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**INTRODUCTION
TO GROUP THEORY
WITH APPLICATIONS**

Gerald Burns

**IBM THOMAS J. WATSON RESEARCH CENTER
YORKTOWN HEIGHTS, NEW YORK**



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**To my parents
for their patience and kindness**

PREFACE

This book was developed from notes used for a group theory course given at the IBM Research Center at three different times over a period of six years. Its goal is to provide a "feel" for the subject. Examples are given for each new concept. Theorems are motivated; they are not simply stated, proved, and used several chapters later. Rather the importance of a theorem is stressed, and examples of its use given. Long proofs, beautifully presented elsewhere (see Wigner), are not included here. This offers the serious student of group theory the opportunity to become acquainted with other books. This volume follows the philosophy that one is motivated to understand proofs and the beauty of theorems if their usefulness is understood beforehand, and in this pragmatic approach, the book differs from others. As Maimonides ("Guide for the Perplexed") said: "We must first learn the truths by tradition, after this we must be taught how to prove them."

The presentation grows progressively more difficult as the introductory chapters (Chapters 1–6 or 7) unfold. The last one or two sections of each chapter are the more difficult ones; they may be skipped on a first reading. The remaining chapters may be read in any order, although there is clearly a connection between Chapters 8 and 13, 9 and 10, as well as 11 and 12.

This book exhibits a leaning toward point groups and the 32 crystallographic point groups. However, this is only partially done because of my involvement in solid state physics. Rather, it is done because the point group operations are easy to grasp and provide a convenient tool to use as examples in the study of group theory. Space groups appear in Chapter 1 as well as in some of the later chapters.

They almost always occur in the last section of the chapter and may be ignored if there is no interest in that topic. On the other hand, if one is interested in space groups, a modest working knowledge can be developed with very little extra effort.

Although the book has been used as a textbook, it also has been successfully used without the aid of an instructor. There are enough examples to apply one's knowledge immediately. The notes, appendixes, and problems at the end of each chapter broaden the subject matter of the chapter itself. As much as possible I have tried to keep the text on the subject of group theory, without teaching or reviewing large chunks of physics or chemistry. This has the advantage of enabling one to concentrate and use more group theory for a given amount of study.

ACKNOWLEDGMENTS

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Chapter 1

SYMMETRY OPERATIONS

... the recognition that almost all the rules of spectroscopy follow from the symmetry of the problem is the most remarkable result.

Wigner, "Group Theory", Author's Preface

Very little formalism need be learned before the power of group theory can be applied to problems in physics and chemistry and much of this formalism is covered in Chapters 2–4. This chapter, independent of group theory, is presented first for two reasons: (1) It is a self-contained topic enabling a scientist to describe, by means of a symbol, the symmetry operations possessed by a molecule or crystal and conversely, to see the symbol and understand the symmetry operations. (2) The symmetry operations of the molecules or crystals can then be used as examples to understand the ideas in group theory better.

1-1 Introduction

Symmetry is possessed by atoms, molecules, and infinite crystals (henceforth called crystals until the boundary conditions are discussed in Chapter 12). That is, we can operate on them with a **symmetry operation (or covering operation)** which interchanges the positions of various atoms but results in the molecule or crystal looking exactly the same as before the symmetry operation (the molecule or crystal is in an equivalent position) and when the operation is continuously repeated the molecule or crystal continues to be in an equivalent position.

Figure 1-1 shows a planar C_6H_6 molecule (benzene). The symmetry operations of this molecule are: rotations about the z-axis by $\pm\pi/3$, $\pm 2\pi/3$, π , 2π ; rotations by π about six axes in the plane of the molecule

