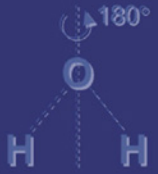
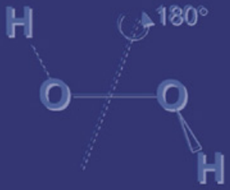
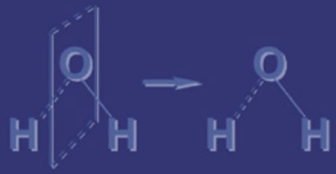
INTRODUCTION TO SYMMETRY AND GROUP THEORY FOR CHEMISTS

By

Arthur M. Lesk







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Preface

This book is based on a one-semester course for advanced undergraduates specializing in physical chemistry. I am aware that the mathematical training of most science majors is more heavily weighted towards analysis – typically calculus and differential equations – than towards algebra. But it remains my conviction that the basic ideas and applications of group theory are not only vital, but not difficult to learn, even though a formal mathematical setting with emphasis on rigor and completeness is not the place where most chemists would feel most comfortable in learning them.

The presentation here is short, and limited to those aspects of symmetry and group theory that are directly useful in interpreting molecular structure and spectroscopy. Nevertheless I hope that the reader will begin to sense some of the beauty of the subject. Symmetry is at the heart of our understanding of the physical laws of nature. If a reader is happy with what appears in this book, I must count this a success. But if the book motivates a reader to move deeper into the subject, I shall be gratified.

Cambridge,
January 2004

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Chapter 1

THE RELATIONSHIP BETWEEN GROUP THEORY AND CHEMISTRY

1.1 Introduction

Group theory is a branch of mathematics that describes the properties of an abstract model of phenomena that depend on symmetry. Despite its abstract tone, group theory provides practical techniques for making quantitative and verifiable predictions about the behavior of atoms, molecules and solids. Once the basic ideas are clear, these techniques are easy to apply, requiring only simple arithmetic calculations.

In this introductory treatment of the applications of group theory to chemistry, all mathematical tools are introduced and developed as they are needed. Familiarity is assumed with only the basic ideas of Euclidean geometry, trigonometry and complex numbers.

1.2 Applications of group theory

Group theory has been useful in chemistry in several ways. First, it has provided simple, qualitative explanations for the behavior of matter. For example, why can the states of electrons in any atom be classified, to a good approximation, by the four quantum numbers n, l, m_l and m_s? Why, in their ground states, is BeH_2 a linear molecule but H_2O bent? Why do certain transitions not appear in an absorption spectrum? Lengthy computations can provide correct but uninformative answers to these questions; group theory can provide perspicuous explanations of the factors that determine these answers.

At a more recondite level, group theory has helped in writing the grammars of the languages we use to describe the physical world. The principles of quantum mechanics can be stated with conciseness, clarity, and confidence because the properties of wave functions and linear operators are well-characterized by mathematics.

Together, qualitative understanding plus formal theory produce predictive tools. The following questions survey the topics to be treated: How can we *describe, classify and predict*

1 . . . the modes of vibration of a molecule?

2 . . . the possible shapes of the wave functions characterizing the electronic structures of atoms and molecules?

3 . . . the spectroscopic properties of atoms and molecules; that is, their exchange of energy with radiation?

Chapter 2

SYMMETRY

2.1 A bridge from geometry to arithmetic

A crucial reason for the importance of group theory in chemistry is that it provides a quantitative description of the symmetry properties of atoms, molecules, and solids. It would be incorrect, however, to think that group theory is *only,* or even mainly, a theory of geometric symmetry, because group theory also describes the processes of ordinary arithmetic. Indeed the *source* of the power of group theory in dealing with phenomena that depend on symmetry is its establishment of a link between symmetries and numbers. It is the power of this analogy, which provides arithmetic representations of geometrical operations, that makes it possible to derive geometric conclusions from simple numerical calculations.

2.2 Classifying symmetry operations

A fundamental concept in the analysis of the symmetry of an object, such as a cube or a water molecule, is the idea of a *covering operation.* A covering operation is a geometrical transformation of an object that leaves it unchanged in appearance. For example, the rotation of a water molecule by 180° around an axis bisecting the H–O–H angle has the effect of exchanging the positions of the two hydrogens, so that the molecule looks the same before and after the rotation, as shown in Figure 2.1.

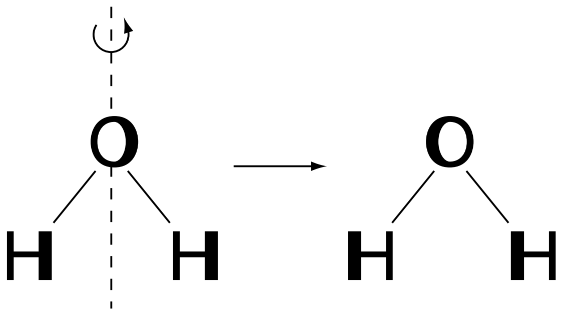


Figure 2.1. Rotation by 180° is a symmetry operation of the water molecule.

A test for recognizing a covering operation is that it would go unnoticed by an observer who was temporarily not looking while the operation was being performed.

Many covering operations correspond to simple rotations – it is easy, and most helpful, to try them out with molecular models. In addition, a "mirror reflection" of the distribution of matter in the water molecule in a plane passing through the oxygen atom and perpendicular to the molecule is a covering operation. It is illustrated in Figure 2.2.

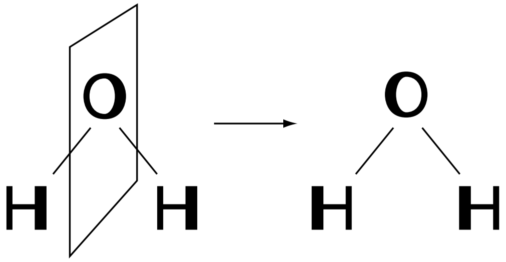


Figure 2.2. Reflection in a mirror plane is another symmetry operation of the water molecule.

The complete list of covering operations of any object is a precise description of its symmetry.

2.3 Full analysis of the symmetry of the water molecule: Introduction to notation

There is one covering operation that even the most asymmetric object must have: the operation of leaving it alone. Like multiplying a number by 1, there is no effect, but this operation, called the *identity,* is as important in the study of symmetry as the number 1 is to multiplication in arithmetic. The identity operation will be denoted here by the letter E.

The *rotation* by 180° is denoted by the symbol C_2 (C is curved, like the orbit of an atom undergoing rotation, and the subscript 2 indicates that the angle of rotation is 360°/**2**). A rotation by $120° = 360°/3$ would be denoted by the symbol C_3, What is the effect of the operation C_1?

The *mirror* symmetry, the reflection in a plane perpendicular to the molecular plane, is denoted by the symbol σ_v. All mirror reflections are denoted by the Greek letter σ: the subscript v indicates that the plane of symmetry would be *v*ertical if the molecule were drawn on a blackboard in the usual way.

A fourth covering operation of the water molecule is *reflection* IN the plane of the molecule. This is also a vertical mirror; it is denoted by the symbol σ_v'.

Table 2.1 summarizes the symmetry operations of the water molecule, and records the final position of each atom after each operation.

Table 2.1. Symmetries of the water molecule.

		Final position of atom originally located at:		
Symmetry operation	Symbol	H_1	O	H_2
Identity	E	H_1	O	H_2
Twofold rotation	C_2	H_2	O	H_1
Reflection in mirror perpendicular to molecular plane	σ_v	H_2	O	H_1
Reflection in molecular plane	σ_v'	H_1	O	H_2

In the table, the symbols H_1, O, and H_2 denote fixed locations in space, occupied *initially* (before the symmetry operation) by hydrogen and oxygen atoms. It is customary to say, for example, that H_1 is *carried into* H_2 by the twofold rotation C_2. This statement means that the hydrogen atom initially at the point H_1 is moved by the operation to the point H_2; or, if H_1 and H_2 denote the atoms themselves rather than the positions in space, that H_1 is moved to the position originally occupied by H_2. H_1 is carried into H_2 does *not* mean that both hydrogen atoms are at the same point in space after the operation.

Table 2.1 shows that σ_v' has the same effect on the water molecule as the identity and that σ_v has the same effect as C_2. Are all four operations really needed to describe the symmetry of the water molecule, or would E and C_2, for example, be enough?

A comparison of the symmetry properties of the water molecule with those of hydrogen peroxide shows that all four operations are necessary. Although E and C_2 are covering operations of H_2O_2, as shown in Figure 2.3, H_2O_2 has no plane of symmetry. Therefore it is essential to include all four covering operations in a description of the symmetry of the water molecule, to indicate that water has a higher symmetry than hydrogen peroxide.

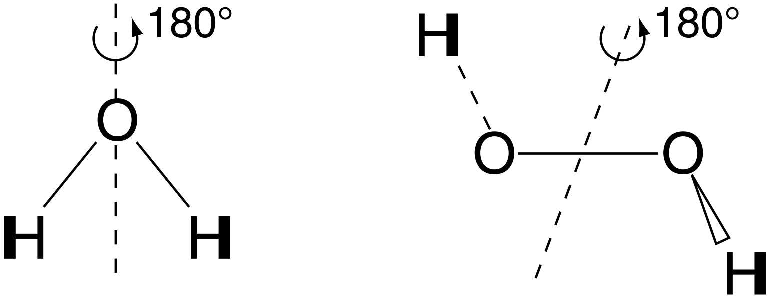


Figure 2.3. C_2 is a symmetry operation of both water and hydrogen peroxide, but hydrogen peroxide has no plane of mirror symmetry. The orientation of the symmetry axis in H_2O_2 is perpendicular to the O–O bond and bisects the angle between the H–O–O and O–O–H planes.

Is the set E, C_2, σ_v and σ_v' a complete description of the symmetry of the water molecule, or do additional covering operations exist? One way to try to generate additional covering operations is by applying two known covering operations in succession; for example, C_2 followed by σ_v.

This compound operation must also be a covering operation of the water molecule – it satisfies the criterion of undetectability by a temporarily distracted observer. However, it is not a *new* covering operation, but is equivalent to σ_v'.

The equivalence of two geometrical operations must be verified on an adequately asymmetric object. For example, E and σ_v' have the same effect on the water molecule, but they are certainly not the same geometrical manipulation. Figure 2.4a shows that a consideration of the water molecule alone cannot determine whether the compound operation (C_2 followed by σ_v) is equal to σ_v' or to E; but that, for the case of a square rendered asymmetric by labeling the corners (Figure 2.4b), the compound operation (C_2 followed by σ_v) is equivalent to σ_v' and unequal to E.

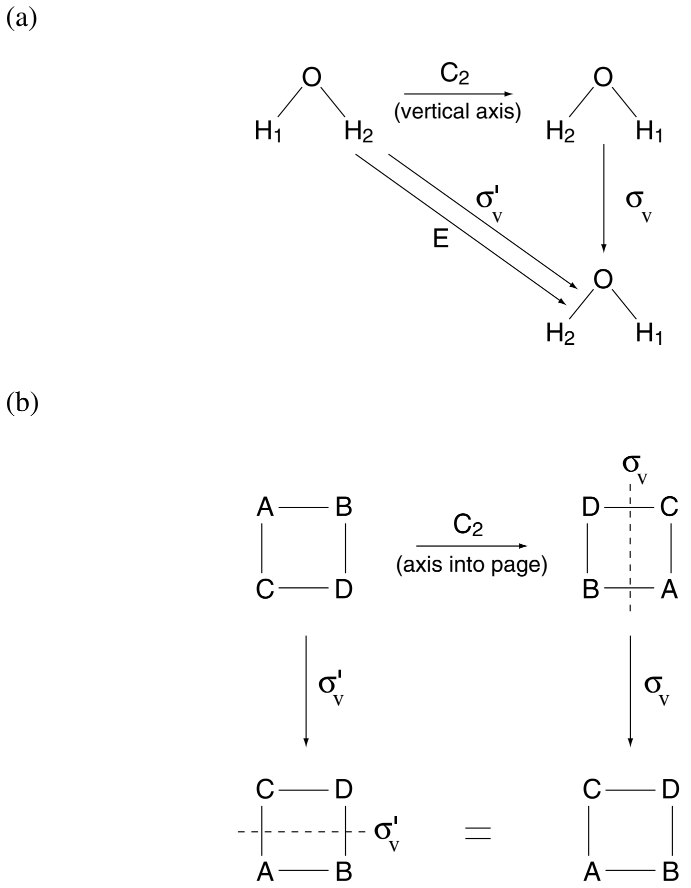


Figure 2.4. (a) For the water molecule the compound operation C_2 followed by σ_v has the same effect as the identity E or σ_v'. (b) For a suitably-labeled square the compound operation C_2 followed by σ_v has the same effect as σ_v', but is not equivalent to the identity E.

Thus the assertion that the compound operation (C_2 followed by σ_v) is equivalent to σ_v' means not only that both produce the same result if applied to the water molecule, but that both produce the same result if applied to any object whatever, even an operation for which none of the transformations σ_v, C_2 or (C_2 followed by σ_v) is a covering operation.

Is it possible that consideration of other examples might expose a case in which (C_2 followed by σ_v) does not give the same result as σ_v'? Rather than proceeding inductively with additional tests, it will prove more effective to treat the geometric manipulations as independent entities, without reference to illustrative objects on which they operate. The development of numerical representations of symmetry operations will then provide straightforward arithmetic tests for equality.

2.4 Products of covering operations: multiplication tables

It is usual to refer to the compound operation produced by applying two operations in succession as the *product* of the two operations. In order to investigate further whether the products of the known covering operations of the water molecule produce any new ones, it is helpful to construct a complete *multiplication table,* shown in the box. Each entry in the table gives the operation resulting from applying first the operation at the head of the column containing the entry, and then the operation at the left of the row.

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

No new covering operations have been generated – perhaps we have already found all of them.

2.5 What is a group?

The fact that the product of any two of the four covering operations of the water molecule is again one of the four can be expressed by the statement that the set E, C_2, σ_v, and σ_v' is *closed* under the rule of combination used. This is one of the defining properties of a *group.* The set of all covering operations of an object forms its *symmetry group.*

Other examples of sets that are closed under some rule of combination are familiar. Consider the numbers 1 and -1, combining according to the rules of ordinary multiplication:

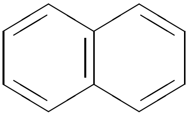
	1	-1
1	1	-1
-1	-1	1

or the complex numbers $1, -1, i$ and $-i$, again under multiplication:

	1	-1	i	$-i$
1	1	-1	i	$-i$
-1	-1	1	$-i$	i
i	i	$-i$	-1	1
$-i$	$-i$	i	1	-1

As an important step towards appreciating the abstract concept of a group, try to recognize what the set of covering operations of the water molecule and these numerical examples have in common.

In many extremely important cases, the analogy between a group of symmetry operations and a group of real numbers is more than superficial. For example, consider the molecule α−chloronaphthalene:



1==Cl0-190

The covering operations of this molecule are only the identity E and a reflection in the plane of the molecule, denoted simply as σ. Compare the multiplication table of this group with that of the group formed by 1 and -1 under multiplication:

	E	σ
E	E	σ
σ	σ	E

	1	-1
1	1	-1
-1	-1	1

The two multiplication tables have exactly the same structure. Whenever it is possible to establish a one-to-one correspondence between the elements of two groups, in such as way that the product of any two elements in one group corresponds to the product of corresponding elements in the other group, the two groups are said to be *isomorphic.* In this example the correspondence is $E \leftrightarrow 1$ and $\sigma \leftrightarrow -1$. Because all properties of a group depend on its multiplication table, any property of a group is also a property of all isomorphic groups.

In particular, a group of numbers isomorphic to a symmetry group is an example of a *representation* of the symmetry group. Group representations are of the utmost importance in chemistry because they make it possible to achieve the effects of geometrical reasoning by means of calculations with the numerical representations.

Problem 2–1. Is the symmetry group of the water molecule (Box, p. 8) isomorphic with the group formed by $1, i, -1$ and $-i$ under multiplication?

Problem 2–2. Consider the symmetry group of an object for which the only covering operations are the identity and rotations by $120°$ (= C_3) and $240°$ (= C_3^2) around the same axis. The multiplication table for this group is:

	E	C_3	C_3^2
E	E	C_3	C_3^2
C_3	C_3	C_3^2	E
C_3^2	C_3^2	E	C_3

Can you determine all the possible sets of three complex numbers that satisfy the same multiplication table?

Chapter 3

GROUP THEORY

3.1 Definition of a group

A group consists of a set (of symmetry operations, numbers, etc.) together with a rule by which any two elements of the set may be combined – which will be called, generically, multiplication – with the following four properties:

1 *Closure:* The result of combining any two elements – the product of any two elements – is another element in the set.

2 Group multiplication satisfies the *associative law:* $a \cdot (b \cdot c) = (a \cdot b) \cdot c$ for all elements a, b and c of the group.

3 There exists a *unit element,* or *identity,* denoted E, such that $E \cdot a = a$ for any element of the group.

4 For every element a of the group, the group contains another element called the *inverse,* a^{-1}, such that $a \cdot a^{-1} =$ E. Note that as E·E = E, the inverse of E is E itself.

Problem 3–1. Verify that the set of covering operations of the water molecule is a group, with the definition of the product of two operations as the compound operation resulting from applying them in succession.

