3 \\
S_5^9 &= C_5^4 \text{ then } \sigma \\
S_5^{10} &= E \\
S_5^{11} &= C_5 \text{ then } \sigma
\end{aligned}
$$

We see that for S_5 through S_5^{10} (in general, S_n through S_n^{2n}), the operations are all different ones, but commencing with S_n^{2n+1} repetition of the sequence begins. Of the 10 operations, however, 4 plus E can be expressed as a single operation only by using symbols S_5^n, whereas the other 5 can be written either as C_5^n or as σ. Thus there are operations which, although they may be accomplished by using C_5^n and σ successively, cannot be represented as unit operations in any other way than S_5^n. We also see that in general the element S_n with n odd generates $2n$ operations.

3.7 PRODUCTS OF SYMMETRY OPERATIONS

In Sections 3.3–3.6 we have often discussed the question of how we can represent the net effect of applying one symmetry operation after another to a molecule, but only in a limited way. In this section we shall discuss this question with regard to a broader range of possibilities. First, we shall establish a conventional shorthand for stating that "operation X is carried out first and then operation Y, giving the same net effect as would the carrying out of the single operation Z." This we express symbolically as

$$YX = Z$$

Note that the order in which the operations are applied is the order in which they are written from *right to left*, that is, YX means X first and then Y. In general, the order makes a difference although there are cases where it does not. When the result of the sequence XY is the same as the result of the sequence YX, the two operations, X and Y, are said to *commute.* It is also normal to speak of an operation that produces the same result as does the successive application of two or more others as the *product* of the others.

One way in which we may approach the problem of finding a single operation which is the product of two others is to consider a general point with coordinates $[x_1, y_1, z_1]$. On applying a certain operation, this point will be shifted to a new position with coordinates $[x_2, y_2, z_2]$; if still another operation is applied, it will again be shifted so that its coordinates are now $[x_3, y_3, z_3]$. The net effect of applying the two operations successively is to shift the point from $[x_1, y_1, z_1]$ to $[x_3, y_3, z_3]$. We now look for a way of accomplishing this in one step. The operation which does so will be the product of the first two.

Let us illustrate this procedure by proving the statement made earlier that, if there are two twofold axes at right angles to one another, there must necessarily be a third at right angles to both. Suppose that the two given axes coincide with the x and y axes; we can designate them $C_2(x)$ and $C_2(y)$. On applying first $C_2(x)$ and then $C_2(y)$ to a general point, the following transformations of its coordinates take place:

$$[x_1, y_1, z_1] \xrightarrow{C_2(x)} [x_1, -y_1, -z_1] \xrightarrow{C_2(y)} [-x_1, -y_1, z_1]$$

That is , the value of x_3 is $-x_1$, the value of y_3 is $-y_1$, and the value of z_3 is z_1. If now we apply $C_2(z)$ to the general point, it is shifted to $[-x_1, -y_1, z_1]$. Thus we may write

$$C_2(y)C_2(x) = C_2(z)$$

Thus, whenever $C_2(x)$ and $C_2(y)$ exist, $C_2(z)$ must also exist, because it is their product.

As a second example of how the existence of two symmetry elements may automatically require that a third one exist, we shall consider a case having a C_4 axis and one plane containing this axis. We have already seen that the operation C_4 will generate a second plane from the first one at right angles to it. It is also true, however, though less obvious, that when the C_4 axis and one of these planes exist there must then be a second plane also containing C_4 at an angle of 45° to the first one. We can prove this by the method just used. The effect of reflecting a general point $[x_1, y_1, z_1]$ through the xz plane is given by

$$\sigma(xz)[x_1, y_1, z_1] \rightarrow [x_1, -y_1, z_1]$$

whereas the effect of a clockwise C_4 rotation about the z axis upon the point is given by

$$C_4(z)[x_1, y_1, z_1] \rightarrow [y_1, -x_1, z_1]$$

From these relations we can determine the effect of applying successively $\sigma(xz)$ and then $C_4(z)$, namely,

$$C_4(z)\sigma(xz)[x_1, y_1, z_1] \rightarrow C_4(z)[x_1, -y_1, z_1] \rightarrow [-y_1, -x_1, z_1]$$

Now let us consider the effect of reflecting the point through a plane σ_d, which also contains the z axis and bisects the angles between the $+y$ and $-x$ axes and the $+x$ and $-y$ axes. This transformation is

$$\sigma_d[x_1, y_1, z_1] \rightarrow [-y_1, -x_1, z_1]$$

We see that

$$C_4(z)\sigma(xz) = \sigma_d$$

which means that the existence of $C_4(z)$ and $\sigma(xz)$ automatically requires that σ_d exist. The C_4 rotation then generates from σ_d another plane, σ_d', which passes through the first and third quadrants. The final result is that, if there is one plane containing a C_4 axis, there is automatically a set of four planes.

It may be shown in a very similar way that if $C_4(z)$ and $C_2(y)$ axes exist a C_2 axis lying in the first and third quadrants of the xy plane at 45° to $C_2(y)$ must also exist. This is left as an exercise.

Examination of the shifts in a general point may also be employed to show a commutative relation, for example, that $C_2(z)$ and $\sigma(xy)$ commute. Thus, we may write, in a notation that uses $\bar{x}$ instead of $-x$, $\bar{y}$ instead of $-y$, and $\bar{z}$ instead of $-z$:

$$C_2(z)[x, y, z] \rightarrow [\bar{x}, \bar{y}, z]$$

$$\sigma(xy)[x, y, z] \rightarrow [x, y, \bar{z}]$$

$$C_2\sigma[x, y, z] \rightarrow C_2[x, y, \bar{z}] \rightarrow [\bar{x}, \bar{y}, \bar{z}]$$

and

$$\sigma C_2[x, y, z] \rightarrow \sigma[\bar{x}, \bar{y}, z] \rightarrow [\bar{x}, \bar{y}, \bar{z}]$$

We see also that the product in each case is equivalent to i.