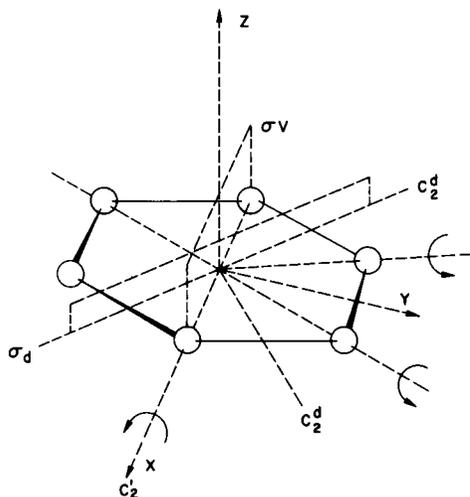


Fig. 1-1 Planar benzene (C_6H_6) showing some of the symmetry operations.

as shown in the figure; reflections across six planes that contain the z -axis, two of which are shown; reflection across the plane of the molecule; inversion through the center of the molecule; and four "improper" rotations which will be discussed later. It will be shown in the next chapter that the set of independent covering operations forms a group in the mathematical sense. It is just these groups which will be studied in most of the remainder of this book. In this chapter we will develop an understanding of the symmetry operations and their notation, and of the classification of molecules and crystals into the point groups (32 in the case of crystals). (Again we emphasize that in the next chapter a group will be defined in the mathematical sense. In this chapter the word is used in a more literal sense.)

1-2 Point Symmetry Operations

In this section we discuss symmetry operations for which one point in the body is kept fixed. These are the **point symmetry operations** usually associated with a molecule or crystal. For molecules the number of such operations is finite. At the end of this chapter other types of symmetry operations without any fixed point are discussed as well as several systems with an infinite number of symmetry operations.

a. Principal axis

For noncubic crystals or for molecules there is usually one axis having higher rotational symmetry than the others (more symmetry operations). For example, an axis with 4-fold symmetry will automatically have 2-fold symmetry and thus have four symmetry operations (rotation by $\pi/2$, π , $3\pi/2$, 2π). An axis with just 2-fold symmetry has just two symmetry operations (rotation by π and 2π). Thus a 4-fold axis is said to have higher symmetry than a 2-fold axis. The axis with the highest symmetry is defined as the **z-axis** or the **principal axis**.

In the case of orthorhombic crystals there are three mutually perpendicular axes of 2-fold symmetry. The choice of z-axis is arbitrary in this case. (Often crystallographers will call the longest cell dimension the x-axis.) Similarly, for other crystals with several principal axes there is a certain arbitrariness but this presents no fundamental problem in the mathematics as will be seen later.

b. Symmetry operations

The symmetry operations are defined and discussed in Table 1-1. We can summarize them briefly in Schoenflies' notation:

E	identity	σ_h	reflection in a horizontal plane
i	inversion	σ_v	reflection in a vertical plane
C_n	rotation by $2\pi/n$ (proper rotation)	σ_d	reflection in a diagonal plane
σ	reflection	S_n	improper rotation ($S_n = \sigma_h C_n$)

Note that all the symmetry operations involve a movement of the body. A **symmetry element** is a geometric entity such as a center of inversion, an axis of rotation, or a plane. Symmetry operations can be carried out with respect to these symmetry elements or combinations of them.

The existence of certain symmetry operations implies the existence of others. For example, if an object has a C_n axis and a C_2' symmetry axis perpendicular to the C_n axis is added, there must be at least nC_2' axes. Similarly, the existence of a C_n axis and one σ_v plane implies at least n σ_v planes. Also, a C_n axis and σ_h imply certain improper rotations.

c. Examples (see Fig. 1-2)

Example 1. H_2O . This molecule possesses symmetry elements E and C_2 (the 2-fold axis being the principal axis shown). It also possesses