Problem 3–2. For each of the following: Is it a group? If not, which condition(s) fail? If the specified set does form a group under the specified operation, state what the identity element is, and give a formula for the the inverse of any element.
(a) All integers – positive, negative and zero – under multiplication.
(b) The five integers $-2, -1, 0, 1, 2$ under addition.
(c) All odd integers under addition.
(d) All odd integers under multiplication.
(e) All even integers under addition.
(f) All even integers under multiplication.
(g) All real numbers under multiplication.
(h) All numbers of the form $n_1 + n_2\sqrt{5}$ where n_1 and n_2 are integers (negative, zero or positive), under multiplication.
(i) The set of all rotations around a single axis; the rule of combination is successive application.

3.2 Subgroups

A *subgroup* is a set of elements selected from a parent group that themselves form group, with the additional condition that the product of two elements in the subgroup must be the same as the product of the same two elements considered as members of the larger group. For example, the group formed by 1 and -1 under multiplication is a subgroup of the group formed by $1, i, -1$ and $-i$ under multiplication:

	$\mathbf{1}$	$\mathbf{-1}$	i	$-i$
$\mathbf{1}$	$\mathbf{1}$	$\mathbf{-1}$	i	$-i$
$\mathbf{-1}$	$\mathbf{-1}$	$\mathbf{1}$	$-i$	i
i	i	$-i$	-1	1
$-i$	$-i$	i	1	-1

In contrast, although the integers $\ldots, -2, -1, \quad 0, \quad 1, \quad 2\ldots$ form a group under *addition,* the group formed by 1 and -1 under *multiplication* is not a subgroup even though both 1 and -1 are contained in the set of all integers.

Problem 3–3. Find all subgroups of the symmetry group of the water molecule, in two ways: (a) For each symmetry element, try to find a specific conformation of a related molecule, or of any geometric object, that has all the symmetry elements except the one considered.

continues. . .

The symmetry group of that molecule or object is a subgroup of the symmetry group of the water molecule.

(b) Make several copies of the multiplication table of the group. Cross out all reasonable combinations of rows, and corresponding columns – this has the effect of deleting certain elements – and determine whether that which is left forms a group. Note that there is a total of 15 possibilities – see how many you can eliminate without actually trying them. Make sure that you get the same answer both ways!

3.3 Examples of groups

	Elements of the group	Rule of combination
1.	covering operations of an object	Successive application
2.	All real numbers	Addition
3.	All complex numbers	Addition
4.	All real numbers except 0	Multiplication
5.	All complex numbers except $(0, 0)$	Multiplication
6.	All integers	Addition
7.	Even integers	Addition
8.	The n complex numbers of the form $\cos\frac{2\pi k}{n} + i\sin\frac{2\pi k}{n}, k = 0, \ldots, n-1$	Multiplication
9.	All permutations of an ordered set of objects	Successive application

A permutation is a specification of a way to reorder a set. For example, the group of permutations of two objects contains two elements: the identity, *first* → *first, second* → *second* and the exchange, *first* → *second, second* → *first*. This group is isomorphic to the group formed by 1 and -1 under multiplication.

10.	All 2×2 arrays of complex numbers of the form $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ such that $ad - bc \neq 0$	$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \cdot \begin{pmatrix} a' & b' \\ c' & d' \end{pmatrix} = \begin{pmatrix} aa' + bc' & ab' + bd' \\ ca' + dc' & cb' + dd' \end{pmatrix}$
11.	All 2×2 arrays of complex numbers of the form $\begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}$ such that $aa^* + bb^* = 1$	Same as example 10
12.	All possible rotations in three-dimensional space	Successive application

Problem 3–4. The group of permutations of three objects contains six elements (written in terms of cardinal rather than as ordinal numbers to save space):

Initial position		Final position					
1	→	1	2	3	1	3	2
2	→	2	3	1	3	2	1
3	→	3	1	2	2	1	3

Write the multiplication table for the group of permutations of three objects.

Problem 3–5. Do you expect the group of permutations of three objects to be isomorphic to the symmetry group of the water molecule? Explain your reasoning. Are the groups isomorphic?

Problem 3–6. Find the subgroups of the group of permutations of three objects.

Problem 3–7. Verify that the 2×2 complex arrays of example 10 at the beginning of this chapter form a group. Hints: (a) The difficulty in verifying closure is the proof that if the condition $ad - bc \neq 0$ holds for two 2×2 arrays, it holds for their product. Show by direct calculation that $(aa' + bc')(cb' + dd') - (ab' + bd')(ca' + dd') = (ad - bc)(a'd' - b'c')$. (b) Verify the associative law by direct calculation. (c) Verify that the identity element is $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$. (d) Verify that if $ad - bc = D \neq 0$, then the inverse of $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ is $\begin{pmatrix} d/D & -b/D \\ -c/D & a/D \end{pmatrix}$.

Problem 3–8. For all twelve examples of groups in this section, determine which groups are subgroups of others, and which groups are isomorphic to others. Prepare a chart showing diagrammatically the chains of subgroups, and connect the isomorphs by dotted lines. (Warning! The relationship between examples 11 and 12 is quite tricky.)

Chapter 4

POINT GROUPS – THE SYMMETRY GROUPS OF SMALL MOLECULES

4.1 Introduction

A *point group* is the symmetry group of an object of finite extent, such as an atom or molecule. (Infinite lattices, occurring in the theory of crystalline solids, have translational symmetry in addition.) Specifying the point group to which a molecule belongs defines its symmetry completely.

There is quite a range of the possible types of symmetry that a molecule can exhibit. The only covering operation of an asymmetric molecule such as morphine is the identity: the symmetry group of methane, a molecule of very high symmetry, contains fourteen covering operations.

This chapter surveys the varieties of symmetry observed in molecules. First, the different types of covering operations are defined and illustrated. A consideration of possible compatible combinations of symmetry elements leads to a catalog of the common point groups.

4.2 Axes of rotation: C_n

A molecule has an *axis of rotation of degree n,* or an $n-$*fold rotation axis,* if rotation by $\frac{1}{n}$th of a full turn is a covering operation. If $n = 2$, the rotation is by half a turn, or 180°, as in the case of the C_2 axis of the water molecule. The symbol C_n denotes an $n-$fold axis.

Axes of rotation are among the most common of molecular symmetry operations. A onefold axis is a rotation by a full turn, equivalent to the identity. A twofold rotation axis, as in the example of the water molecule, is sometimes called a *dyad.* Cyclopropane has a threefold axis perpendicular to the plane containing the carbon atoms; it also has three twofold axes. Can you visualize them?

4.3 Mirror planes: σ

A molecule has a *plane of symmetry,* or *mirror plane,* if reflection of all atoms in the plane is a covering operation.

Any planar molecule has mirror symmetry, because reflection in the molecular plane leaves the positions of all atoms unaltered. For planar molecules, mirror reflection in the molecular plane is equal to the identity. A molecule may have several mirror planes: recall that the water molecule has two – it is symmetric both with respect to the molecular plane and with respect to a plane perpendicular to the molecule.

Mirror planes are denoted by the Greek letter σ. Mirror planes in a molecule that has an axis of rotation are further classified according to the relative orientation of the axis and the mirror plane. Because it is usual to draw molecules with the principal rotation axis vertical, a mirror plane *containing* the principal rotation axis is called a *vertical mirror* and denoted σ_v. A mirror plane perpendicular to the rotation axis is called a *horizontal mirror* and denoted σ_h.

A special type of vertical plane of symmetry occurs if there are two or more twofold axes perpendicular to the principal axis, and a mirror plane bisects the angle between two of these twofold axes, as in benzene. Such a plane is called a *diagonal mirror plane,* denoted σ_d.

For example, the symmetry group of benzene contains six dyads perpendicular to the principal C_6 axis, and six vertical mirror planes containing the principal axis. These mirror planes can be divided into two sets of three: those passing through atoms and those passing between atoms. The product of C_6 with any of the mirror reflections is another reflection in the same set. It is conventional to distinguish these two sets by calling members of one of them σ_v and members of the other σ_d; but the choice of *which* are the σ_v and which are the σ_d is arbitrary.

Examples of different types of mirror planes are:

- a plane of symmetry in the absence of a rotation axis (other than C_1), σ : HOCl, chloronaphthalene.
- vertical mirror symmetry planes, σ_v : water, methane.
- horizontal mirror symmetry planes, σ_h : *trans*-1,2,−dichloroethylene.
- diagonal mirror symmetry planes, σ_d: benzene, ferrocene in its staggered conformation.

Problem 4–1. (a) Locate the four mirror planes of cyclopropane. (b) How many of the mirror planes of benzene can you find? (c) How many mirror planes does ethane have in the staggered, eclipsed, and gauche conformations?

Problem 4–2. Classify all the mirror planes of cyclopropane, benzene, and the staggered, eclipsed, and gauche conformations of ethane as vertical, horizontal or diagonal mirrors.

4.4 Stereographic projection diagrams

Stereographic projection diagrams, or *stereograms,* are a technique for concise depiction of sets of point symmetry operations. Figure 4.1 contains simple examples of stereographic projection diagrams, in which the symbols $\times$, $\circ$, and $\otimes$ stand for points in space related by symmetry operations. Figure 4.1a shows the simplest possible stereogram, illustrating the identity alone; Figure 4.1b illustrates the symmetry group of the water molecule; and Figure 4.1c illustrates the symmetry group of cyclopropane.

Problem 4–3. In Figure 4.1c, what symmetry operation or combination of symmetry operations takes the $\times$ just above the horizontal line (just above the 3 o'clock line) into (a) the $\circ$ closest to the top of the circle (b) the $\times$ closest to the top of the circle, (c) the $\times$ next to the $\times$ in part (b) of this problem.

A stereogram is to be interpreted as a schematic diagram of an object viewed *down* the principal axis. Horizontal mirror planes and equatorial rotation axes lie in the plane of the diagram. Points in space are designated by $\times$ if they lie above the plane of the diagram and by $\circ$ if they lie below it.

The first step in constructing a stereogram is to place a $\times$ in a position just to the right of the vertical axis of the diagram, as in Figure 4.1a. The initial point occupies a *general position* in space; that is, a point that does not lie on an axis or plane of symmetry. The diagram is built up by applying each operation in turn to every point currently plotted, and adding the points generated to the diagram. For example, the reflection of an $\times$ in a horizontal mirror is an $\circ$, lying directly beneath it; they are written together: $\otimes$. At the end of this process, the stererograms will contain all points generated from the original point by any combination of operations from the group.

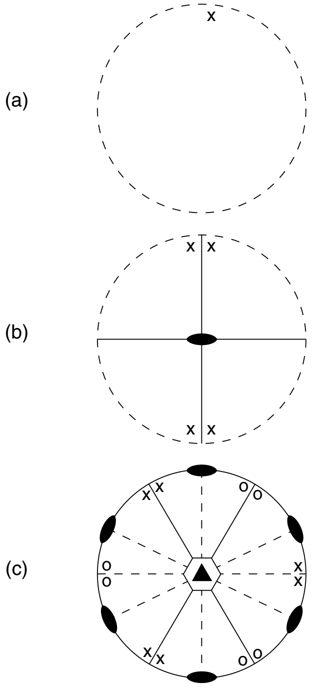


Figure 4.1. Stereographic projection diagrams.

Additional features of the diagram represent symmetry operations themselves. The degree of the principal axis is indicated by the number of sides of a polygon at the center of the diagram, as in Figure 4.1c. (A dyad is symbolized by the lozenge, as in the center of Figure 4.1b.) The circle circumscribing the diagram is solid if a σ_h is present and broken if no σ_h is present. Solid diameters indicate the orientation of vertical or diagonal mirrors. Broken diameters with the dyad symbol at either end indicate the orientations of equatorial two-fold axes.

Problem 4–4. Construct stereographic projection diagrams for the symmetry groups of HOCl, cyclopropane, allene, and benzene.

4.5 Inversion: *i*

The operation of inversion of an atom with respect to an origin means that a line segment is drawn from the atom to the origin, the line segment is extended by an equal distance, and the atom is moved to the endpoint of the extended line segment. After inversion, the atom is as far away from the origin as it was before, but in the opposite direction. A molecule is said to have inversion symmetry – symbol i – if the operation of inversion of all atoms with respect to the center of gravity of the molecule is a covering operation. Benzene has inversion symmetry, as does *trans-1,2,*-dichloroethylene, but cyclopropane does not.

Analytically, inversion has the effect of reversing the signs of all coordinates, measured from the origin of the inversion.

Problem 4–5. What conformation of ethane has inversion symmetry?

4.6 Rotatory reflections, or improper rotations, S_n

A twofold rotation around the molecular axis of *cis-1,2*-dichloroethylene is not a covering operation, because the rotation exchanges hydrogens and chlorines. However, the compound operation of the twofold rotation followed by a reflection in a plane perpendicular to the molecular axis – a C_2 followed by a σ_h — *is* a covering operation. The combination of an $n-$fold rotation and a reflection in a perpendicular plane is called a *rotatory-reflection* or *improper rotation,* symbolized S_n.

Not all rotatory-reflections are unfamiliar operations. An S_1 is just a C_1 followed by a σ_h – this is equivalent to the mirror reflection alone. S_2 is equal to the inversion, because the rotation reverses the signs of the coordinates measured along axes (of the coordinate system) perpendicular to the axis (of rotation), and the reflection reverses the sign of the third coordinate.

In drawing stereographic projection diagrams, it is conventional to indicate improper axes, S_n, by an *open* polygon at the center, and a proper axis, C_n, by a filled polygon (see Figure 4.1c).

4.7 ***Catalogue raisonée*** of the common point groups: symbols, molecular examples, and macroscopic examples

I. Groups containing a principal rotation axis

Symbol	*Symmetry Elements*	*Molecular Examples*	*Macroscopic Examples*
C_1	E	C-FClBrI, myoglobin	a tree
C_n	E, C_n (and, necessarily)	C_2: hydrogen peroxide	
	$C_n^2, C_n^3 \ldots C_n^{n-1}$	C_3: m,m′,m″-trichloro-triphenyl radical	three-bladed propellor
C_{nv}	E, C_n, σ_v but not σ_h,	C_{2v}: water, phenanthrene	tennis racket
	and powers of C_n, plus	C_{3v}: chloroform, ammonia	
	additional σ_v's	C_{4v}: B_5H_9 (square pyramid)	
C_{nh}	E, C_n, σ_h, etc.		
	C_{1h} contains only E and σ_h;	C_{1h}: HOCl, chloronaphthalene	a boat,
	it is sometimes called C_s	C_{2h}: trans-1,2-dichloroethylene	human body (external view)
S_n	E, S_n, etc.		
$S_1 = C_{1h}$	E, σ		
$S_2 = C_i$	E, i	C_i: staggered 1,2-dichloro,1,2-difluoroethane	
$S_n = C_n$			
S_4	$E, S_4, S_4^2 = C_2, S_4^3$		
S_6	$E, S_6, S_6^2 = C_3, S_6^3 = i, S_6^4 = C_3^2, S_6^5$		

Dihedral groups: groups containing n dyads perpendicular to a principal axis
D_n is the symmetry group of a regular $n-$sided polygon.

$D_2 = V$	$E, C_2(x), C_2(y), C_2(z)$	D_2: twisted ethylene (neither planar nor perpendicular)
D_3	$E, 2C_3, 3C_2$	D_3: Co(en)$_3^{+++}$ (en = $H_2NCH_2CH_2NH_2$)
D_4		

D_{nd}	Elements of D_n, plus σ_d, etc.	
$D_{2d} = V_d$	$E, C_2, 2C_2', 2\sigma_d, 2S_4$	D_{2d}: allene, cyclooctatetraene
		D_{3d}: cyclohexane, chair form
$\ldots$		D_{5d}: staggered ferrocene

D_{nh}	Elements of D_{nd} plus σ_h, etc.	
$D_{2h} = V_h$	$E, 3C_2, i, \sigma_v, \sigma_h, \sigma_d$	D_{2h}: ethylene, naphthalene
D_{3h}	$E, 2C_3, 3{C_2}', 2S_3, 3\sigma_v, \sigma_h$	D_{3h}: cyclopropane, eclipsed ethane
D_{6h}		D_{6h}: benzene

II. Groups of high symmetry: no principal axis, more than one C_n with $n > 2$

Symbol	*Symmetry Elements*	*Molecular Examples*	*Macroscopic Examples*
T_d	$E, 8C_3, 3C_2, 6\sigma_d, 6S_4$	methane	triangular pyramid
O_h	$E, 8C_3, 6C_2, 6C_4, 3C_2(= C_4^2), i, 6S_4, 8S_6, 9\sigma$ $i, 6S_4, 8S_6, 9\sigma$	Fe(CN)$_6^{--}$, cubane	regular octahedron
I_h	$E, 12C_5, 12C_5^2, 20C_3, 15C_2,$ $i 12S_{10}, 12S_{10}^3, 20S_6, 15\sigma$	some viruses	regular icosahedron

III. Continuous groups: symmetry groups of linear molecules

Symbol	*Symmetry Elements*	*Molecular Examples*	*Macroscopic Examples*
$C_{\infty v}$	$E, 2C_\phi, \infty\sigma_v$	heteronuclear diatomics, HF, HCN	baseball bat bowling pin
$D_{\infty h}$	$E, 2C_\phi, \infty C_2', i, 2iC_\phi, \infty iC2'$	homonuclear diatomics, N_2, CO_2	dumbbell

$\infty\sigma_v$ means that there are an infinite number of vertical mirror planes, at all different orientations to the principal axis.

$\infty C_2'$ means that there are an infinite number of dyad axes, all perpendicular to the principal axis but at all different orientations to it.