In these examples, where only C_2 and C_4 rotations and certain kinds of planes are concerned, the transformation of the coordinates $[x, y, z]$ to $[x, \bar{y}, \bar{z}]$ by a twofold rotation about the x axis, for example, is fairly obvious by inspection. It is also obvious that a fourfold rotation about the x axis will transform the coordinates into $[x, \bar{z}, y]$. It is also easy to see by inspection the effects of the inversion operation, an improper rotation by $2\pi/2$ or $2\pi/4$ and reflection in a plane that is the xy, xz, or yz plane or a plane rotated by

45° from these. However, the transformations effected by more general symmetry operations, such as rotation by $2\pi/n$ or $m2\pi/n$ and reflections in planes other than those just mentioned, are not easily handled by the simple methods and notation used above. Further discussion along this line will therefore employ some geometrical methods and also the more powerful methods of matrix algebra, which will be introduced in Chapter 4.

3.8 EQUIVALENT SYMMETRY ELEMENTS AND EQUIVALENT ATOMS

If a symmetry element A is carried into the element B by an operation generated by a third element X, then of course B can be carried back into A by the application of X^{-1}. The two elements A and B are said to be equivalent. If A can be carried into still a third element C, then there will also be a way of carrying B into C, and the three elements, A, B, and C, form an equivalent set. In general, any set of symmetry elements chosen so that any member can be transformed into each and every other member of the set by application of some symmetry operation is said to be a set of equivalent symmetry elements.

For example, in a plane triangular molecule such as BF_3, each of the twofold symmetry axes lying in the plane can be carried into coincidence with each of the others by rotations of $2\pi/3$ or $2 \times 2\pi/3$, which are symmetry operations. Thus all three twofold axes are said to be equivalent to one another. In a square planar AB_4 molecule, there are four twofold axes in the molecular plane. Two of them, C_2 and C_2', lie along BAB axes, and the other two, C_2'' and C_2''', bisect BAB angles. Such a molecule also contains four symmetry planes, each of which is perpendicular to the molecular plane and intersects it along one of the twofold axes. Now it is easy to see that C_2 may be carried into C_2' and vice versa, and that C_2'' may be carried into C_2''' and vice versa, by rotations about the fourfold axis and by reflections in the symmetry planes mentioned, but there is no way to carry C_2 or C_2' into either C_2'' or C_2''' or vice versa. Thus C_2 and C_2' form one set of equivalent axes, and C_2'' and C_2''' form another. Similarly, two of the symmetry planes are equivalent to each other, but not to either of the other two, which are, however, equivalent to each other.

As other illustrations of equivalence and nonequivalence of symmetry elements, we may note that all three of the symmetry planes in BF_3 that are perpendicular to the molecular plane are equivalent, as are the three in NH_3, whereas the two planes in H_2O are not equivalent. The six twofold axes lying in the plane of the benzene molecule can be divided into two sets of equivalent axes, one set containing those that transect opposite carbon atoms and the other set containing those that bisect opposite edges of the hexagon.

Equivalent atoms in a molecule are those that may all be interchanged with one another by symmetry operations. Naturally, equivalent atoms must be of the same chemical species. Examples of equivalent atoms include all of the hydrogen atoms in methane, ethane, benzene, or cyclopropane, all of the fluorine atoms in SF_6, and all of the carbon and oxygen atoms in $Cr(CO)_6$. Examples of chemically identical atoms which are not equivalent in molecular environment are the apical and equatorial fluorine atoms in PF_5; no symmetry operation possible for this molecule ever interchanges these fluorine atoms. The α and β hydrogen and carbon atoms of naphthalene are not equivalent. All six carbon atoms of cyclohexane are equivalent in the chair configuration, but four are different from the other two in the boat configuration.

3.9 GENERAL RELATIONS AMONG SYMMETRY ELEMENTS AND OPERATIONS

We present here some very general and useful rules about how different kinds of symmetry elements and operations are related. These deal with the way in which the existence of some two symmetry elements necessitates the existence of others, and with commutation relationships. Some of the statements are presented without proof; the reader should profit by making the effort to verify them.

Products

1. The product of two proper rotations must be a proper rotation. Thus, although rotations can be created by combining reflections (see rule 2), the reverse is not possible. The special case $C_2(x)C_2(y) = C_2(z)$ has already been examined (page 30).

2. The product of two reflections, in planes A and B, intersecting at an angle ϕ_{AB}, is a rotation by $2\phi_{AB}$ about the axis defined by the line of intersection. The simplest proof of this is a geometric one, as indicated in Figure 3.3. It is clear that this rule has some far-reaching consequences. If the two planes are separated by the angle ϕ_{AB}, a C_n axis, where $n = 2\pi/2\phi_{AB}$, is required to exist. Here n must be an integer, and the C_n axis will then assure that a total of n such planes exists. Thus, the two planes imply that the entire set of operations constituting the C_{nv} group (see below) is present.

3. When there is a rotation axis, C_n, and a plane containing it, there must be n such planes separated by angles of $2\pi/2n$. This follows from rule 2.

4. The product of two C_2 rotations about axes that intersect at an angle θ is a rotation by 2θ about an axis perpendicular to the plane of the C_2 axes. This can be proved geometrically by a diagram similar to Figure 3.3. It also implies that a C_n axis and one perpendicular C_2 axis require the existence of a set of n C_2 axes and thus generate what we shall soon recognize as the D_n group of operations.