Chemical Applications

of Group Theory

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Preface

This book is the outgrowth of a one-semester course which has been taught for several years at the Massachusetts Institute of Technology to seniors and graduate students in chemistry. The treatment of the subject matter is unpretentious in that I have not hesitated to be mathematically unsophisticated, occasionally unrigorous, or somewhat prolix, where I felt that this really helps to make the subject more meaningful and comprehensible for the average student. By the average student, I mean one who does not aspire to be a theoretician but who wants to have a feel for the strategy used by theoreticians in treating problems in which symmetry properties are important and to have a working knowledge of the more common and well-established techniques. I feel that the great power and beauty of symmetry methods, not to mention the prime importance in all fields of chemistry of the results they give, make it very worthwhile for all chemists to be acquainted with the basic principles and main applications of group theoretical methods.

Despite the fact that there seems to be a growing desire among chemists at large to acquire this knowledge, it is still true that only a very few, other than professional theoreticians, have done so. The reason is not hard to discover. There is, so far as I know, no book available which is not likely to strike some terror into the hearts of all but those with an innate love of apparently esoteric theory. It seemed to me that ideas of the sort developed in this book would not soon be assimilated by a wide community of chemists until they were presented in as unpretentious and down-to-earth a manner as possible. That is what I have tried to do here. I have attempted to make this the kind of book which "one can read in bed without a pencil," as my colleague, John Waugh, once aptly described another textbook which has found wide favor because of its down-to-earth character.*

* This statement is actually (and intentionally) not applicable to parts of Chapter 3 where I have made no concessions to the reader who refuses to inspect steric models in conjunction with study of the text.

Perhaps the book may also serve as a first introduction for students intending to do theoretical work, giving them some overall perspective before they aim for depth.

I am most grateful for help I have received from many quarters in writing this book. Over the years students in the course have offered much valuable criticism and advice. In checking the final draft and the proofs I have had very welcome and efficient assistance from Dr. A. B. Blake and Messrs. R. C. Elder, T. E. Haas, and J. T. Mague. I, of course, assume sole responsibility for all remaining errors. Finally, I wish to thank Mrs. Nancy Blake for expert secretarial assistance.

F. Albert Cotton

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Introduction

The experimental chemist in his daily work and thought is concerned with observing and, to as great an extent as possible, understanding and interpreting his observations on the nature of chemical compounds. Today, chemistry is a vast subject. In order to do thorough and productive experimental work, one must know so much descriptive chemistry and so much about experimental techniques that there is not time to be also a master of chemical theory. Theoretical work of profound and creative nature requires a vast training in mathematics and physics which it is now the business of specialists to deal with. And yet, if one is to do more than merely *perform* experiments, one must have some theoretical framework for thought. In order to formulate experiments imaginatively and interpret them correctly, an understanding of the ideas provided by theory as to the behavior of molecules and other arrays of atoms is essential.

The problem in educating student chemists—and in educating ourselves—is to decide what kind of theory and how much of it is desirable. In other words, to what extent can the experimentalist afford to spend time on theoretical studies and at what point should he say, "beyond this I have not the time or inclination to go"? The answer to this question must of course vary with the special field of experimental work and with the individual. In some areas fairly advanced theory is indispensable. In others relatively little is really useful. For the most part, however, it seems fair to say that molecular quantum mechanics, that is, the theory of chemical bonding and molecular dynamics, is of general importance.

As we shall see in Chapter 5, the number and kinds of energy levels which an atom or molecule may have are rigorously and precisely determined by the symmetry of the molecule or of the environment of the atom. Thus, from symmetry considerations alone, we can always tell

what the qualitative features of a problem must be. We shall know, without any quantitative calculations whatever, how many energy states there are and what interactions and transitions between them *may* occur. To put it another way, symmetry considerations *alone* can give us a complete and rigorous answer to the question "What is possible and what is completely impossible?" Symmetry considerations alone *cannot*, however, tell us how likely it is that the possible things will actually take place. Symmetry can tell us that, *in principle*, two states of the system *must* differ in their energy, but only by computation or measurement can we determine how great the difference will be. Again, symmetry can tell us that only certain absorption bands in the electronic or vibrational spectrum of a molecule may occur. But to learn where they will occur and with what intensity, calculations must be made.