Chapter 5

INTRODUCTION TO LINEAR ALGEBRA

5.1 Introduction

The fundamental theme of linear algebra is the quantitative representation of geometric objects and relationships. Table 5.1 lists the most important of these correspondences between geometry and algebra.

5.2 Systems of coordinates

A coordinate system is a mathematical device for naming positions in space. From the geometric standpoint, a coordinate system is an artificial construct, because the structure of an object is defined by the relationships between its component parts, independent of any external references. Nevertheless a description of geometric objects by means of a coordinate system is a convenient way to describe *numerically* the internal structure of an object and the relationships between different positions and orientations of an object in space.

Table 5.1. Algebra-geometry dictionary

Algebra	***Geometry***
vector	point in space
norm of a vector	distance from the origin of coordinates to the point represented by the vector
inner product of two normalized vectors	cosine of the angle between the lines joining the origin to the points represented by the two vectors
inner product of two vectors = 0	the lines joining the points to the origin are perpendicular
matrix	a linear transformation changing the positions and scalings of a set of points
multiplication of a vector by a matrix	determining the final position of a transformed point
determinant of a matrix	under some circumstances, a measure of the distortion of lengths and angles introduced by a transformation
orthogonal matrix	transformation that keeps all lengths and angles constant

5.3 Vectors

In linear algebra, a *vector* is defined as a sequence of numbers. A vector may be written either in row form: (x, y, z) or in column form: $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$. Frequently we shall use a boldface letter, **x**, to stand for an entire vector: $\mathbf{x} = (x, y, z)$.

The geometric interpretation of a vector as a position in space requires reference to a coordinate system. Any point in three-dimensional space corresponds to a triplet of real numbers, the x, y and z coordinates of the point with respect to a set of Cartesian axes. Conversely, any vector consisting of three real numbers specifies a point in space. The position in space associated with a particular vector will change if a different coordinate system is selected.

A different sense of the word vector in use in physical science is that of a quantity having magnitude and direction. In the language of classical physics, the term *radius vector* – a "vector" from the origin to the point – is the closest equivalent of the idea of a vector introduced here.

Problem 5–1. Visualize or construct graphs in two dimensions, of the geometric interpretations of the 2-vector (3, 4) with respect to two or more Cartesian coordinate systems. These coordinate systems may differ with respect to the position of the origin and directions of the axes; however, the axes must in every case be perpendicular to one another. Keep the scale the same.
Which of the following are independent of the coordinate system?
(a) The point in space (that is, relative to the walls of the room you are in) represented by the vector.
(b) The direction (relative to the walls of the room you are in) of the line joining the origin to the point represented.
(c) The distance from the point represented to the origin.
(d) The length of the projection of the vector along the $x-$axis.

5.4 Norm or length of a vector

The *norm* of a vector, $\parallel (x, y, z) \parallel = \sqrt{x^2 + y^2 + z^2}$, is the distance from a point to the origin of a system of coordinates, or the length of the radius vector.

Problem 5–2. Multiplication of a vector by a real number is defined as multiplying each component by the number: $c\mathbf{x} = c(x, y, z) = (cx, cy, cz)$. Show that if c is a real constant,
$\parallel c(x, y, z) \parallel = c \parallel (x, y, z) \parallel$.

Problem 5–3. Show that if $\parallel (x, y, z) \parallel = 0$, then $x = y = z = 0$.

5.5 Angles and inner products

What is the angle between the lines joining each of two points to the origin? If vectors (x_1, y_1, z_1) and (x_2, y_2, z_2) specify the points, then the cosine of the angle between the lines joining them to the origin is:

$$\cos\theta = \frac{(x_1x_2 + y_1y_2 + z_1z_2)}{\parallel (x_1, y_1, z_1) \parallel \parallel (x_2, y_2, z_2) \parallel}$$

The expression $x_1x_2+y_1y_2+z_1z_2$ is called the *inner product* or *dot product* of the vectors (x_1, y_1, z_1) and (x_2, y_2, z_2), and is denoted

$$(x_1, y_1, z_1) \cdot (x_1, y_1, z_1).$$

Problem 5–4. (a) Express the norm of a vector in terms of an inner product. (b) Express the cosine of the angle between two vectors in terms of inner products.

Problem 5–5. A point on the $x-$axis is represented by a vector of the form $(X, 0, 0)$, where X is a real number. (a) Find the general form of the vectors that represent points of the $y-$ and $z-$axes. (b) Show that the inner product of any vector representing a point on the $x-$axis with any vector representing a point on the $y-$ or $z-$axes is zero.

5.6 Generalizations to n dimensions

A useful feature of the algebraic representations of geometric quantities is the ease with which one can work in dimensions higher than three. Although it is difficult to visualize the angle between two five-dimensional vectors, there is no particular problem involved in taking the dot product between two vectors of the form $(x_1, x_2, x_3, x_4, x_5)$.

A vector with n components is called an *n-vector.* Thus (x, y, z) is a 3-vector, and vectors representing points in the Euclidean plane, (x, y), are 2-vectors.

5.7 Orthogonality and normality

Two vectors are said to be *orthogonal* if they are perpendicular. Vectors are orthogonal if and only if their inner product is zero.

For many applications, the direction in which a vector points is more significant than its length. It is often convenient to multiply a vector by a constant so that its length is equal to 1. Multiplication of a vector by a constant does not change its direction. The resulting vector of length 1 is said to be *normalized.* The normalization constant, N, by which a vector should be multiplied is equal to the inverse of its norm or length. If (x, y, z) is the original vector, N must satisfy the equations:

$$\| (Nx, Ny, Nz) \| \quad = \quad 1, \qquad\qquad \text{or}$$

$$\begin{aligned}(Nx, Ny, Nz) \cdot (Nz, Ny, Nz) &= N^2x^2 + N^2y^2 + N^2z^2 \\ &= N^2(x^2 + y^2 + z^2) \\ &= N^2 \parallel (x, y, z) \parallel^2 = 1\end{aligned}$$

Therefore multiplication of the components of a vector by

$$N = 1/ \parallel (x, y, z) \parallel$$

will produce a vector of unit length.

Any vector of the form $(x, y, z)/ \parallel (x, y, z) \parallel$ is normalized.

Normalized vectors are sometimes written with circumflex accent marks (or "hats"): $\hat{x} = x/ \parallel x \parallel$. The "hat" is a reminder that the length of the vector is 1.

Problem 5–6. Draw on a graph the 2–vectors $(3, 3)$ and $(2, -2)$. Observe that they are perpendicular and verify that their dot product is zero.

Problem 5–7. Show that the lines joining two points to the origin are perpendicular if and only if the inner product of the corresponding vectors is zero?

Problem 5–8. Normalize the vector (3, 4, 12); that is, find the vector of length 1 with the same direction.

Problem 5–9. What is the norm of the vector $(13\ 3\ 4\ 5\ 12\ 13\ 12)$?

5.8 Linear transformations and matrices

inxxlinear transformation The most important class of geometrical manipulations is the set of linear transformations, for which the effect on a point is given by the linear equations:

$$\begin{aligned}x_f &= a_{11}x_i + a_{12}y_i + a_{13}z_i \\ y_f &= a_{21}x_i + a_{22}y_i + a_{23}z_i \\ y_f &= a_{31}x_i + a_{32}y_i + a_{33}z_i\end{aligned}$$

in which (x_i, y_i, z_i) and (x_f, y_f, z_f) are vectors representing the ***i***nitial and ***f***inal points, and the a_{ij} are real numbers characterizing the transformation. All the covering operations we have dealt with are of this type.

Matrix notation is a shorthand way of writing such systems of linear equations, that avoids tedious copying of the symbols x_i, y_i and z_i. The application of the identity matrix:

$$\begin{pmatrix} x_f \\ y_f \\ z_f \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

is an abbreviation of the system of equations:

$$\begin{aligned} x_f &= 1x_i + 0y_i + 0z_i \\ y_f &= 0x_i + 1y_i + 0z_i \\ z_f &= 0x_i + 0y_i + 1z_i \end{aligned}$$

In general, the array of numbers:

$$\begin{pmatrix} a_{11} & a_{12} & a_{12} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

is called a *matrix.* The numbers a_{ij} are its *elements:* the first subscript specifies the row and the second subscript specifies the column in which the element appears. A matrix characterizes a linear transformation completely, in a form containing no explicit reference to particular initial and final points. Thus, in addition to *abbreviating* the description of a transformation in terms of a set of linear equations, matrix form emphasizes that the transformation is a mathematical entity in its own right, independent of the points on which it operates. A three-by-three matrix expresses a transformation in three-dimensional space. Matrices of other dimensions express transformations in other dimensions.

Each of the symmetry operations we have defined geometrically can be represented by a matrix. The elements of the matrices depend on the choice of coordinate system. Consider a water molecule and a coordinate system so oriented that the three atoms lie in the x–z plane, with the $z-$axis passing through the oxygen atom and bisecting the H–O–H angle, as shown in Figure 5.1.

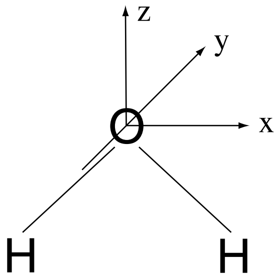


Figure 5.1.

Figure 5.1. Coordinate system for the water molecule.

The operation σ_v, the mirror reflection in the y–z plane, has the effect *in this coordinate system* of reversing the sign of the $x-$coordinate of any point it operates on. This effect is specified by the equations:

$$x_f = -x_i, \qquad y_f = y_i, \qquad z_f = z_i$$

or by the matrix equation:

$$\begin{pmatrix} x_f \\ y_f \\ z_f \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

The identity operation is expressed by the identity matrix:

$$I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

There is an identity matrix of every size, for every dimension.

Problem 5–10. Using the same coordinate system, write the sets of linear equations corresponding to C_2 and σ'_v. What are the corresponding matrices? Make sure that the results are correct even for points that do not lie on the x–z plane.

Problem 5–11. Make up matrices corresponding to the operations C_3, $C_3^2 = -C_3$, and σ_h. Assume that the axis lies along the $z-$axis of the coordinate system. Make up the matrix corresponding to the inversion.

5.9 Successive transformations; matrix multiplication

Because the successive application of two linear transformations is itself a linear transformation, it must also correspond to a matrix. The matrix corresponding to a compound transformation can be computed directly from the matrices corresponding to the individual transformations. Let us derive the formulas; for simplicity we shall work in two dimensions. Given two linear transformations:

$$\begin{aligned} x_f &= a_{11}x_i + a_{12}y_i \\ y_f &= a_{21}x_i + a_{22}y_i \end{aligned}$$

and

$$\begin{aligned} x'_f &= b_{11}x'_i + b_{12}y'_i \\ y'_f &= b_{21}x'_i + b_{22}y'_i \end{aligned}$$

use the final point of the first transformation as the initial point of the second. That is, let

$$\begin{aligned} x'_i &= x_f = a_{11}x_i + a_{12}y_i \qquad \text{and} \\ y'_i &= y_f = a_{21}x_i + a_{22}y_i \end{aligned}$$

Then:

$$\begin{aligned} x'_f &= b_{11}(a_{11}x_i + a_{12}y_i) + b_{12}(a_{21}x_i + a_{22}y_i) \\ y'_f &= b_{21}(a_{11}x_i + a_{12}y_i) + b_{22}(a_{21}x_i + a_{22}y_i) \end{aligned}$$

or:

$$\begin{aligned} x'_f &= (b_{11}a_{11} + b_{12}a_{21})x_i + (b_{11}a_{12} + b_{12}a_{21})y_i \\ y'_f &= (b_{21}a_{11} + b_{22}a_{21})x_i + (b_{21}a_{12} + b_{22}a_{22})y_i \end{aligned}$$

The last set of equations is in the standard form for a linear transformation. Its matrix form is:

$$\begin{pmatrix} x'_f \\ y'_f \end{pmatrix} = \begin{pmatrix} b_{11}a_{11} + b_{12}a_{21} & b_{11}a_{12} + b_{12}a_{21} \\ b_{21}a_{11} + b_{22}a_{21} & b_{21}a_{12} + b_{22}a_{22} \end{pmatrix} \begin{pmatrix} x_i \\ y_i \end{pmatrix}.$$

The matrix corresponding to the compound transformation is derived from the individual transformation matrices by the rule of matrix multiplication introduced in the examples of matrix groups (section 3–3), examples 10 and 11.

In more than two dimensions, the calculation is similar. The general result is that: if the matrix

$$C = \begin{pmatrix} c_{11} & \ldots & c_{1n} \\ \ldots & & \ldots \\ c_{n1} & \ldots & c_{nn} \end{pmatrix}$$

corresponds to the compound transformation of applying first the matrix

$$A = \begin{pmatrix} a_{11} & \ldots & a_{1n} \\ \ldots & & \ldots \\ a_{n1} & \ldots & a_{nn} \end{pmatrix}$$

and then the matrix

$$B = \begin{pmatrix} b_{11} & \ldots & b_{1n} \\ \ldots & & \ldots \\ b_{nl} & \ldots & b_{nn} \end{pmatrix}$$

we say that C is the product of B and A: $C = B \times A$. The elements of C are given by the formula:

$$c_{ik} = \sum_{j=1}^{n} b_{ij} a_{jk}$$

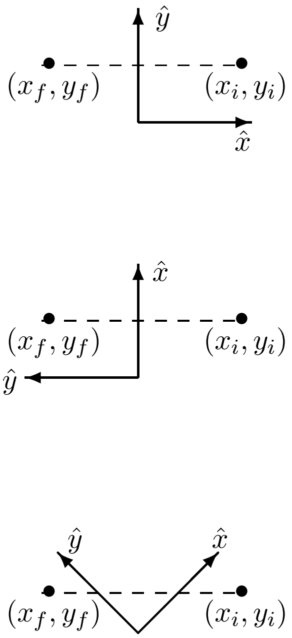
If the rows of B and the columns of A are considered as vectors, then the element c_{ik} is the dot product of the ith row of B with the kth column of A:

$$\begin{array}{ccccc} C & = & B & \times & A \\ \begin{pmatrix} & \vdots & \\ \cdots & c_{ik} & \cdots\cdots \\ & \vdots & \\ & \vdots & \end{pmatrix} & = & \begin{pmatrix} b_{i1} & b_{i2} & \ldots & b_{in} \\ & & & \\ & & & \end{pmatrix} & \times & \begin{pmatrix} a_{1k} \\ a_{2k} \\ \vdots \\ a_{nk} \end{pmatrix} \\ c_{ik} & = & (\, b_{i1} \quad b_{i2} \quad \ldots \quad b_{in} \,) & \cdot & (\, a_{1k} \quad a_{2k} \quad \ldots \quad a_{nk} \,) \end{array}$$

5.10 The effect on a matrix of a change in coordinate system

The elements of the matrix that corresponds to a geometrical operation such as a rotation depend on the coordinate system in which it is expressed. Consider a mirror reflection, in two dimensions, expressed in three different coordinate systems, as shown in Figure 5–2. The mirror itself is in each case vertical, independent of the orientation of the coordinate system.

Coordinate system



Equations of mirror reflection	**Matrix**
$\begin{aligned} x_f &= -x_i \\ y_f &= y_i \end{aligned}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$
$\begin{aligned} x_f &= x_i \\ y_f &= -y_i \end{aligned}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
$\begin{aligned} x_f + y_f &= x_i + y_i \\ x_f - y_f &= -x_i + y_i \end{aligned}$	or
$\begin{aligned} x_f &= y_i \\ y_f &= x_i \end{aligned}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

Figure 5.2. Expression of a reflection in a mirror plane in three different coordinate systems. Note that the points (x_i, y_i) and (x_f, y_f) don't change position. Only the coordinate axes change.

The relationships between the matrices representing the reflection in different coordinate systems are expressible in terms of the matrix S that defines the relationships between the coordinate systems themselves. Suppose $(\hat{x}, \hat{y})$ and $(\hat{x}', \hat{y}')$ are two pairs of normalized vectors oriented along the axes of two Cartesian coordinate systems related by a linear transformation:

$$\begin{pmatrix} \hat{x}' \\ \hat{y}' \end{pmatrix} = S \begin{pmatrix} \hat{x} \\ \hat{y} \end{pmatrix}$$

If the matrix A represents the mirror reflection in the $(\hat{x}, \hat{y})$ coordinate system, then the matrix that represents the reflection in the $(\hat{x}', \hat{y}')$ coordinate system is the triple matrix product $S^{-1}AS$, where S^{-1} is the inverse of S. Such a change in representation induced by a change in coordinate system is called a *similarity transformation.*

Problem 5–12. Verify that the three sets of equations and matrices in Figure 5.2 express the same mirror reflection, in the three different coordinate systems. Proceed as follows: First plot and connect the points of the triangle $(1, 1), (5, 1), (3, 4)$ on standard axes, corresponding to the top frame of Figure 5.2. Apply the transformation equations and the matrix from the top frame of Figure 5.2 and plot the result on the same axes. Do the results look as if the triangle has been subjected to a mirror reflection? Then determine the coordinates of the initial points in the other two coordinate systems. Apply the other two sets of transformation equations and matrices, plot, the results with respect to the other coordinate axes on separate pieces of paper. Verify that if you hold all three pieces of paper up to a light, and superpose the origins of the sets of coordinates, the original triangle and its mirror image will overlay one another but the coordinate axes will not.