Table 1-1 Symmetry operations

E	Identity. The molecule or crystal is not rotated at all or rotated by 2π about any axis. All objects possess this symmetry operation. Taking r as a vector from the origin to any point, $Er \rightarrow r$.
i	Inversion. The molecule is inverted through some origin, the center of inversion. Benzene (Fig. 1-1) has this symmetry element. (However, your right hand does not. Upon inversion it looks like your left hand, which is clearly distinguishable from what it looked like before the operation.) The operation is $i(x, y, z) \rightarrow (-x, -y, -z)$.
C_n	Rotation. Sometimes called a proper rotation. A rotation of the molecule by $2\pi/n$ about an axis, in the sense of a right hand screw by convention . If the axis is not the principal axis, often, but not always, there will be a prime or other superscript; C_n' or C_n^x . Benzene (Fig. 1-1) has C_6, C_3, C_2 about its principal axis. C_n^m is defined as $(C_n)^m$, so $C_6^2 = C_3$ and $C_6^3 = C_2$ but C_3^2 is a new symmetry operation. (It can be written as $C_3^2 = C_3^{-1}$ where C_3^{-1} would be a rotation of $2\pi/3$ in the opposite sense but this will not be used in this book.) C_6^5 is also a new symmetry operation. Thus, about the z-axis of benzene there are six independent symmetry operations: E, $C_6, C_3, C_2, C_3^2, C_6^5$. In the plane of the benzene molecule there are three 2-fold rotations of the C_2' type (through the origin and two carbon atoms) and three 2-fold rotations of the C_2^d type (through the origin and the midpoint between carbon atoms). For example, $C_4(x, y, z) \rightarrow (y, -x, z)$.
σ	Reflection. Reflection of the molecule in a plane. The particular plane of reflection will sometimes be specified by a subscript. Reflection in a plane means: transfer all of the points to the other side of the plane an equal distance along perpendiculars to the plane. So for reflection across the x-plane, which contains the yz-axis, we have $\sigma(x, y, z) \rightarrow (-x, y, z)$.
σ_h	Reflection in the horizontal plane. The plane of reflection is perpendicular to the principal axis and contains the origin. Benzene has one σ_h .
σ_v	Reflection in a vertical plane. The plane contains the principal axis. Benzene has three σ_v through the z-axis and the three C_2' axes.
σ_d	Reflection in a diagonal plane. This plane also contains the principal axis and bisects the angle between the 2-fold axes perpendicular to the principal axis. Benzene has three σ_d through z and the three C_2' axes. (Actually for benzene the distinction between σ_v and σ_d is arbitrary.)
S_n	Improper rotation. A rotation by $2\pi/n$ followed by a reflection in a horizontal plane, i.e., $S_n = \sigma_h C_n$. Again $S_n^m = (S_n)^m = (\sigma_h C_n)^m$. ($S_3^2 \neq S_3^{-1}$ but $S_3^2 = C_3^2$.) Benzene has $S_6, S_3, S_2 (=i), S_3^2, S_6^5, E$. (Note $S_2 = i$ always.) A molecule possessing S_n need not possess σ_h and C_n . For example, methane CH_4 . For S_4 we have $S_4(x, y, z) \rightarrow (y, -x, -z)$.

one σ_v (plane of oxygen and two hydrogens) and another σ_v' perpendicular to the first. Clearly there are no other operations C_n , S_n , i , or σ_h . (Thus the molecule has four symmetry operations.)

Example 2. NH_3 . The molecule has six symmetry operations E , C_3 , C_3^2 , and three σ_v .

Example 3. PF_3Cl_2 . The three F atoms are in the xy -plane (every $2\pi/3$) and the Cl atoms are along the z -axis. The symmetry operations are E , C_3 , C_3^2 , $3C_2'$, σ_h , $3\sigma_v$, S_3 , S_3^5 . (Note, if one F is interchanged with one Cl, there are only two symmetry operations. If two F are interchanged with the two Cl so that in the xy -plane there are 2 Cl + 1 F, then the principal axis changes and there are four symmetry operations.)