Some illustrations of these statements may be helpful. Let us choose one illustration from each of the four major fields of application which are covered in Part II. In Chapter 6 the method of constructing hybrid orbitals will be explained. It will be shown, *inter alia*, that a set of sp^3d hybrid orbitals will form bonds directed to the apices of a trigonal bipyramid if the d orbital used is d_{z^2} whereas the set will form good bonds to atoms at the apices of a square pyramid if the d orbital used is $d_{x^2-y^2}$ or d_{xy}. The connection between the symmetry of the resulting set of hybrids and the d orbital used is absolutely rigorous on the basis of symmetry alone, but only by calculations (which are not practicable at present) could we determine which set of hybrids and hence which symmetry would be favored in a particular molecule. In Chapter 7 the symmetry and some other properties of molecular orbitals will be discussed. It will be shown, for example, that in symmetrical molecules the calculation of the energies of pi molecular orbitals can be accomplished by solving several sets of very small equations rather than one large equation, but the numerical accuracy of the results will still depend on how much labor we wish to put into computations. In Chapter 8, using symmetry arguments and only the most elementary quantitative considerations, we will learn how to construct energy level diagrams, which tell us a great deal about the order of the levels and the qualitative features of the spectra of the ions, for metal ions in ligand fields. Finally, in Chapter 9 it will be shown that using symmetry considerations alone we may predict the number of vibrational fundamentals, their activities in the infrared and Raman, and the way in which the various bonds and interbond angles contribute to them for any molecule possessing some symmetry. The actual magnitudes of the frequencies depend on the interatomic forces in the molecule, and these cannot be predicted from symmetry properties.

The main purpose of this book is to describe the methods by which we can extract the information which symmetry alone will provide. An understanding of this requires only a superficial knowledge of quantum mechanics. In several of the applications of symmetry methods, however, it would be artificial and stultifying to exclude religiously *all* quantitative considerations. Thus, in the chapter on molecular orbitals, it is natural to go a few steps beyond the procedure for determining the symmetries of the possible MO's and explain how the requisite linear combinations of atomic orbitals may be written down and how their energies may be estimated. It also appeared desirable to introduce some quantitative ideas into the treatment of ligand field theory.

It has been, necessarily, assumed that the reader has some prior familiarity with the basic notions of quantum theory. He is expected to know in a general way what the wave equation is, the significance of the Hamiltonian operator, the physical meaning of a wave function, and so forth, but no detailed knowledge of mathematical intricacies is presumed. Even the contents of a rather qualitative book such as Coulson's *Valence* should be sufficient, although, of course, further background knowledge will not be amiss.

The following comments on the organization of the book may prove useful to the prospective reader. It is divided into two parts. Part I, which includes Chapters 1 through 5, covers the principles which are basic to all of the applications. The applications are described in Part II, embracing Chapters 6 through 9. The material in Part I has been written to be read sequentially. That is, each chapter builds on the material developed in all preceding chapters. Part II, however, is written so that each chapter is independent of all other chapters in Part II, although each one, of course, depends on all of the material in Part I. The only exceptions to this statement are a few instances in which quantum principles are equally necessary in two places. They are given only once and in the second instance a reference is made to the first. This arrangement is advantageous to a reader whose immediate goal is to study only one particular area of application, since he can proceed directly to it, whichever it may be; it also allows the teacher freedom in selecting which applications to cover in a course too short to cover all of them, or to take them all but in an order different from that chosen here.

Basic Definitions and Theorems

of Group Theory

2.1 The Defining Properties of a Group

A *group* is a collection of *elements* which 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 entirely
with the groups formed by the sets of symmetry operations which may
be carried out on molecules, 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 com-
mutative, 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 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 in speaking 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 the 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 we may write as

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

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, getting 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, this must hold for the continued product of any number of elements, viz.,

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

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, viz.,

$$ABC = D$$

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

obtain

$$ABCC^{-1}B^{-1}A^{-1} = DC^{-1}B^{-1}A^{-1}$$

$$ABEB^{-1}A^{-1} = DC^{-1}B^{-1}A^{-1}$$

.
.
.

$$E \qquad = DC^{-1}B^{-1}A^{-1}$$

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

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

which proves the above rule.