5.11 Orthogonal transformations

Although every symmetry operation can be represented by a matrix, many matrices correspond to linear transformations that do not have the properties of symmetry operations. For example, every symmetry operation has the property that the distance between any two points and the angles between any two lines are not altered by the operation. Such a geometric transformation, that does not *distort* any object that it acts on, is called an *orthogonal transformation.* A matrix that corresponds to such a transformation is called an *orthogonal matrix.*

An algebraic criterion for orthogonality is stated in terms of a relation between a matrix and its *transpose.* The transpose of a matrix A is a matrix A^t such that the i, j^{th} element of A is equal to the j, i^{th} element of A^t. For example, the transpose of $\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$ is the matrix $\begin{pmatrix} 1 & 3 \\ 2 & 4 \end{pmatrix}$. A matrix is called orthogonal if $A^tA = I$ (the identity matrix).

Problem 5–13. Verify that if $A^t A = I$, then $Ax \cdot Ay = x \cdot y$ for any vectors x and y. Why does this imply that the transformation represented by the matrix A does not alter lengths and angles? (Hint: see problem 5–4.)

Problem 5–14. Verify that the matrices constructed in problems 5–9 and 5–10 are orthogonal.

5.12 Traces and determinants

Linear transformations that correspond to nonorthogonal matrices distort lengths or angles. The trace and determinant of a matrix provide partial measures of the distortions introduced.

The trace of a matrix is defined as the sum of the diagonal elements.

$$\mathrm{Tr}\ A = \sum_{i=1}^{n} a_{ii}.$$

For two-by-two arrays, the determinant is

$$\det \begin{pmatrix} a & b \\ c & d \end{pmatrix} = ad - bc.$$

Analogous but more complicated formulas define the determinants of square matrices of higher dimensions. (A square matrix is a matrix which has the same number of rows as columns.) It is not possible to define the determinant of a non-square matrix.

To get an idea of the way that the trace and determinant measure distortions, consider the following examples of matrices that correspond to simple geometric transformations in two dimensions:

Table 5.2. Examples of simple transformations in two dimensions.

Operation	Matrix	Trace	Determinant	Lengths	Angles
				Preserved	
Identity	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	2	1	Yes	Yes
Rotation by 45°	$\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$	$\sqrt{2}$	1	Yes	Yes
Rotation by θ	$\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$	$2\cos\theta$	1	Yes	Yes
Mirror reflection	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	0	-1	Yes	Yes
Inversion	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	-2	1	Yes	Yes
Uniform expansion : $x \longrightarrow 5x, y \longleftarrow 5y$	$\begin{pmatrix} 5 & 0 \\ 0 & 5 \end{pmatrix}$	10	25	No	Yes
Uniform shrinkage : $x \longrightarrow \frac{1}{2}x, y \longleftarrow \frac{1}{2}y$	$\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$	1	$\frac{1}{4}$	No	Yes
Shrinkage of x, expansion of $y : x \longrightarrow \frac{1}{4}x, y = 4y$	$\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & 4 \end{pmatrix}$	$4\frac{1}{4}$	1	No	No
Expansion of x, inversion and expansion of y : $x \longrightarrow 6x; y \longrightarrow -4y$	$\begin{pmatrix} 6 & 0 \\ 0 & -4 \end{pmatrix}$	2	-24	No	No

What conclusions do these examples suggest? First, note that only the first six examples are orthogonal transformations. The determinant of each of these matrices is $+1$ or -1. Every matrix that represents an orthogonal transformation must have determinant ± 1. However, one example shows that the determinant of a nonorthogonal transformation *can* be 1. (Which example?)

The trace is a much less reliable measure of distortion. Only in the special case of shrinkages of all axes or expansions of all axes does the deviation of the trace from 2 measure the distortion of lengths introduced by the transformation.

The importance of the trace and determinant lies in their independence of the coordinate system in which the matrix is expressed. Recalling that a change in coordinate system leads to a change in the matrix representation of a transformation by a similarity transformation, the independence of trace and determinant on coordinate system is expressed by the equations:

$$\mathrm{Tr}\ (S^{-1}AS) = \mathrm{Tr}\ A$$

$$\det\ (S^{-1}AS) = \det A$$

where S is an orthogonal matrix. Thus the trace and determinant provide numerical characteristics of a transformation independent of any coordinate system.

Problem 5–15. Compute the traces and determinants of the following matrices:

$$A = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad B = \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}, \qquad C = \begin{pmatrix} 5 & 4 \\ 4 & 5 \end{pmatrix},$$

$$D = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \qquad E = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Problem 5–16. Verify the information in the rightmost four columns of Table 5.2.

Problem 5–17. Show that: $\mathrm{Tr}\ (A \times B) = \sum_{i,j} a_{ij}b_{ji} = \mathrm{Tr}\ (B \times A)$. Conclude that $\mathrm{Tr}(S^{-1}AS) = \mathrm{Tr}A$, by writing $\mathrm{Tr}\ (S^{-1}AS)$ as $\mathrm{Tr}\ [(S^{-1}A)S]$, then interchanging the order of the factors, and using the associative law for matrix multiplication.

Problem 5–18. In Problem 3–7 it was shown for two-dimensional matrices that $\det(AB) = \det B \det A$. For two-dimensional matrices, prove that $\det(S^{-1}AS) = \det S^{-1} \det A \det S$. Show that $\det S^{-1} = 1/(\det S)$, whenever $\det S \neq 0$. Conclude that $\det\ (S^{-1}AS) = \det A$ whenever $\det S \neq 0$. Prove this in another way, by noting that $\det(A \times B) = \det\ (B \times A)$, and using the fact that $\det I = 1$. (I is the identity matrix.)

5.13 Matrix representation of symmetry groups

We are now ready for the main conclusion of this chapter: If all elements of a symmetry group are represented by orthogonal matrices in a consistent coordinate system, the matrices will form a group under the operation of matrix multiplication that is isomorphic to the symmetry group. The set of matrices is said to be a *representation* of the group.

Problem 5–19. Assemble a set of matrices corresponding to the elements of C_{2v}: $E, C_2, \sigma_v, \sigma_v'$. Verify that under matrix multiplication they form a group isomorphic to C_{2v}.

Problem 5–20. Make sure you understand the definitions of the following terms, introduced in this chapter:

(a) 3-vector
(b) norm of a vector
(c) dot product of two vectors
(d) orthogonality of vectors
(e) normalization of vectors
(f) matrix form of equations of linear transformation
(g) matrix multiplication
(h) transpose of a matrix
(i) orthogonal transformation
(j) orthogonal matrix
(k) similarity transformation
(l) trace of a matrix
(m) determinant of a 2×2 matrix
(n) invariance of trace and determinant under a similarity transformation (change of coordinate system)
(o) matrix representation of a symmetry group

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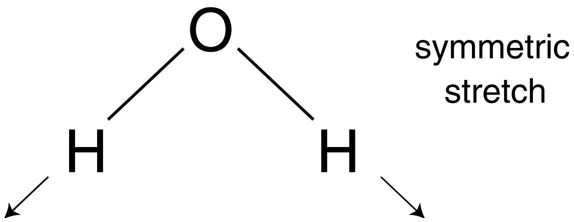
Chapter 6

GROUP REPRESENTATIONS AND CHARACTER TABLES

6.1 Introduction

In order to apply group-theoretical descriptions of symmetry, it is necessary to determine what restrictions the symmetry of an atom or molecule imposes on its physical properties. For example, how are the symmetries of normal modes of vibration of a molecule related to, and derivable from, the full molecular symmetry? How are the shapes of electronic wave functions of atoms and molecules related to, and derivable from, the symmetry of the nuclear framework?

By the symmetry of a normal mode of vibration, we mean the symmetry of the nuclear framework under the distortion introduced by the vibration. Pictorially, the symmetry of the normal mode is equal to the symmetry of the pattern of arrows drawn to indicate the directions of the nuclear displacements. The normal modes of vibration of water are the symmetric and antisymmetric stretches, and the angle bend, shown in Figure 6–1.



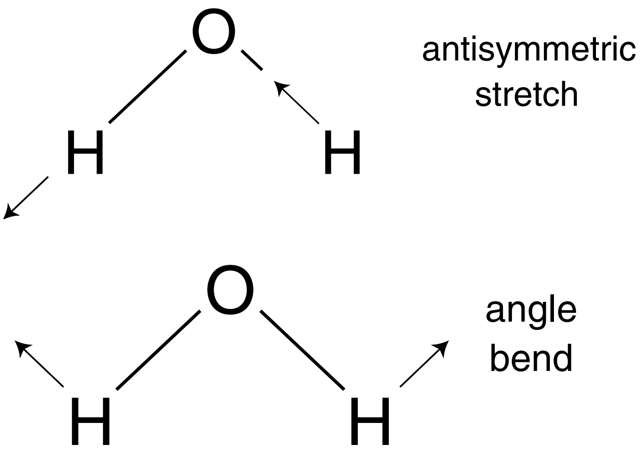


Figure 6.1. Normal modes of vibration of the water molecule.

Although the symmetric stretch and the bend have the full symmetry of the molecule, the antisymmetric stretch does not: the only covering operations of this mode are E and σ'_v. The symmetry group of each normal mode is either the entire symmetry group of the undistorted molecule, or a subgroup.

The electronic states of a diatomic molecule such as H_2 are approximately equal to linear combinations of atomic orbitals. For example, the ground state is approximately proportional to the sum of $1s$ orbitals from the two atoms: $1s_{\mathrm{A}} + 1s_{\mathrm{B}}$. An excited state is approximately proportional to the difference: $1s_{\mathrm{A}} - 1s_{\mathrm{B}}$. Although these LCAO (Linear Combination of Atomic Orbitals) wave functions are not quantitatively correct representations of the true wave functions, their shape, and hence their symmetry, is correct.

The ground state has the full molecular symmetry, but the excited state does not. The symmetry group of the nuclear framework, $\mathrm{D}_{\infty h}$, has the elements: E, C_ϕ (a rotation by ϕ for any angle ϕ), σ_v's at any orientation, the inversion i, S_ϕ for any angle ϕ, and C_2 axes at any orientation in the plane perpendicular to the molecular axis. The symmetry group of the excited state to which $1s_{\mathrm{A}} - 1s_{\mathrm{B}}$ is an approximation contains the elements E, all the C_ϕ's, and all the σ_v's; but *not* the inversion, the S_ϕ's or the equatorial C_2's. The symmetry group of the excited state is therefore $C_{\infty v}$, the symmetry group of a heteronuclear diatomic molecule, and a subgroup of the original group $\mathrm{D}_{\infty h}$. Again, the possible symmetries of the states correspond either to the full symmetry of the nuclear framework or to a subgroup.

These examples suggest the correct result: The possible symmetry types, either for normal modes or electronic wave functions, that are compatible with an overall molecular symmetry, correspond to the full molecular symmetry group or its subgroups. Each normal mode, or electronic state, can be classified as a *symmetry species,* according to the group that describes its symmetry. Therefore it will be useful to prepare, for each molecular symmetry group, a roster of subgroups.

Another fact suggested by the examples is that not every subgroup of the original group need have an associated normal mode or electronic state. Thus there were two normal modes of water with full C_{2v} symmetry and none having C_2 symmetry. It will be useful to have computational tools for predicting which symmetry species will correspond to normal modes or electronic states, and how many; and which symmetry species will not occur.

It has turned out that the most concise description of the symmetry species compatible with a molecular point group, that still includes enough information for useful predictions, is the group character table. The character table of a group is a list of the traces of sets of matrices that form groups isomorphic to the group or to one of its subgroups.

6.2 Group representations

A representation of a symmetry group is a set of square matrices, all of the same dimension, corresponding to the elements of the group, such that multiplication of the matrices is consistent with the multiplication table of the group. That is, the product of matrices corresponding to two elements of the group corresponds to that element of the group equal to the product of the two group elements in the group itself. Representations can be of any dimension; 1×1 arrays are of course just ordinary numbers.

Problems 3–2 and 5–18 contain examples of representations.

If each group element corresponds to a different matrix, the representation is said to be *faithful.* A faithful representation is a matrix group that is isomorphic to the group being represented.

If the same matrix corresponds to more than one group element, the representation, the representation is called *unfaithful.* Unfaithful representations of any group are available by assigning the number 1 to every element, or by assigning the identity matrix of some dimension to every element. (But the number 1 is a *faithful* representation of the group C_1.) The collection of matrices occurring in an unfaithful representation of a group, if taken each only once, forms a group isomorphic to a *subgroup* of the original group. Thus to any unfaithful representation of a group there corresponds a faithful representation of a subgroup.

Examples of group representations:

	Group	Operation		Representation
1.	C_1	E	$\leftrightarrow$	1
2.	C_2	E	$\leftrightarrow$	1
		C_2	$\leftrightarrow$	-1
3.	C_2	E	$\leftrightarrow$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
		C_2	$\leftrightarrow$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
4.	C_3	E	$\leftrightarrow$	1
		C_3	$\leftrightarrow$	1
		C_3^2	$\leftrightarrow$	1
5.	C_3	E	$\leftrightarrow$	1
		C_3	$\leftrightarrow$	ω_1 or ω_2
		C_3^2	$\leftrightarrow$	ω_2 or ω_1
				where $\omega_1 = -\frac{1}{2} + i\frac{\sqrt{3}}{2}, \quad \omega_2 = -\frac{1}{2} - i\frac{\sqrt{3}}{2}$.
6.	C_3	E	$\leftrightarrow$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
		C_3	$\leftrightarrow$	$\begin{pmatrix} \cos\frac{2\pi}{3} & \sin\frac{2\pi}{3} \\ -\sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} \end{pmatrix}$
		C_3^2	$\leftrightarrow$	$\begin{pmatrix} \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} \\ \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} \end{pmatrix}$
7.	C_{2v}	E	$\leftrightarrow$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
		C_2	$\leftrightarrow$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
		σ_v	$\leftrightarrow$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
		σ_v'	$\leftrightarrow$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
8.	C_{2v}	E	$\leftrightarrow$	1 or 1 or 1
		C_2	$\leftrightarrow$	-1 $\quad -1$ $\quad 1$
		σ_v	$\leftrightarrow$	-1 $\quad 1$ $\quad 1$
		σ_v'	$\leftrightarrow$	1 $\quad -1$ $\quad 1$

Note that the three representations in example 8 are derived from the matrices in example 7 by copying off the corresponding diagonal elements.

Problem 6–1. Show that if a set of matrices $A, B, \ldots$ represents a group, then applying the same similarity transformation to all elements of the group: $A' = S^{-1}AS$, $B' = S^{-1}BS$, $\ldots$ produces another representation of the same group.

It is reasonable to hope to assemble a complete set of representations to provide a full and non-redundant description of the symmetry species compatible with a point group? The problem is that there are far too many representations of any group. On the one hand, matrices in representations derived from expressing symmetry operations in terms of coordinates – as in problem 5–18 – depend on the coordinate system. Thus there are an infinite number of matrix representations of C_{2v} equivalent to example 7, derivable in different coordinate systems. These add no new information, but it is not necessarily easy to recognize that they are related. Even in the cases of representations not derived from geometric models via coordinate systems, an infinite number of other representations are derivable by similarity transformations.

Secondly, there are too many representations available by repeating or combining representations in *block form.* Thus, the representation in Figure 6.2 is different from any of the representations of C_3 in examples 4, 5 or 6, but it contains no new information:

$$E \quad \leftrightarrow \quad \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

continues…

$$C_3 \quad \leftrightarrow \quad \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \omega_1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \cos\frac{2\pi}{3} & \sin\frac{2\pi}{3} & 0 & 0 \\ 0 & 0 & 0 & -\sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \cos\frac{2\pi}{3} & \sin\frac{2\pi}{3} \\ 0 & 0 & 0 & 0 & 0 & -\sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} \end{pmatrix}$$

$$C_3^2 \quad \leftrightarrow \quad \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \omega_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} & 0 & 0 \\ 0 & 0 & 0 & \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} \\ 0 & 0 & 0 & 0 & 0 & \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} \end{pmatrix}$$

Figure 6.2. A reducible representation of C_3. Recall that $\omega_1 = -\frac{1}{2} + i\frac{\sqrt{3}}{2}, \quad \omega_2 = -\frac{1}{2} - i\frac{\sqrt{3}}{2}$.

Matrices such as these for which all elements are zero except for clusters, or blocks, of elements around the diagonal, are said to be in *block form.* In a set of matrices, all in block form *with the same distribution of blocks* of non-zero elements, the blocks can be thought of as independent submatrices. Multiplication of two such matrices preserves the block form, and the value of any element in a block of the product depends only on the elements in the corresponding blocks of the factors.

In the case of the representation of C_3 in Figure 6.2, it is obvious that the matrices are merely combinations of of simpler representations. But if the three matrices were subjected to a similarity transformation, they would no longer be in block form, and it would not be obvious that the representation is composite. Applying the reverse similarity transformation would put the matrices back into block form. If there exists a similarity transformation such that applying it to each matrix in a representation puts every matrix into congruent block form, the representation is said to be *reducible.* If no such similarity transformation exists, the representation is said to be *irreducible.*

The set of irreducible representations forms the complete catalog of the symmetry species compatible with a symmetry group. For a finite group, the number of irreducible representations is no greater than the number of elements of the group. Groups with infinite numbers of elements, such as $C_{\infty v}$ and $D_{\infty h}$ have infinite numbers of irreducible representations.

Problem 6–2. Of the eight examples of representations listed in this section, which are faithful? For each unfaithful representation, which subgroup of the original group does it faithfully represent?