At this stage it is worthwhile to deal with a point of **notation**. Proper or improper rotations about the principal axis have no superscripts apart from exponents when appropriate; rotations perpendicular to the principal axis are primed in the present examples or have some other superscript. In the next example the 2-fold rotations perpendicular to the principal axis are labeled C_2^x or C_2^y to denote rotations about the x - or y -axis, respectively. Similarly, rotations about the $[110]$ and $[\bar{1}\bar{1}0]$ axes are usually denoted by C_2'' or will be written as $C_2[110]$ and $C_2[\bar{1}\bar{1}0]$ if such differentiation really should be needed. There are no hard and fast rules for these descriptive superscripts. As will be seen in the next chapter, the symmetry operations are often gathered together in classes where detailed superscripts are irrelevant. Similar descriptive superscripts sometimes will be used for σ_v if it is necessary to differentiate among the various vertical planes. σ_v^x means reflection across a plane perpendicular to the x -direction. Similarly, $\sigma[110]$ means reflection across a plane perpendicular to the $[110]$ direction. (We will continue to use the Schoenflies notation for point symmetry operations until Chapter 11, where some of the other notations are discussed.)

Note the **origin** in the figures: For the H_2O example we assumed the plane of the molecule was the σ_v plane. Care must always be exercised with respect to this problem since other workers might use the σ_v' for the plane of the molecule or put the origin at a different position in the molecule. These are not fundamental problems but it is important to keep them in mind. For H_2O the origin can be anywhere on the z -axis.

Example 4. PbTiO_3 . A unit cell of the crystal is shown in Fig. 1-2d, so we can think of $1/8$ of a Pb ion at each corner, $1/2$ of an oxygen at the center of each face, and the Ti ion at the center of the cell. In a