2.2   Some Examples of Groups

Groups may be either finite or infinite, that is, they may contain a limited or unlimited number of elements. The symmetry groups with which we shall be concerned are mostly finite, but two, namely those to which linear molecules may 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 both an infinite and a finite group.

As an infinite group we may take all of the integers, both positive, 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 our 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 $(+n) + (-n) = 0$.

As another example of a group, this a finite one of order six, let us take the set of elements E (the identity), A, B, C, D, F. A consideration of the defining rules will show that every group has what we may call a multiplication table, that is, a tabular array of all the one-against-one or binary combinations of group elements. The multiplication table for the above group of six elements we shall take to be the following one, with the convention that each entry is the combination of the element at the top of its column with that at the left of its row in the order (column) (row).

Since inspection of the table shows that this group is not Abelian, it is obviously necessary that the above order of combination be specified and that it be remembered in using the multiplication table subsequently.

	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

Let us observe that this table has certain features which are necessary consequences of the defining rules. If it did not have them, we should be forced to conclude either that the set of elements did not actually constitute a group or, if the set does actually constitute a group, that a mistake had been made in working out the table.

(i) Note that each column and each row is a shuffled list of the elements, each occurring once and only once. That this must be so is easily seen if we consider, for instance, a column. The six entries in this column, say the column under C, are CE, CA, CB, CC, CD, CF. If any two products were the same, say the product of CA and CF, then we could write $CA = CF$, which would necessarily mean $A = F$. Thus two elements in the group would be identical, and thus two entire columns and two entire rows would have to be identical. This is not true, so we have shown that the initial assumption must be an impossibility.

(ii) Note that the products E are either on the diagonal or placed symmetrically with respect to it. This is because either an element is its own reciprocal (as for E, A, B, and C), or, in this case, since D is reciprocal to F, F is reciprocal to D.

(iii) The identity occurs only once in each column or row, because each element can have only one reciprocal. This is merely a special case of (i) above.

There are other features of this particular table which are not general, but specific to this group, such as the nonexistence of any commutative multiplications other than those involving E or producing E.

One special kind of group, of which there are many representatives among the symmetry groups, is the *cyclic group*. This is a set of elements X, X^2, X^3, X^4 ... X^n such that $X^n = E$. It may be noted that a cyclic group must be Abelian. The set of elements X, X^2 ... X^{n-1}, X^n, where n is a number such that $X^{n+1} = X$, is called the *period* of the element X, and this entire set of n elements may be symbolized by $\{X\}$.

2.3 Subgroups

Inspection of the multiplication table for the group *EABCDF*, given above, will show that within this group of order 6 there are smaller groups. *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, viz., *E*, *A*; *E*, *B*; *E*, *C*; and the group of order 3, viz., *E*, *D*, *F*. The last should be recognized also as a cyclic group since $D^2 = F$, $D^3 = DF = FD = E$; it is thus a cycle of *D*, namely *D*, D^2 and $D^3 = E$. But to return to the main point, these smaller groups which may be found within a larger group are called subgroups. There are, of course, groups which 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 which are logical consequences of the definition and not of any additional or special characteristics of a particular group. Indeed there are. We may note that the orders of the group above and its subgroups are 6 and 1, 2, 3; in short, the orders are all factors of the order of the main group. We shall now prove the theorem that:

The order of any subgroup, g, of a group of order h must be a divisor of h.
In other words, $h/g = k$ with *k* some integer.

PROOF. Suppose the set of *g* elements, $A_1, A_2, A_3 \ldots A_g$, form 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 2*g* members of the group. If $h > 2g$, we can choose still another element of the group, namely *C*, which is not one of the A_i or 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 which 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 this point where there are no more. Then $h = kg$, where k is, of course, an integer. Then $h/g = k$, which is what we set out to prove. While 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 which 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 get

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

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