Problem 6–3. Of the eight examples of representations listed at the beginning of this section, which are obviously reducible, and which are obviously irreducible?

Problem 6–4. (a) Multiply the two matrices that represent C_3 and C_3^2. What element of the group does the result represent? (b) If you noticed that $C_3^2 \cdot C_3 = C_3^3 = E$, how could you have avoided the work of calculating the matrix product in part (a)?

Problem 6–5. Consider the symmetry group C_{1h}, with elements E and σ. Choosing a two-dimensional coordinate system such that the $x-$axis is in the mirror plane and the $y-$axis is perpendicular to it gives the following representation of C_{1h} :

$$E = \begin{array}{c} x \rightarrow x \\ y \rightarrow y \end{array} \quad \leftrightarrow \quad \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\sigma = \begin{array}{c} x \rightarrow \ \ x \\ y \rightarrow -y \end{array} \quad \leftrightarrow \quad \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

This representation is in block form, and is obviously reducible. Consider another coordinate system, rotated in the $x - y$ plane by 45°. Verify that in this new coordinate system the formulas giving the effect of σ are $x \rightarrow -y$ and $y \rightarrow -x$. Find the matrix relating the two coordinate systems and verify that a similarity transformation applied to the matrices of this new representation produces the old representation. How does this demonstrate the reducibility of the new representation?

Problem 6–6. A $n \times n$ matrix A in block form containing two blocks of size m and $k = n - m$ satisfies the condition $A_{ij} = 0$ whenever $i > m$ and $j \leq m$, *or* $i < m$ and $j \geq m$. Show that if both A and B are two $n \times n$ matrices in this block form, then $C = A \times B$ has the same property.

6.3 Character tables

To tabulate the properties of symmetry species, it would be useful to work with quantities that are independent of the coordinate system, such as the traces or determinants of the matrices of a representation. But because all symmetry operations are orthogonal transformations, the determinants are all ± 1. The determinants of the matrices of the representations, although independent of the coordinate system, do not contain enough information.

The traces, however, are convenient and adequate representatives of the symmetry species. The character table of a group is a listing of the traces of the matrices forming the sets of irreducible representations of the group.

For example, the character table of C_{2v} appears in reference books as follows:[1]

C_{2v}	E	C_2	σ_v	σ'_v
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

The top line identifies the group and contains headings for the columns associated with each covering operation. The symbols A_1, A_2, B_1 and B_2 are the names of the four symmetry species corresponding to the irreducible representations. The lines of numbers to the right of the symmetry species designations are the traces of the matrices of the representations. In this case, the characters themselves represent the group, albeit unfaithfully. This is not always true.

The symbols for the symmetry species contain a coded description of their symmetry properties:

(a) The letter specifies the dimensionality of the representation:

A or B	one-dimensional
E	two-dimensional
F or T	three-dimensional

(b) For one-dimensional representations, A implies that an object or pattern transforming according to that symmetry species is *symmetric* with respect to the principal axis of rotation, as in the ground state of $H_2^+ \sim 1s^A + 1s^B$. B implies that the object goes into its negative upon rotation.

(c) If the group contains the inversion, symmetry species may be symmetric or antisymmetic under *i.* The letters *g,* for *gerade* (= even), and *u,* for *ungerade* (= odd), appear as subscripts in the symmetry species symbol.
(d) Subscripts 1 or 2 imply, respectively, symmetry or antisymmetry with respect to a subsidiary symmetry element such as a mirror plane or an equatorial dyad axis.
(e) $'$ and $''$ imply symmetry and antisymmetry with respect to a plane of symmetry.

For C_{2v}, the representation A_1 is symmetric with respect to every operation. Such a one-dimensional representation, in which every element is assigned the number 1, occurs for every group, and is called the *totally symmetric representation.* Two representations are symmetric with respect to C_2; each is denoted A. Two are symmetric with respect to σ_v, and are given a subscript 1; the representations antisymmetric with respect to σ_v bear the subscript 2. Because this suffices to give each symmetry species a unique symbol, $'$ and $''$ need not be used in this case.

Because the trace of a matrix is independent of the coordinate system, matrices representing operations that have the same effect in different coordinate systems must have the same trace. It is possible to use this fact to abbreviate the character tables. For example, consider the long and short versions of the character table of C_{3v} :

Long version:

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
A_1	1	1	1	1	1	1
A_2	1	1	1	−1	−1	−1
E	2	−1	−1	0	0	0

Short version:

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

The coefficient of the symmetry element, in the top line, tells how many different equivalent operations of this type occur. However, not all symmetry elements of the same type are always equivalent. Thus, in the symmetry group of benzene, the thirteen C_2 operations fall into three distinct classes: the one dyad perpendicular to the molecular plane, the six that pass through opposite atoms in the ring, and the six that pass in between the atoms, through the centers of the bonds. Each of these operations is equivalent only to the others within the same class.

Consider for example the abbreviated form of the character table of D_{3h}:

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	1	1	-1	1
A_1''	1	-1	1	-1	1	-1
A_2''	1	-1	1	-1	-1	1
E'	2	2	-1	-1	0	0
E''	2	-2	-1	1	0	0

In this table all one-dimensional representations are symmetrical with respect to C_3, the principal axis, so all are designated A. Subscripts 1 and 2 refer to the operations C_2', and $'$ and $''$ refer to σ_h.

Note that because the identity operation must always be represented by the identity matrix, the trace of the matrix representing the identity is equal to the dimensionality of the representation.

Problem 6–7. Analyze the symbols for the symmetry species of D_{3h}, making sure you understand the components of the symbol and the transformation properties.

Problem 6–8. Cyclopropane, C_3H_3, has D_{3h} symmetry. What is the symmetry species of a molecular orbital approximately equal to $2s_A + 2s_B + 2s_C$? ($2s_A$ is a 1s orbital centered on atom A, etc.) What is the symmetry species of a molecular orbital of the form $2p_{\pi A} + 2p_{\pi B} + 2p_{\pi C}$?

6.4 Properties of character tables

There are certain general properties of character tables that will be useful in applications. The number of representations of a given dimension is usually determined by two rules:

(a) The number of irreducible representations is equal to the number of classes – the number of sets of equivalent elements – of the group.

(b) The sum of the squares of the dimensions of the irreducible representations is equal to the total number of elements in the group (for groups with finite numbers of elements, *not* $C_{\infty v}$ or $D_{\infty h}$).

An extremely useful mode of calculation with characters arises from considering the characters of any representation as a vector. Thus the four character vectors of C_{2v} are:

$$\begin{array}{lcrrrr} A_1 & = & (1, & 1, & 1, & 1) \\ A_2 & = & (1, & 1, & -1, & -1) \\ B_1 & = & (1, & -1, & 1, & -1) \\ B_2 & = & (1, & -1, & 1, & -1) \end{array}$$

Then if Γ is the character vector of any irreducible representation of any group:
(c) $\Gamma \cdot \Gamma =$ the number of elements of the group (Finite groups),
and for any *two* character vectors Γ_1 and Γ_2 :
(d) $\Gamma_1 \cdot \Gamma_2 = 0$. (Finite *and* infinite groups.)

These rules apply to the *long* forms of the character tables, so that in applying them using the abbreviated forms, due account must be taken of the number of elements in each class.

The mutual orthogonality of the character vectors is reminiscent of the axes of a Cartesian coordinate system, and suggests the valuable idea that the character vectors of a group form a *basis* for the symmetry. Any vector can be *resolved into components of different symmetry types.* The projection of any vector onto any symmetry species is calculable. So we have returned to the geometrical point of view!

Problem 6–9. Verify rules (a), (b), (c) and (d) for the character systems of C_{2v}, C_3, and D_{3h}, using the character tables in the preceding section.

6.5 Calculations with character tables

Analysis of symmetry

One application of character tables is the identification of the symmetry species of given objects. For example, what is the symmetry species of a displacement Δz in the positive z direction in the symmetry group C_{2v}, assuming that the C_2 axis is along z?

All four operations take the displacement vector Δz into itself:

$$\begin{aligned} E\Delta z &= 1\Delta z \\ C_2\Delta z &= 1\Delta z \\ \sigma_v\Delta z &= 1\Delta z \\ \sigma_v'\Delta z &= 1\Delta z \end{aligned}$$

The four numbers on the right-hand sides of these equations, $(1, 1, 1, 1)$, are the character vector for the totally-symmetric representation A_1. Accordingly, we say that Δz transforms as A_1 in C_{2v}.

Bases for representations

If a set of objects is such that operation on any of them by any element of a group produces a linear combination of the same set of elements, then the operations can be expressed in terms of a set of matrices that represent the group. Such a set of objects is said to form a *basis* for the representation. Thus Δz forms a basis for the representation A_1 of C_{2v}.

Displacements along x and y form a basis for a two-dimensional representation of D_{3h} :

$$E\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}=\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}\qquad \chi(E)=2$$

$$\sigma_h\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}=\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}\qquad \chi(\sigma_h)=2$$

(Note that σ_h alters only z if the C_3 axis is taken along the $z-$axis).

$$C_3\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}=\begin{pmatrix}\cos\frac{2\pi}{3}&\sin\frac{2\pi}{3}\\-\sin\frac{2\pi}{3}&\cos\frac{2\pi}{3}\end{pmatrix}\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}\qquad \chi(C_3)=2\cos\tfrac{2\pi}{3}=-1$$

$$S_3\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}=C_3\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}\qquad \chi(S_3)=-1$$

One possible axis for the C_2' operations is the $x-$axis itself – the others are 120° away. For this choice,

$$C_2'\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}=\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}\qquad \chi(C_2')=0$$

A possible orientation of σ_v is in the x–z plane:

$$\sigma_v\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}=\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}\Delta x\\ \Delta y\end{pmatrix}\qquad \chi(\sigma_v)=0$$

This character vector, $\Gamma = (\,2,\quad 2,\quad -1\quad -1,\quad 0,\quad 0\,)$, identifies E' as the symmetry species of the pair (x, y).

With a little practice, such identification of symmetry species will become easy. For example, in the case just considered, as soon as it is recognized that all the operations take x and y into linear combinations of themselves, the inference is immediate that the representation is two-dimensional. The only two-dimensional representations are E' and E''. To select the correct one, we need check only a single operation for which the characters in E' and E'' are different – σ_h or S_3. σ_h is the easier to check. Since x and y are symmetric under σ_h, $\chi(\sigma_h) = 2$ and the symmetry species is E'.

Similar analysis assigns a symmetry species to rotations about the three coordinate axes: R_x, R_y and R_z. These may be visualized as directed loops around the axes. A symmetry operation that reverses the *sense* of the rotation is said to take the rotation into its negative. Thus in C_{2v}, $ER_x = +R_x$, $C_2R_x = -R_x$, and $\sigma_vR_x = -R_x$ and $\sigma_v'R_x = +R_x$. Remember that the molecular plane is the y–z plane. The character vector is $(\,1\quad -1\quad -1\quad 1\,)$; therefore R_x transforms according to symmetry species B_2.

The symmetry species of translations and rotations are used so frequently that they are generally included in the character tables.

Problem 6–10. Verify that displacements along x and y transform according to symmetry species B_1 and B_2, respectively, in C_{2v}, provided that the molecular plane is taken to be the $y - z$ plane.

Problem 6–11. Verify that R_y and R_z transform according to symmetry species B_1 and A_2, respectively, in C_{2v}.

Problem 6–12. According to which symmetry species do x, y, z, R_x, R_y and R_z transform in D_{3h}, if the principal axis is along the $z-$axis?

Notes

1 Character tables for point groups are available on the Web.
See: http://www.mpip-mainz.mpg.de/∼gelessus/group.html

Chapter 7

MOLECULAR VIBRATIONS

7.1 Introduction

Molecular vibrations provide important information about molecular structures and energetics.

Vibrational frequencies give insight into the nature of the forces responsible for chemical binding. Typical force constants for stretching of chemical bonds are in the range $5 - 20 \times 10^{-8}$ newton/Ångstrom.

The energy that a molecule can take up in vibrational motion contributes to the heat capacity and other thermodynamic properties. The specific heats of crystalline solids, predominantly vibrational in origin, are of great historical importance. The law of Dulong and Petit, dating from 1819, stated that the specific heats of solids approximates 6 cal/deg·mole. *First,* this law provided a means of estimating atomic weights of metals. *Next,* the successful explanation of this law was an important test of the classic kinetic theory, and the law of equipartition of energy. *Then,* the *deviations* from the law observed at low temperature gave important clues to the quantum-mechanical nature of matter – the theory of specific heats of solids by Einstein (1907) and Debye (1912) are also landmarks in the history of physics.

The excitation of molecular vibrations by light produces the phenomena of infrared and Raman spectra. Measurements of these spectra have become standard techniques for analysis of chemical structures; and, through the measurements of force constants, for calculation of the thermodynamic properties of molecules.

Problem 7–1. Consider the following table of force constants:

Molecule	Force constant for bond stretching	
H_2	5.3	$\times 10^{-8}$ newton/Å
O_2	11.7	
N_2	22.7	
HCl	4.9	
CO	18.8	
Cl_2	3.3	

What general conclusions can you draw with respect to the dependence of force constant on (a) the type of bonding: ionic or covalent, and (b) the number of pairs of electrons participating in a bond; that is, single, double, or triple bonding?

Problem 7–2. What type of bond is found in the carbon monoxide molecule, CO? This molecule is very slightly polar; but, surprisingly, the negative end of the molecule is the *carbon* atom. (Why is this surprising?) Compare the force constant of CO with that of a molecule with a typical double bond, O_2, and with that of a molecule with a typical triple bond, N_2. Suggest a reasonable qualitative description of the electronic structure of CO that explains these observations.

7.2 Classical description of molecular vibrations

The dynamical problem to be solved in describing molecular vibrations is analogous to the calculation of the motion of a set of masses connected by springs. The equations of motion can be stated, according to classical mechanics, by applying Newton's second law to a set of atoms acted on by forces acting counter to displacements from a set of equilibrium positions.

The force on any atom depends on the positions of *all* the atoms. When the atoms are all at their equilibrium positions, all displacements are zero, and all forces vanish. If the restoring forces are strong relative to available energies, all displacements will remain small, and the following approximations are justified:

(a) The contributions to the force on each atom may be regarded as a sum of independent contributions from individual components of individual displacements, ignoring the effect of one displacement on the forces associated with any other.

For example, for water, the $x-$component of the force on the oxygen atom F_x^{O}, is the sum of 9 independent contributions from each component of the displacement of each of the three atoms. In general, if there are N atoms in a molecule, each force component is a sum of $3N$ terms.
(b) The magnitude of the components of the restoring forces are approximately linearly proportional to the displacements of the atom *exerting* the restoring force.

A typical contribution to the restoring force – for example, the contribution to the $x-$component of the force on the oxygen atom, arising from the $y-$component of the displacement of one of the hydrogen atoms – then takes the form: $-F_{x,y}^{\mathrm{O,H_1}} y_{\mathrm{H_1}}$. (To avoid proliferation of symbols, here x, y, and z rather than Δx, Δy, and Δz represent the *displacements* of an atom from its equilibrium position.) The largest terms are of course expected to be those of involving displacements of the atom itself, such as $-F_{z,z}^{\mathrm{O,O}} z_{\mathrm{O}}$, the $z-$component of the force on the oxygen atom arising from the $z-$displacement of the oxygen atom.

If the atoms are numbered from 1 to N, the x-components of the force on the i^{th} atom is:

$$F_x^i = -\sum_j (F_{xx}^{ij} x_j + F_{xy}^{ij} y_j + F_{xz}^{ij} z_j)$$

Problem 7-3. Write analogous expressions for F_y^i and F_z^i, the y and z components of the force on the i^{th} atom.

To achieve a still more abbreviated notation, let us write $(x_i, y_i, z_i) = (x_1^i, x_2^i, x_3^i)$. Then we can replace the three terms in x, y, and z with a summation over components i from 1 to 3 :

$$F_x^i = F_1^i = -\sum_{k=1}^{N} \sum_{j=1}^{3} F_{1k}^{ij} x_k^j$$

or, in general:

$$F_\ell^i = -\sum_{k=1}^{N} \sum_{j=1}^{3} F_{\ell k}^{ij} x_k^j$$

This equation is sufficiently complex that it is worth stating in words: The ℓ^{th} component of the restoring force on the i^{th} atom is a sum, over the components k of the displacements of the atoms j, of terms proportional to the displacement x_k^j. The proportionality constant is $F_{\ell k}^{ij}$.

Finally, these equations can be written in matrix form: $\mathbf{F} = -\mathcal{F}\mathbf{x}$, in which the force vector $\mathbf{F} = (F_x^1, F_y^1, F_z^1, F_x^2, F_y^2, F_z^2, \ldots F_x^N, F_y^N, F_z^N)$, and the displacement vector $\mathbf{x} = (x_1, y_1, z_1, x_2, y_2, z_2, \ldots x_N, y_N, z_N)$ or $(x_1^1, y_1^1, z_1^1, x_1^2, y_1^2, z_1^2, \ldots x_1^N, y_1^N, z_1^N)$, and the elements of $\mathcal{F}$ are the force constants $F_{\ell k}^{ij}$. As a consequence of Newton's third law, $F_{\ell k}^{ij} = F_{k\ell}^{ji}$, so that the matrix $\mathcal{F}$ is symmetric.

Problem 7–3. Get a large piece of paper and write out the force equation for H_2O, in the form of two nine-vectors and a nine-by-nine matrix. Which values in this matrix are expected to be the smallest?