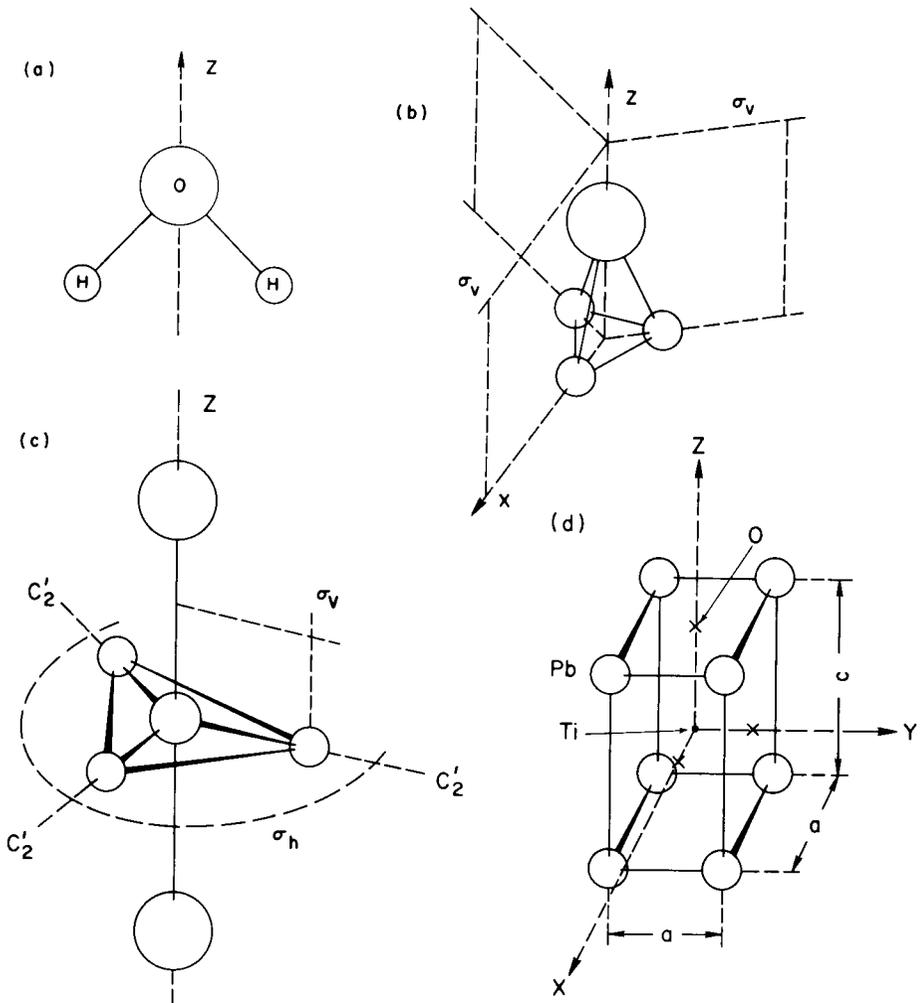


Fig. 1-2 Diagrams of various molecules showing some of the symmetry operations. (a) H_2O : In the example σ_v' is the plane of the paper and σ_v is perpendicular to the paper; (b) NH_3 ; (c) PF_3Cl_2 ; (d) PbTiO_3 shown in a conceptual tetragonal distortion.

tetragonally distorted cell, which might be obtained by stretching the cubic cell along the c -axis, the symmetry operations are: E , C_4 , C_2 , C_4^3 , C_2^x , C_2^y , two C_2'' , σ_h , two σ_v , two σ_d , S_4 , i , S_4^3 . If the Ti ion is moved up along the z -axis, which symmetry operations are still appropriate? If the cell were cubic, not stretched along the z -axis, what are the symmetry operations? (48 operations — don't forget the four C_3 and four C_3^2 .)

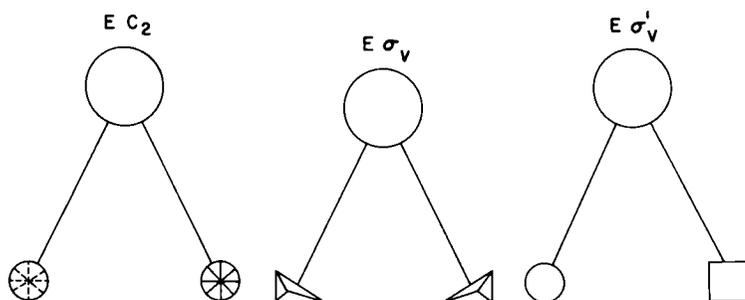


Fig. 1-3 Various conceptual H_2O -like molecules that have lower symmetry than H_2O .

At this point we bring up a very important point. In H_2O , for example, only two symmetry operations are needed to transform the two H ions into themselves or each other. The two operations could be either E and C_2 or E and σ'_v . We might ask why we should say that H_2O has four symmetry operations when it appears that two symmetry operations will suffice. The answer is simple. After we are convinced that the point symmetry operations listed in Table 1-1 are sufficient to describe any type of molecule, we want to find the **maximum number** of independent symmetry operations consistent with the molecule. If we describe the molecule with less than the maximum number of symmetry operations, we are really describing a molecule with lower symmetry. Figure 1-3 shows examples of similar molecules that have lower symmetry than H_2O .

d. Inverse of symmetry operations

It should be noted in the examples given that, within any set of symmetry operations for a given molecule or crystal, the inverse of each symmetry element is also included in the set. The **inverse** of a symmetry operation A is a symmetry operation B such that the successive application of A and then B will return the molecule or crystal to exactly the same (not just an equivalent) position as if no operations were applied at all: $BA = E$. Thus, for any molecule or crystal in the examples given, if the set of symmetry operations is denoted by $\{A_i\}$ then for each A_i in the set there is an A_j , also in the set, such that $A_j A_i = E$. (In the next chapter we show that a left inverse is also a right inverse, $A_j A_i = A_i A_j = E$.) Note that E, i, and any σ are their own inverses. For the Examples: (1) H_2O : $C_2 C_2 = E$, i.e., C_2 is also its own inverse; (2) NH_3 : $C_3 C_3^2 = E$ and $C_3^2 C_3 = E$; (3) PF_3Cl_2 : $S_3^5 S_3 = E$ and $S_3 S_3^5 = E$; etc. In general:

Symmetry operation	Inverse	
C_n^m	C_n^{n-m}	
S_n^m	S_n^{n-m}	all m, n even
S_n^m	S_n^{2n-m}	m odd, n odd

$S_n^m = C_n^m$ for n odd and m even and $E, i,$ and σ are their own inverses.