Problem 7–4. For CO_2, structure O=C=O, consider the independent force constants expressing the proportionalities of the components of restoring forces to displacements along the molecular axis, taken to be z: F_{zz}^{OO}, F_{zz}^{CC}, F_{zz}^{OC}, and $F_{zz}^{\mathrm{OO}'}$. Estimate the *relative* magnitudes of these numbers and arrange them in expected order from largest to smallest.

Applying Newton's second law to this force field:

$$\begin{aligned} m_i \ddot{x}_\ell^i &= F_\ell \\ m_i \ddot{x}_\ell^i &= -\sum_{k=1}^{3}\sum_{j=1}^{N} F_{\ell k}^{ij} x_k^\ell \end{aligned}$$

or, in matrix form:

$$\mathbf{m}\ddot{\mathbf{x}} = -\mathcal{F}X$$

in which the vector $\mathbf{m}\ddot{\mathbf{x}}$ has components of the form $m_i \ddot{x}_\ell^i$. This is a system of coupled linear differential equations.

A clue to the kinds of solutions to expect from this type of system of equations is available from the simple case of a single equation in the same form: $m\ddot{x} = -Fx$. The function $x(t) = X\cos\omega t$ is a solution, because $\dot{x} = \omega X\sin\omega t$ and $\ddot{x} = -\omega^2 X\cos\omega t = -\omega^2 X$. Substituting this in the differential equation produces:

$$-m\omega^2 X = -FX \qquad \text{or} \qquad (F - m\omega^2)X = 0$$

There can be a solution with non-zero amplitude (that is, $X \neq 0$), only if ω is equal to $\sqrt{F/m}$. The system can execute periodic motions only for a unique frequency.

7.3 Eigenvalue problems

Returning to the full system of equations, we expect the modes of molecular vibration to appear as periodic solutions of the form:

$$x_\ell^i = X_\ell^i \cos \omega t$$

where the X_ℓ^i are constants specifying the relative amplitudes of the atomic displacements. Substituting $x_\ell^i = X_\ell^i \cos \omega t$, and $\ddot{x}_\ell^i = -\omega^2 X_\ell^i \cos \omega t$, the system of equations that must be satisfied is:

$$\begin{aligned} -\omega^2 m_i X_\ell^i &= -\sum_{k=1}^{3}\sum_{j=1}^{N} F_{\ell k}^{ij} X_k^j && \text{or} \\ \sum_{k=1}^{3}\sum_{j=1}^{N}[F_{\ell k}^{ij} - \omega^2 m_j \delta_{ij}]X_k^j &= 0 && \text{or, in matrix form,} \\ (\mathcal{F} - \omega^2 \mathbf{M})\mathbf{X} &= 0 \end{aligned}$$

in which $\mathbf{M}$ is a diagonal matrix, $M_{ij} = m_i \delta_{ij} = m_i$ if $i = j$ and 0 if $i \neq j$.

This form of equation is called a *secular equation.*

For every choice of ω, this is a system of linear equations to be solved for the X_k^j. Although $X_k^j = 0$ for all j and k will always satisfy the system of equations, for some values of ω there may be additional, non-trivial solutions.

Problem 7–5. Consider the two-dimensional system of equations:

$$\begin{aligned} ax + by &= 0 \\ cx + dy &= 0 \end{aligned}$$

or, in matrix form:

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Prove that if $\det \begin{pmatrix} a & b \\ c & d \end{pmatrix} = ad - bc \neq 0$, then the only solution of the system of equations is the trivial one: $x = y = 0$. [Hint: Multiply the first equation by c and the second by a, and subtract them; verify the result: $(bc - ad)y = 0$. This implies that if $y \neq 0$, $bc - ad = 0$. Hence, there can be a solution of the simultaneous equations for which $y \neq 0$ *only* if $bd - ac = 0$. Show analogously that $(ad - bc)x = 0$.]

Problem 7–6. Consider the same question from the point of view of matrix algebra. If the inverse of $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ exists, multiply both sides of the equation by the inverse, and conclude that for any solution, $\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} \begin{pmatrix} 0 \\ 0 \end{pmatrix}$. Evaluate x and y, and conclude again that if $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ has an inverse, $x = y = 0$ is the only solution.
Why is this criterion for the existence of a non-trivial solution equivalent to the one in Problem 7–5?

In general, a matrix equation in the form $\mathbf{A} \cdot \mathbf{x} = \mathbf{0}$ will have solutions other than $\mathbf{x} = \mathbf{0}$ only if $\det\ \mathbf{A} = 0$. In the case of vibrations, there will be non-trivial solutions only if $\det(\mathcal{F} - \omega^2\mathbf{M}) = 0$. This is an example of an *eigenvalue* problem.

Problem 7–7. Find the *eigenvalues* of the matrix $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$: These are by definition the numbers ω that satisfy the equation $\det\begin{pmatrix} a-\omega & b \\ c & d-\omega \end{pmatrix} = 0$. How many of them are there? What are the conditions on the matrix elements a, b, c and d to ensure that all the eigenvalues are real numbers?

For any real value of ω for which $\det(\mathcal{F} - \omega^2\mathbf{M}) = 0$, there will be a solution of $(\mathcal{F} - \omega^2\mathbf{M})X = 0$ for which $X \neq 0$. This solution will consist of a set of amplitudes X^i_ℓ, such that there exists a motion of the nuclei of frequency ω. The displacements of any atom at any time are $X^i_\ell \cos \omega t$. If $\omega = 0$, the motion will be non-periodic – a combination of translation and rotation. If $\omega \neq 0$, the motion will be periodic – a vibration. Any such motion is called a *normal mode* of vibration of the system.

A normal mode is to be thought of as a collective motion of the system of nuclei, much as a choreographed passage in a ballet is a collective motion of the *corps.*

The important characteristics of normal modes that make them so useful in describing vibrational motions are:
(a) Excitation of any normal mode is independent of the excitation of other normal modes. That is, provided the mathematical assumptions of low energy are valid, energy will not be transferred from one mode to another.

(b) A molecule has only a finite number of normal modes of vibration. For a linear molecule with N atoms there are $3N - 5$; for a non-linear molecule there are $3N - 6$. Any vibrational motion may validly be regarded as a superposition of the normal modes of vibration.
(c) The displacements defining any normal mode must transform according to one of the irreducible representations of the symmetry group of the molecule with the nuclei in the equilibrium position.

The simplest illustration of molecular vibration is a homonuclear diatomic molecule, which can vibrate in only one direction – parallel to its internuclear axis. If the coordinates of the nuclei are x_1 and x_2; the force matrix equation relating restoring forces to displacements is:

$$\begin{pmatrix} F_x^1 \\ F_x^2 \end{pmatrix} = \begin{pmatrix} -k & k \\ k & -k \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

in which k is the force constant for bond stretching. The equations of motion are:

$$\begin{pmatrix} m\ddot{x}_1 \\ m\ddot{x}_2 \end{pmatrix} = \begin{pmatrix} -k & k \\ k & -k \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

where m is the mass of either nucleus. These equations will have non-trivial solutions of the form $x_i = X_i \cos \omega t, i = 1, 2$; only if:

$$\begin{pmatrix} -k - m\omega^2 & k \\ k & -k - m\omega^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$

which requires that:

$$\det \begin{pmatrix} -k - m\omega^2 & k \\ k & -k - m\omega^2 \end{pmatrix} = 0$$

The value of the determinant is $(-k - m\omega^2)^2 - k^2$. It will be zero only if $-k - m\omega^2 = \pm k$; or $\omega = 0,\ \omega = \sqrt{2k/m}$.

Let us solve for the amplitudes in each of these cases:
(a) $\omega = 0$

$$\begin{pmatrix} -k & +k \\ +k & -k \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = 0$$

This is equivalent to $k(x_1 - x_2) = 0$, implying that the displacements $x_1 = x_2 =$ any real constant. The physical interpretation of this result is that there is a mode of motion that is non-periodic, because $\omega = 0$; and in which both nuclei move in tandem, since $x_1 - x_2 =$ a constant. This is a *translation* parallel to the internuclear axis. Of course in reality there are also translational motions in the two directions perpendicular to the molecular axis; these, and rotations, are other possible motions of the molecule. We did not put them into the equations (no y or z), so they do not come out of the equations.

(b) $\omega^2 = 2k/m, -k - m\omega^2 = +k$

$$\begin{pmatrix} +k & +k \\ +k & +k \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = 0$$

This is equivalent to $+k(x_1 + x_2) = 0$, or $x_1 = -x_2$. This is a periodic motion, of frequency $\sqrt{2k/m}$, in which the displacements of the atoms are exactly *out* of phase. This is the *vibration.*

The solution of the eigenvalue equation has *automatically* given us the desired decomposition of the motion of this simple system.

Problem 7–8. Consider the case of a *heteronuclear* diatomic molecule constrained to move in one dimension. Let the masses of the nuclei be denoted by m and M, and the force constant by k. Set up and solve the secular equation: determine that the allowed modes of motion are the overall translation and vibration. Determine the vibrational frequency in terms of m, M and k.

7.4 Determination of the symmetries of the normal modes

Any displacement of the atoms in a molecule can be described in terms of displacements in Cartesian coordinate systems centered at each atom. Thus, for water we may imagine three sets of axes, originating at the equilibrium positions of each of the three atoms, as shown in Figure 7.1.

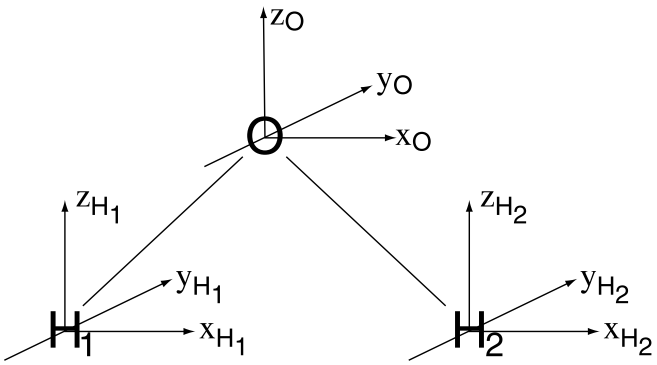


Figure 7.1. Coordinate systems fixed on each atom of the water molecule.

Then the vector $(x_{\mathrm{H}_1}, y_{\mathrm{H}_1}, z_{\mathrm{H}_1})$ specifies the displacement of one of the hydrogen atoms, and $(x_{\mathrm{O}}, y_{\mathrm{O}}, z_{\mathrm{O}})$ and $(x_{\mathrm{H}_2}, y_{\mathrm{H}_2}, z_{\mathrm{H}_2})$ the displacements of the other atoms. We may combine these three 3-component vectors into one 9-component vector:

$$(x_{\mathrm{H}_1}, y_{\mathrm{H}_1}, z_{\mathrm{H}_1}, x_{\mathrm{O}}, y_{\mathrm{O}}, z_{\mathrm{O}}, x_{\mathrm{H}_2}, y_{\mathrm{H}_2}, z_{\mathrm{H}_2})$$

to describe the displacement of all three atoms at once.

Since any general displacement is a superposition of translational, rotational and vibrational displacements it is possible to redescribe the motion of the molecule in terms of overall translations and rotations, and the normal modes of vibration. Using the character tables, it is possible to decompose the symmetry of the general displacement into the symmetries of the different types of motion.

Consider the effect of the operations of C_{2v} on the vector of displacements. The identity, of course, has no effect on any displacement: $Ex_i = x_i$. The rotation C_2 leaves unchanged only the component z_{O}. Its full effect is as follows:

$$\begin{array}{rcrcrcrcrcr}
C_2 x_{\mathrm{H}_1} & = & -x_{\mathrm{H}_2} & \quad & C_2 x_{\mathrm{O}} & = & -x_{\mathrm{O}} & \quad & C_2 x_{\mathrm{H}_2} & = & -x_{\mathrm{H}_1} \\
C_2 y_{\mathrm{H}_1} & = & -y_{\mathrm{H}_2} & & C_2 y_{\mathrm{O}} & = & -y_{\mathrm{O}} & & C_2 y_{\mathrm{H}_2} & = & -y_{\mathrm{H}_1} \\
C_2 z_{\mathrm{H}_1} & = & z_{\mathrm{H}_2} & & C_2 z_{\mathrm{O}} & = & z_{\mathrm{O}} & & C_2 z_{\mathrm{H}_2} & = & z_{\mathrm{H}_1}
\end{array}$$

These results may be summarized in matrix form:

$$C_2 \begin{pmatrix} x_{\mathrm{H}_1} \\ y_{\mathrm{H}_1} \\ z_{\mathrm{H}_1} \\ x_{\mathrm{O}} \\ y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ x_{\mathrm{H}_2} \\ y_{\mathrm{H}_2} \\ z_{\mathrm{H}_2} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_{\mathrm{H}_1} \\ y_{\mathrm{H}_1} \\ z_{\mathrm{H}_1} \\ x_{\mathrm{O}} \\ y_{\mathrm{O}} \\ z_{\mathrm{O}} \\ x_{\mathrm{H}_2} \\ y_{\mathrm{H}_2} \\ z_{\mathrm{H}_2} \end{pmatrix}$$

Problem 7–9. Verify the effect of C_2 on the displacements. Determine the matrices specifying the effects of σ_v and σ_v' on the displacements.

This procedure generates a representation of the group C_{2v}, called Γ_{tot}, for which the vector of displacements forms the basis. The character of the operation C_2 in Γ_{tot} is the trace of the matrix representing C_2; it has the value -1.

Because the traces contain sufficient information to decompose Γ_{tot} into irreducible representations, it is necessary to compute only the diagonal elements of the matrices of the representation. If a particular atom changes position under a symmetry operation, its displacements can contribute no diagonal elements to the matrix; therefore, for that symmetry operation, such an atom may be ignored. For example, the displacements of the *hydrogen* atoms in water do not contribute to the character of C_2 in Γ_{tot}. The displacement of H_1 means that the elements $(1,1)$, $(2,2)$ and $(3,3)$ of the matrix are zero.

This suggests a simple rule for the calculation of the characters of the matrices in Γ_{tot}: Each displacement that is taken into itself contributes $+1$ to the character of the operation; each displacement that is taken into its negative contributes -1; and all displacements of atoms that change position contribute 0.

Problem 7–10. Verify that this rule correctly predicts that $\chi(E) = 9$ and $\chi(C_2) = -1$. Compute $\chi(\sigma_v)$ and $\chi(\sigma_v')$.

Problem 7–11. Will this rule always work? If not, under what circumstances will it be valid? Can you suggest a more general rule that will always work?

The character vector of Γ_{tot} is $(\,9 \quad -1 \quad 1 \quad 3\,)$. Γ_{tot} is not an irreducible representation of C_{2v}, but it can be resolved into irreducible components, using the character vectors of the irreducible representations as a basis. The number of times a particular irreducible representation is contained in Γ_{tot} is equal to the dot product of $\Gamma_{\text{tot}} = (\,9 \quad -1 \quad 1 \quad 3\,)$ with the character vector of the irreducible representation, divided by the number of elements of the group. This statement is a consequence of the orthogonality relations for characters, stated in section 6–4, which originally suggested the metaphor of treating the characters of the irreducible representations as vectors.

Applying the orthogonality relations:

$$\begin{aligned}
\frac{1}{4}(\Gamma_{\text{tot}} \cdot \mathrm{A}_1) &= \frac{1}{4}(9 \times 1 \;+\; -1 \times 1 \;+\; 1 \times \;\; 1 \;+\; 3 \times \;\; 1) = 3 \\
\frac{1}{4}(\Gamma_{\text{tot}} \cdot \mathrm{A}_2) &= \frac{1}{4}(9 \times 1 \;+\; -1 \times 1 \;+\; 1 \times -1 \;+\; 3 \times -1) = 1
\end{aligned}$$

Problem 7–12. Verify that $\frac{1}{4}(\Gamma_{\text{tot}} \cdot \mathrm{B}_1) = 2$, and that $\frac{1}{4}(\Gamma_{\text{tot}} \cdot \mathrm{B}_2) = 3$.

The resolution of the reducible representation Γ_{tot} into its irreducible components is:

$$\Gamma_{\text{tot}} = 3\mathrm{A}_1 + \mathrm{A}_2 + 2\mathrm{B}_1 + 3\mathrm{B}_2$$

Any displacement of the nuclei in the water molecule is a superposition of motions of the symmetry species comprising Γ_{tot}.

Subtracting the symmetries of the translational and rotational motions leaves the symmetries of the normal modes of vibration. For C_{2v}, the symmetries of translations and rotations are: $\begin{array}{cccccc} T_x & T_y & T_z & R_x & R_y & R_z \\ \mathrm{B}_1 & \mathrm{B}_2 & \mathrm{A}_1 & \mathrm{B}_2 & \mathrm{B}_1 & \mathrm{A}_2 \end{array}$ (see section 6.5) Therefore, removing these from Γ_{tot}:

$$\Gamma_{\text{vibration}} = 2\mathrm{A}_1 + \mathrm{B}_2.$$

The conclusion is that the three normal modes of vibration of the water molecule are of symmetry species $\mathrm{A}_1, \mathrm{A}_1$ and B_2.

Problem 7–13. Determine the symmetry species of the normal modes of vibration of the cyclopropilium cation, $\mathrm{C}_3\mathrm{H}_3^+$. This molecule is planar and has D_{3h} symmetry.

Problem 7–14. Determine the symmetry species of the normal modes of cyclopropane.

7.5 Use of internal coordinates

The set of displacements used to generate the reducible representation Γ_{tot} is not the only possible basis. A particular type of coordinate that simplifies the calculation of normal modes is a set of *internal* coordinates.

Whereas the coordinates used in the previous section describe displacements of nuclei relative to axes fixed in space, internal coordinates describe displacements of nuclei relative to one another.

For the water molecule, a reasonable set of internal coordinates would be the lengths of the O–H bonds – let us call them r_1 and r_2 – and the H–O–H angle, θ. Displacements of these coordinates form a basis for a reducible representation of C_{2v} that is composed of symmetry species of vibrational motions only.

To compute the character vector of the representation generated, apply the same rule that was used to compute the characters of Γ_{tot}. Under E, all three displacements in internal coordinates are unchanged, so that $\chi(E) = 3$. C_2 leaves the angle bend unchanged, contributing 1 to the character, but takes the displacement associated with r_1 into that associated with r_2, and *vice versa.* Therefore $\chi(C_2) = 1$. Similarly, $\chi(\sigma_v) = 1$ and $\chi(\sigma_v') = 3$.

The character vector $\Gamma_{\text{vibrational}} = (3\ 1\ 1\ 3)$ may now be reduced as before, giving $\Gamma_{\text{vibrational}} = 2\text{A}_1 + \text{B}_2$ as expected.

Problem 7–15. Verify for the displacements that $\chi(\sigma_v) = 1$ and that $\chi(\sigma_v') = 3$

Problem 7–16. Verify by decomposing $\Gamma_{\text{vibrational}} = (3\ 1\ 1\ 3)$ that $\Gamma_{\text{vibrational}} = 2\text{A}_1 + \text{B}_2$.

Problem 7–17. Compute the symmetry species of the normal modes of vibration of CH_3 (symmetry group D_{3h}) using internal coordinates.

Problem 7–18. Set up and solve the secular equation for the normal modes of water in internal coordinates.

Chapter 8

ELECTRONIC STRUCTURE OF ATOMS AND MOLECULES

8.1 The quantum-mechanical background

In the quantum-mechanical description of atoms and molecules, electrons have characteristics of waves as well as particles. In the familiar case of the hydrogen atom, the orbitals $1s, 2s, 2p, \ldots$ describe the different possible "standing wave" patterns of electron distribution, for a single electron moving in the potential field of a proton. The motion of the electrons in any atom or molecule is described as fully as possibly by a set of wave functions associated with the ground and excited states.

The hydrogen atom orbitals are functions of three variables; the coordinates of the electron. Their physical interpretation is that the square of the amplitude of the wave function at any point is proportional to the probability of finding a particle at that point. Mathematically, the electron density distribution is equal to the square of the absolute value of the wave function:

$$\rho(x, y, z) = |\psi(x, y, z)|^2$$

In this way the notion of a delocalized electron or electron cloud follows naturally from the wave-like characterization of the electron.

In addition to their spatial coordinates, electrons are characterized by a spin, described by a coordinate s, which can have two discrete values, usually called "up" and "down." Wave functions for a system containing more than one electron are analogous functions of the coordinates of all the electrons:

$$\psi(x_1, y_1, z_1, s_1, x_2, y_2, z_2, s_2 \ldots x_n, y_n, z_n, s_n).$$

The equation that must be solved to determine a wave function is the Schrödinger equation:

$$\mathcal{H}\psi = \mathcal{E}\psi$$

Here ψ is the wave function, $\mathcal{E}$ is the value of the energy; and $\mathcal{H}$ is the Hamiltonian *operator.* The Hamiltonian is the sum of the quantum-mechanical expressions for the kinetic and potential energies of the system.

The mathematical notion of an *operator* may be unfamiliar: it is a rule for modifying a function. A comparison of the ideas of operator and function may be useful: Whereas a function acts to take an argument, called the independent variable, as input, and produces a value, called the dependent variable; an operator takes a *function* as input and produces a function as output. Multiplication of a function by a constant, taking a square or square root, differentiation or integration, are examples of *operators.* Table 8.1 contains examples of functions and operators.

Table 8.1. Comparison of functions and operators

Function	*Input (a number)*	*Output (a number)*
square	3	9
	1	1
	-5	25
multiply by 4	3	12
	1	4
	-5	-20

Operator	*Input (a function)*	*Output (a function)*
square	$f(x) = x$	$g(x) = x^2$
	$f(x) = 3x$	$g(x) = 9x^2$
	$f(x) = x^2$	$g(x) = x^4$
	$f(x) = x - 2$	$g(x) = x^2 - 4x + 4$
multiply by 4	$f(x) = x$	$g(x) = 4x$
	$f(x) = 3x$	$g(x) = 12x$
	$f(x) = x^2$	$g(x) = 4x^2$
	$f(x) = x - 2$	$g(x) = 4x - 8$
differentiate	$f(x) = x$	$g(x) = 1$
	$f(x) = 3x$	$g(x) = 3$
	$f(x) = x^2$	$g(x) = 2x$
	$f(x) = x - 2$	$g(x) = 1$

An operator L is called *linear* if for any two functions f_1 and f_2, and any number a,

$$L(f_1 + f_2) = Lf_1 + Lf_2 \quad \text{and} \quad L(af) = a(Lf)$$

A fundamental principle of quantum mechanics states that any physically observable quantity corresponds to a linear operator.

Problem 8–1. Which of the operators in Table 8.1 are linear?

The expression $\mathcal{H}\psi$ in the Schrödinger equation is the function resulting from the application of the operator $\mathcal{H}$ to the function ψ. A verbal statement of the Schrödinger equation is: the function resulting from the application of $\mathcal{H}$ to ψ must be the same as the function resulting from multiplying ψ by a constant $\mathcal{E}$. Usually both the function ψ and the number $\mathcal{E}$ are unknown, and the Schrödinger equation is solved for both simultaneously.

The Hamiltonian for the electrons in an atom or molecule is the sum of terms in kinetic and potential energies: $\mathcal{H}$ = T + V. The kinetic energy operator for a particle of mass m is $\mathrm{T} = -\frac{h^2}{8\pi^2 m}\nabla^2$, in which the Laplacian operator $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

T is called a *differential operator.* The potential energy operator V contains expressions for the Coulomb forces among and between the nuclei and electrons. For the hydrogen atom, containing only one pair of particles, V$= -e^2/r$, in which e is the absolute value of the charge of the electron and r the distance from electron to proton. The effect of V on a function ψ is simply to multiply ψ by $-e^2/r$. V is called a *multiplicative operator*.

The Schrödinger equation for the hydrogen atom is:

$$-\frac{h^2}{8\pi^2 m}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] - \frac{e^2}{r}\psi = \mathcal{E}\psi$$

Note that, in the absence of a magnetic field, the terms in the Schrödinger equation depend only on the spatial coordinates of the electron, not on the spin. This is a second-order partial differential equation. Inasmuch as it describes a set of wave patterns, one might suspect that meaningful solutions might exist only for certain allowed values of $\mathcal{E}$, corresponding to “resonant frequencies.” It is this property of the Schrödinger equations for atomic and molecular electrons that leads to the correct prediction of discrete values of allowed energy levels observed in atomic and molecular spectroscopy.

A characteristic of such an equation is that it has solutions only for certain values of a parameter, just as in the case of the matrix equations for determining vibrational frequencies (see section 7.3). A value for $\mathcal{E}$ for which a solution to the Schrödinger equation exists is called an *eigenvalue,* and the solution ψ is called an *eigenfunction.*

Problem 8–2. The wave function corresponding to the ground state of the hydrogen atom is proportional to e^{-r}. Verify that $\psi = e^{-r}$ is a solution of the Schrödinger equation for the hydrogen atom. Find the value of $\mathcal{E}$, equal to the binding energy of the hydrogen atom, in terms of m, h and e. Hint: it will be easier to evaluate ∇^2 in spherical polar coordinates: r, θ, ϕ. Because e^{-r} has no angular variation, use the formula $\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial\psi}{\partial r})$ (+ terms that are zero if $\frac{\partial\psi}{\partial\theta} = \frac{\partial\psi}{\partial\phi} = 0$).

Problem 8–3. A hydrogen-like ion is an atomic ion containing only one electron, for example, He^{+}, Li^{2+} ... Write down the Schrödinger equation for a general hydrogen-like ion, of nuclear charge Z. Compare with the Schrödinger equation for the hydrogen atom itself, and try to guess a wave function ψ_Z and energy $\mathcal{E}_Z$ that are solutions. Choose a form of ψ_Z that reduces to e^{-r} when $Z = 1$. How should the binding energy in this series depend on Z?

The Schrödinger equations for many-electron systems are generalizations of the one-electron problem. The wave function is a function of the space and spin coordinates of all the electrons:

$$\psi(x_1, y_1, z_1, s_1, x_2, y_2, z_2, s_2 \ldots x_N, y_N, z_N, s_N).$$

The kinetic energy operator T is the sum of the kinetic energies of the individual electrons:

$$\mathrm{T} = \sum_i -\frac{h^2}{8\pi^2 m}\nabla_i^2 = \sum_i -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x_i^2} + \frac{\partial^2\psi}{\partial y_i^2} + \frac{\partial^2\psi}{\partial z_i^2}\right)$$

The result of the operation of T on ψ is the sum of $3n$ terms of the form $-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x_i^2}$. The potential energy V will be a sum of the Coulomb potentials over all pairs of particles.

The hydrogen molecule, H$_2$, has two nuclei, A and B, and two electrons, referred to as 1 and 2. The potential energy is the sum of the repulsion between the two nuclei, the attractions of the electrons to the nuclei and the repulsion between electrons:

$$V = \frac{e^2}{R_{\mathrm{AB}}} - \frac{e^2}{r_{1\mathrm{A}}} - \frac{e^2}{r_{1\mathrm{B}}} - \frac{e^2}{r_{2\mathrm{A}}} - \frac{e^2}{r_{2\mathrm{B}}} + \frac{e^2}{r_{12}}$$

A general molecular system contains n electrons, indexed by $i = 1, 2 \ldots n$; and M nuclei indexed by $A = 1 \ldots M$. Let Z_A denote the atomic number of nucleus A, and R_{AB}, r_{iA} and r_{ij} the distances from the nucleus A to nucleus B, from electron i to nucleus A, and from electron i to electron j, respectively. For example, $r_{iA} = \sqrt{(x_i - X_A)^2 + (y_i - Y_A)^2 + (z_i - Z_A)^2}$. Note that symbols referring to nuclei are capitalized, and those referring to electrons are lower case.

The Hamiltonian operator for the electrons of the system, assuming fixed nuclei, is:

$$\begin{aligned}\mathcal{H} &= T + V \\ &= -\sum_{i=1}^{n} \frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) + \\ &\sum_{\substack{A=1 \\ A<B}}^{M} \sum_{B=1}^{M} \frac{Z_A Z_B e^2}{R_{AB}} - \sum_{A=1}^{M} \sum_{i=1}^{n} \frac{Z_A e^2}{r_{iA}} + \sum_{\substack{i=1 \\ i<j}}^{n} \sum_{j=1}^{n} \frac{e^2}{r_{ij}}\end{aligned}$$

The conditions $A < B$ and $i < j$ are imposed on the summations so that each pair of particles will be counted only once.

In the absence of a magnetic field, the spin does not appear explicitly. We shall see that electron spin constrains the solutions of the many-electron Schrödinger equation as a condition on the symmetry of the wave function with respect to exchange of electrons.

Problem 8–4. What is the Schrödinger equation for the Helium atom?

Problem 8–5. Is the wave function $\psi(r_1, r_2) = e^{-2r_1 - 2r_2}$ a solution of the Schrödinger equation for Helium?

Problem 8–6. What is the Schrödinger equation for Beryllium Hydride, BeH_2?

8.2 Symmetry properties of wave functions

The importance of symmetry in the study of the electronic structure of atoms and molecules depends on the fact that wave functions must transform according to one of the symmetry species of the symmetry group of the molecule. Stated precisely, the eigenfunctions of a Hamiltonian form bases for irreducible representations of the symmetry group of the Hamiltonian. This principle allows wave functions to be classified according to symmetry species; it assists in constructing eigenfunctions of a Hamiltonian; and it aids in the prediction and analysis of spectra.

The application of any symmetry operation to the nuclear framework of an atom or molecule does not alter the Hamiltonian, because a symmetry operation produces an identical distribution of the positive charges that create the potential in which the electrons move. Thus any covering operation of the nuclear framework of an atom or molecule corresponds to an element of the symmetry group of the Hamiltonian. Applying any covering operation of the Hamiltonian to *both* the Hamiltonian and to an eigenfunction corresponds merely to changing the indices of identical particles, the nuclei, and thus must maintain the validity of the Schrödinger equation:

$$\text{If } \mathcal{H}\psi = \mathcal{E}\psi, \qquad (S\mathcal{H})(S\psi) = \mathcal{E}(S\psi)$$

But if S is a symmetry operation of the nuclei, then

$$S\mathcal{H} = \mathcal{H},$$

and

$$\mathcal{H}(S\psi) = \mathcal{E}(S\psi),$$

showing that $S\psi$ is also an eigenfunction of $\mathcal{H}$, with the same eigenfunction $\mathcal{E}$.

Thus, given an eigenfunction of an atomic or molecular Hamiltonian, the operations of the symmetry group of the nuclei generate additional eigenfunctions of $\mathcal{H}$ with the same eigenvalue. Of course, there are no guarantees that there will be as many independent eigenfunctions as there are elements of the group. On one hand, if the eigenfunctions have some of the same symmetry elements as the Hamiltonian, these common symmetry operations will generate no new eigenfunctions. On the other hand, if there is more than one eigenfunction with a given eigenvalue, it will be impossible to generate all possible eigenfunctions with the same eigenvalue by a finite number of symmetry operations. For even if there are only two independent eigenfunctions ψ_1 and ψ_2 with the eigenvalue $\mathcal{E}$, then, because $\mathcal{H}$ is a *linear* operator, all linear combinations of the form $a_1\psi_1 + a_2\psi_2$ are also eigenfunctions, with the same eigenvalue:

$$\mathcal{H}(a_1\psi_1 + a_2\psi_2) = \mathcal{E}(a_1\psi_1 + a_2\psi_2)$$

Problem 8–7. Show that the preceding equation follows from the properties of linear operators.

For the symmetry groups of nonlinear molecules, it should be expected that for any eigenvalue $\mathcal{E}$, there are only a small finite number of linearly independent eigenfunctions $\varphi_1, \varphi_2 \ldots \varphi_n$. That is, for every function ψ such that $\mathcal{H}\psi = \mathcal{E}\psi$, it should be possible to express ψ as a linear combination: $\psi = a_1\varphi_1 + a_2\varphi_2 \ldots + a_n\varphi_n$ for some set of constants $a_1, \ldots a_n$. Thus there is a good analogy between these basis functions and coordinate axes. Like coordinate axes, the choice of basis functions $\varphi_1, \ldots \varphi_n$ is not unique.

The statement that $\varphi_1, \ldots \varphi_n$ forms a complete set of linear independent eigenfunctions of $\mathcal{H}$ with eigenvalue $\mathcal{E}$ is equivalent to the following formulas:

- $\mathcal{H}\varphi_i = \mathcal{E}\varphi_i$ for $i = 1, \ldots n$. (The φ_i are eigenfunctions of $\mathcal{H}$ with eigenvalue $\mathcal{E}$.)
- If $\mathcal{H}\psi = \mathcal{E}\psi, \psi = a_1\varphi_1 + a_2\varphi_2 \ldots + a_n\varphi_n$ (any eigenfunction with the same eigenvalue is a linear combination of the φ_j or, the set is *complete).*
- $\varphi_i \neq a_1\varphi_1 + a_2\varphi_2 \ldots + a_{i-1}\varphi_{i-1} + a_{i+1}\varphi_{i+1} + \ldots + a_n\varphi_n$. (None of the φ_i can be represented as a linear combination of the *others;* or, the set is *linearly independent.*)

Such a set of eigenfunctions must form the basis for a representation of the symmetry group of the Hamiltonian, because for every symmetry operation S, $\mathcal{H}\varphi_i = \mathcal{E}\varphi_i$ implies that $\mathcal{H}(S\varphi_i) = \mathcal{E}(S\varphi_i)$ and hence that the transformed wave function $S\varphi_i$ must be a linear combination of the basic set of eigenfunctions $\varphi_1, \ldots \varphi_n$.

This representation will almost always be irreducible. The most famous of the exceptional cases is the hydrogen atom: One linearly independent set of eigenfunctions corresponding to the eigenvalue $\mathcal{R}/4$ ($\mathcal{R}$ is the Rydberg constant) is the set of *four* orbitals corresponding to the states $2s, 2p_{-1}, 2p_0$ and $2p_1$; but these form a basis for a *reducible* representation of the obvious symmetry group of the hydrogen atom. The representation that they generate is reducible to the sum of a one-dimensional representation for which the $2s$ orbital is a basis, and a three-dimensional one for which the $2p$ orbitals form a basis.

The reason that these eigenfunctions form a basis for a reducible representation is that there is no operation of the apparent symmetry group of the hydrogen atom that transforms a $2p$ orbital into a $2s$ orbital. However it was pointed out in 1935 by Fock and Bargmann, independently, that the true symmetry group of the Hamiltonian of the hydrogen atom is not the group corresponding to the spherical symmetry of the potential, but a larger group. The eigenfunctions of the hydrogen atom form bases for *irreducible* representations of the larger group.