Note that for inverse operations it is not necessary to define which operation must be applied first, as mentioned above. However, if the symmetry operation B is applied to the molecule first, followed by A , by **convention** this is written as AB .

1-3 The Stereographic Projection

A stereographic projection is a useful and clear way of visualizing and understanding the effects of symmetry operations on molecules and crystals. The **stereographic projection** is usually defined as follows. A point in the $+z$ hemisphere is projected on the xy -plane by determining the intersection of that plane and the line connecting the point with the south pole of the unit sphere. If the point to be projected is in the $-z$ hemisphere, then the north pole is used. A stereogram is usually drawn with the z -axis (principal axis) projected onto the xy -plane. A **general point** or **general equivalent position** (this might be called an arbitrary point) on the unit sphere is projected onto the xy -plane and is labeled by a circle (o) or cross (x) if it is in the $+z$ or $-z$ hemisphere, respectively. A dot is often used instead of a cross.

Starting with a circle to denote a general point, we apply each independent symmetry operation to this first point, and map the resultant position with a circle or cross as appropriate, until all the independent symmetry operations have been applied. There will always be as many circles and crosses as independent symmetry operations because a general point has been used and the operations are independent. Figure 1-4 shows the stereograms for the four examples considered previously.

Example 1. H_2O . $E, C_2, \sigma_v, \sigma_v'$. Start with the circle at position 1 and apply E , resulting in 1; apply C_2 to 1, resulting in 2; apply σ_v to 1, resulting in 3; apply the other σ_v to 1 resulting in 4. Note that the order of the symmetry operations as well as the starting point is irrelevant. Note also the convention of thick lines representing the two σ_v and the symbol in the center representing C_2 .

Example 2. NH_3 . $E, C_3, C_3^2, 3\sigma_v$. E applied to 1 gives 1; C_3 applied to 1 gives 2; C_3^2 applied to 1 gives 3; each of the three σ_v applied to 1 gives 4, 5, and 6.

Example 3. PF_3Cl_2 . $E, C_3, C_3^2, 3C_2', \sigma_h, 3\sigma_v, S_3, S_3^5$. Here, the results labeled with the first entry refer to the circle and with the second, to the cross. Note the convention on the diagram to show the three C_2' axes and the thick line for the circle to designate σ_h .

Example 4. PbTiO_3 . When stretched, as discussed, the symmetry operations are: $E, i, C_4, C_2, C_4^3, 2C_2', 2C_2'', \sigma_h, 2\sigma_v, 2\sigma_d, S_4, S_4^3$. Note the obvious convention for C_4, C_2, C_4^3 .

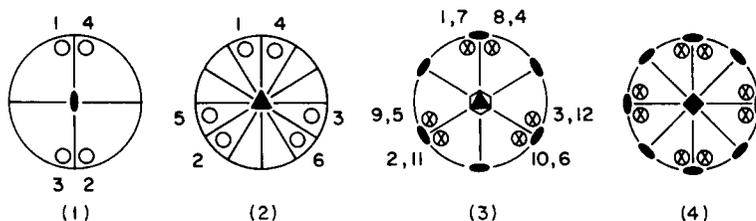


Fig. 1-4 Stereograms for some of the examples.

It should be emphasized again that **general points** or **general equivalent positions** are pictured. If an atom is located on a symmetry element, then a symmetry operation will carry it into itself and fewer circles and crosses will be required on the stereogram to describe all the independent symmetry operations. For example, for H_2O , if an atom were located on one of the σ_v planes, then all four symmetry operations would produce only two circles. If it were located on the C_2 axis, only one circle would result. Such positions are known as **special points**. However, general equivalent positions will always be shown on stereograms. This is consistent with the idea of describing the maximum number of point symmetry operations consistent with a given molecule. For example, compare the stereograms of the molecules in Fig. 1-3 with those for water in Fig. 1-4.

Stereograms for all 32 point groups are in Appendix 1 where two diagrams are shown for each point group. One shows the transformations of an arbitrary point and the other shows the symmetry elements.