8.3 Molecular wave functions

Although computer technology and programming are now sufficiently advanced that the wave functions and properties of atoms and small molecules can be calculated to an accuracy adequate for detailed comparison with experiments, it is nevertheless worthwhile to consider some of the more important types of approximate molecular wave functions. The degree of success of these approximations provides a diagnostic probe of the essential features of the chemical bond. Also, approximate wave functions suggest simplifying concepts, in many cases adequate to describe and predict the major qualitative features of molecular electronic structure and spectra.

8.3.1 Properties of the exact wave functions

The wave functions describing the electronic states of a many-electron atom or molecule are functions of all the coordinates of all the electrons:

$$\psi(x_1, y_1, z_1, s_1, x_2, y_2, z_2, s_2 \ldots x_n, y_n, z_n, s_n).$$

Wave functions for ground and excited states satisfy the Schrödinger equation: $\mathcal{H}\psi_i = \mathcal{E}_i\psi_i$. The square of the absolute value of ψ gives the probability of finding electrons at any point specified by the arguments x_i, y_i, z_i.

The form of the wave function is restricted by the indistinguishability of different electrons. For example, consider two two-electron wave functions:

$$\psi_\mathrm{A}(x_1, y_1, z_1, s_1, x_2, y_2, z_2, s_2) \qquad \text{and}$$

$$\psi_\mathrm{B}(x_1, y_1, z_1, s_1, x_2, y_2, z_2, s_2) = \psi_\mathrm{A}(x_2, y_2, z_2, s_2, x_1, y_1, z_1, s_1)$$

ψ_B is related to ψ_A by exchange of the space and spin coordinates of both electrons. If ψ_A describes a state of two electrons, then ψ_B must describe the same physical state, because the electrons cannot be individually labeled. (Old physicists' adage: “You can't paint electrons red.”) But if both ψ_A and ψ_B describe the same physical state then $|\psi_\mathrm{A}|^2 = |\psi_\mathrm{B}|^2$. Note that it is not necessary for ψ_A to be equal to ψ_B, because any physically observable property of the system will be independent of the sign of ψ. The wave function itself cannot be measured.

It is a characteristic of electrons, that $\psi_\mathrm{A} = -\psi_\mathrm{B}$. Any wave function for electrons must be *antisymmetric* with respect to an exchange of any two electrons. This is the point at which the electron spin enters the symmetry-constrained properties of solutions of the Schrödinger equation.

Problem 8–8. Verify that any wave function for two particles. $\psi(r_1, r_2)$ can be written as a term *symmetric* with respect to exchange of particles and a term *antisymmetric* with respect to exchange of particles, as follows:

$$\psi(r_1, r_2) = \underbrace{\frac{1}{2}\left[\psi(r_1, r_2) + \psi(r_2, r_1)\right]}_{\text{symmetric}} + \underbrace{\frac{1}{2}\left[\psi(r_1, r_2) - \psi(r_2, r_1)\right]}_{\text{antisymmetric}}$$

Problem 8–9. If a two-particle wave function has the form of a *product* $\psi(r_1, r_2) = \phi(r_1)\phi(r_2)$, show that the antisymmetric component of ψ may be written as the determinant of a matrix the elements of which are functions:

$$\det \begin{vmatrix} \phi_1(r_1) & \phi_1(r_2) \\ \phi_2(r_1) & \phi_2(r_2) \end{vmatrix}$$

Problem 8–10. Show that any real functions $f(x, y)$ and $g(x, y)$ satisfying the equation $|f(x, y)|^2 = |g(x, y)|^2$ form a basis for a representation of the permutation group of two objects.

Problem 8–11. Generalize the preceding problem to three variables.

8.3.2 The Hartree-Fock approximation

The *Hartree-Fock* or *self-consistent-field* approximation is a simplification useful in the treatment of systems containing more than one electron. It is motivated partly by the fact that the results of Hartree-Fock calculations are the most precise that still allow the notion of an *orbital,* or a state of a single electron. The results of a Hartree-Fock calculation are interpretable in terms of individual probability distributions for each electron, distinguished by characteristic sizes, shapes and symmetry properties. This pictorial analysis of atomic and molecular wave functions makes possible the understanding and prediction of structures, spectra and reactivities.

Computationally, the simplification introduced by the Hartree-Fock approximation concerns the expression for the component of the potential energy resulting from the repulsion between electrons. These terms in the Hamiltonian depend on the instantaneous positions of all the electrons, because the energy of repulsion between two electrons is inversely proportional to the distance between them.

However, keeping track of the positions of all the electrons all the time is a complicated task. The electron-electron repulsion terms in the potential field in which any electron is moving are constantly changing, because the electrons are in motion relative to one another.

It is simpler to consider the electric field produced by the *distribution* of an electron in an orbital; or, in effect, a time-averaged potential. Adopting this point of view, each electron moves as if in a *static* potential produced by the nucleus and the time-averaged distibutions of the other electrons. As each electron moves in the field of the other electrons, it creates by its own distribution a field affecting the motions of each of the others. Thus the motions of all the electrons are coupled delicately: the term self-consistent field indicates the requirement that all the individual electron distributions must produce the proper potentials for one another's motion.

How accurate are the energies determined by means of the Hartree-Fock approximation? The error, the difference between the Hartree-Fock energy and the exact energy, is called the *correlation energy,* because it arises from neglect of the instantaneous relative motions, or correlation, of the electrons. Correlation energies for atoms are found to be less than 1.5% of total energies. Although this sounds pretty good (though nowhere near the precision of spectroscopic data), it is unfortunately the case that molecular binding energies are also of about this magnitude – so that unless there is good cancellation of the correlation error when subtracting the computed energies of the consitutent atoms from the computed energy of the molecule, the binding energy predicted from Hartree-Fock calculations may be disappointing.

Consider the Nitrogen molecule, N_2. The computed Hartree-Fock energies of atom and diatomic molecule are -54.50 a.u. and -108.99 a.u. respectively, predicting a binding energy of $108.99 - 2 \times 54.40 = 0.19$ a.u. (The atomic unit of energy, or a.u., sometimes called the Hartree, is defined as half the binding energy of the hydrogen atom. 1 a.u. $=$ 27.210 e.v. $=$ 2625.5 kJ/mole.) In fact, the experimental energies of atomic and molecular Nitrogen are -54.61 a.u. and -109.58 a.u., and the experimental binding energy is 0.36 a.u. A more radical case is the Fluorine molecule, in which the correlation error in the atom is so great that the Hartree-Fock approximation does not even predict a stable molecule! (The experimental binding energy of F_2 is 158.78 kJ/mole.)

Note that the final step in computing molecular binding energies involves calculating a small difference between two large numbers, an operation that necessitates great precision in the total energies.

A solution of the equations arising in the Hartree-Fock approximation takes the form of a set of *spin-orbitals* – each consisting of a function of coordinates x, y, and z describing the spatial distribution of a single electron and an indicator of the orientation of the electron spin, usually called "up" and "down." In the *restricted* Hartree-Fock approximation, in which each orbital is *doubly occupied,* the spin-orbitals occur in pairs, both of which have the same spatial part but one of which has spin "up" and the other spin "down." It is the Pauli exclusion principle, a consequence of the necessary antisymmetry of the wave function to electron exchange, that precludes occupancy of the identical spin-orbital by more than one electron, and the laws governing the quantization of angular momentum that restrict the electron spin to have no more than two possible orientations.

The overall many-electron wave function is formed from the Hartree-Fock orbitals as an antisymmetrized product. If the individual spin orbitals are $\varphi_1(r, s)$, $\varphi_2(r, s)$, $\ldots \varphi_n(r, s)$, the overall wave function $\psi(r_1, s_1, r_2, s_2 \ldots r_n,\ s_n)$ is the component of the product $\varphi_1(r_1, s_1)\varphi_2(r_2, s_2) \ldots \varphi_n(r_n, s_n)$ that is antisymmetric with respect to interchange of any pair of electrons.

8.3.3 The Linear Combination of Atomic Orbitals (LCAO) approximation

Several lines of evidence suggest that the states of electrons in molecules are closely related to the states of electron in the free atoms from which the molecules are constructed. First, typical molecular binding energies are a very small fraction of the total binding energies of atoms, so that the formation of a chemical bond should be regarded as a small perturbation of the structure of an atom. For example, the binding energy of the N_2 molecule relative to two Nitrogen atoms is less than 0.5% of the total binding energy, 109.58 atomic units, relative to the fully ionized state of the two separated atoms.

Additional experimental evidence for the preservation of electronic states upon formation of molecules is the insensitivity of X-ray spectra to the chemical environment of an atom, implying that the ionization potentials of inner electrons are relatively unaffected by bonding. Indeed, Moseley's classic experiments on the relationship between X-ray frequencies and atomic number were carried out on atoms in a variety of states of chemical combination.

These facts should not be surprising. The potential field in which electrons move is largest in the immediate vicinity of the nuclei – but in the immediate vicinity of any nucleus the portion of the potential arising from *that* nucleus is much larger than the contributions from the other nuclei. In other words, in the regions of high potential the potential is approximately equal to the potential in a free atom.

These considerations suggest that it might be useful to approximate molecular orbitals as sums of atomic orbitals. Thus for the hydrogen molecule ion H_2^+, a one-electron system, one could consider a wave function – based on the exact orbitals for the separated atoms – of the form $e^{-r_\mathrm{A}} + e^{-r_\mathrm{B}}$, in which r_A and r_B are the distances from any point in space to the two nuclei, as illustrated in Figure 8.1. Recall that e^{-r_A} and e^{-r_B} are the exact solutions for each of the free atoms. Therefore, the wave function $e^{-r_\mathrm{A}} + e^{-r_\mathrm{B}}$ should be asymptotically correct at very large internuclear separations $R_{AB} \to \infty$.

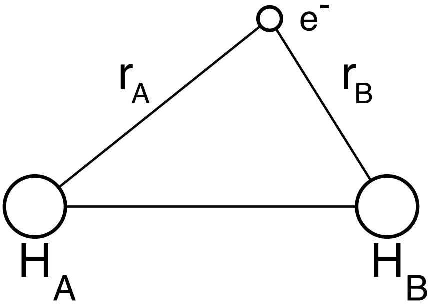


Figure 8.1. The hydrogen molecule ion, H_2^+.

8.4 Expectation values and the variation theorem

Although these approximate wave functions look promising, it is not clear how to test them quantitatively. The Schrödinger equation $\mathcal{H}\psi = \mathcal{E}\psi$ tells us only that the measurement of the energy of a system in a state described by an eigenfunction ψ will give the corresponding eigenvalue $\mathcal{E}$ as the result.

If a system is in a state described by a wave function $\psi(x_1, y_1, z_1, s_1 \ldots x_n, y_n, z_n, s_n)$ that is *not* an eigenfunction of the Hamiltonian, measurements of the energy will give variable results. An expression for the average, or *expectation value,* of the energy measurements is the integral:

$$\frac{\int \psi^* \mathcal{H}\psi \, dx_1 \, dy_1 \, dz_1 \, \ldots \, dx_n \, dy_n \, dz_n}{\int \psi^* \psi \, dx_1 \, dy_1 \, dz_1 \, \ldots \, dx_n \, dy_n \, dz_n}$$

in which ψ^* is the complex conjugate of ψ, and $\psi^*\mathcal{H}\psi$ is the *function* produced by multiplying ψ^* by the function resulting from applying H to ψ. A standard abbreviation for such integrals is:

$$(f, g) = \int f^* g \, dV$$

In this notation, the expectation value of the energy is:

$$\frac{(\psi, \mathcal{H}\psi)}{(\psi, \psi)}$$

Problem 8–12. Verify that if ψ is an eigenfunction of H with eigenvalue $\mathcal{E}$, then the expectation value of the energy is equal to $\mathcal{E}$. The expression (f, g) is called the *inner product off and g.* It has a number of properties analogous to those of the dot product of two vectors. These are illustrated in Table 8.2.

Table 8.2. Analogies between inner product of two vectors and inner product of two functions.

	Property	Vectors	Functions
1.	Definition	$\vec{v} \cdot \vec{w} = \sum_i v_i w_i$	$(f, g) = \int f^* g \, dV$
2.	Linearity upon multiplication by real numbers c, d	$c\vec{v} \cdot d\vec{w} = (cd)\vec{v} \cdot \vec{w}$	$(cf, dg) = cd(f, g)$
3.	nonnegativity of self inner product	$\vec{v} \cdot \vec{v} = \parallel \vec{v} \parallel^2 \geq 0$	$(f, f) = \int \lvert f \rvert^2 \, dV \geq 0$

Problem 8–13. This analogy between inner products of functions and of vectors can be pursued further. Suggest reasonable definitions for (a) the norm of a function, $\parallel f \parallel$, (b) a normalized function, and (c) the cosine of the angle between two functions.

The inner product of two orbitals is sometimes called the *overlap,* the name suggesting the extent to which the orbitals occupy the same region of space; it provides a measure of how closely two functions resemble each other. In particular:

1 The overlap of any normalized wave function with itself is 1.

2 There is a relationship between the overlap of two normalized functions and their mean-squared difference:

$$\int |f - g|^2 \, dV = 2\left(1 - \int f^* g \, dV\right)^2$$

or, in vector notation:

$$\parallel f - g \parallel^2 = 2\,[1 - (f, g)]^2$$

3 The overlap of any two normalized wave functions is less than or equal to 1, with equality holding *only* if the functions are identical.

Problem 8–14. Prove these three properties of orbital overlap.

If the correct wave function and energy are known, there are two ways to assess an approximate wave function:

1 Calculate the difference between the expectation value of the energy given by the approximate wave function and the known true energy, or

2 Calculate the overlap between the approximate wave function and the known true wave function.

If the correct energy values and wave functions are not known, it is not possible to measure the error of an approximate wave function, with respect to energy or to overlap.

However, an important result known as the *variation theorem* ensures that the expectation value of the energy computed with any wave function must be greater than the lowest eigenvalue of the Hamiltonian. For example, the lowest eigenvalue of the Hamiltonian of the hydrogen atom is $-\frac{1}{2}$ atomic units. The variation theorem states that for any normalized function ψ whatsoever, the expectation value $(\psi, \mathcal{H}\psi)$ must be $\geq -\frac{1}{2}$. That is, the expectation value of the energy computed with any trial wave function cannot be *less than* the true ground-state energy.

The conclusions are that: if we are presented with a Hamiltonian for which we do not know the eigenfunctions, and we calculate expectation values of the energy with two or more *approximate* wave functions, we can be sure that the *lowest* calculated expectation value is closest to the true energy. We cannot estimate how far above the true value the results are. Nor can we be sure that the approximate wave function giving the lowest expectation value of the energy has the highest overlap with the true ground state eigenfunction.

Problem 8–15. A normalized hydrogenic $1s$ orbital for a one-electron atom or ion of nuclear charge Z has the form:

$$\psi_Z = \sqrt{\frac{Z^3}{\pi}} e^{-Zr}$$

continues…

Verify that ψ_Z is normalized. The volume integral transformed into spherical coordinates is:

$$\int \psi_Z^*(x,y,z)\;\psi_Z(x,y,z)\;dx\;dy\;dz =$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} \cos\theta d\theta \int_0^{\infty} \psi_Z^*(r)\psi_Z(r)r^2 dr$$

Note that because ψ_Z is independent of the angles θ and ϕ, the integral can be factored into three independent integrals.

Problem 8–16. The $1s$ function with $Z = 1.0$ is an eigenfunction of the Hydrogen atom Hamiltonian $\mathcal{H} = T - 1/r$, (expressed in atomic units.)
To get some idea of the use of trial wave functions and the variation principle, evaluate the expectation value of the energy using the Hydrogen atom Hamiltonian, and normalized $1s$ orbitals with variable Z. That is, evaluate:

$$\mathcal{E}(Z) = (\psi_Z, \left[T - \frac{1}{r}\right] \psi_Z),$$

in which $\psi_Z = \sqrt{\frac{Z^3}{\pi}}e^{-Zr}$. Draw a graph of $\mathcal{E}(Z)$ for values of Z between 0.25 and 4.0. Next, evaluate as a function of Z the overlap of ψ_Z with the *correct* $1s$ wave function for Hydrogen, $\sqrt{\frac{1}{\pi}}e^{-r}$. Draw a graph of the overlap for values of Z between 0.25 and 4.0. What general conclusions can you draw?

Problem 8–17. To show that the general conclusions suggested in the previous example are false, consider the case of the one-dimensional harmonic oscillator, for which $H = T + V = T + \frac{1}{2}kx^2$. The energy levels of the one-dimensional harmonic oscillator with frequency ν are:

$$\mathcal{E}_n = (n + \frac{1}{2})h\nu$$

Denote by φ_n the eigenfunction corresponding to the n^{th} level: $H\varphi_n = \left[(n + \frac{1}{2})h\nu\right]\varphi_n$. The eigenfunctions are orthonormal; that is, $(\varphi_i, \varphi_i) = 1$ for all i, and $(\varphi_i, \varphi_j) = 0$ for $i \neq j$.
Show that for any real number L, no matter how large, and for any real number ε, no matter how small, it is possible to choose numbers a, b, and n so that the trial function $\psi = a\varphi_0 + b\varphi_n$ has these properties:

1 φ is normalized.

2 The overlap of ψ with the true ground state eigenfunction φ_0 is greater than or equal to $1 - \epsilon^2$; that is, the spatial distribution of the trial wave function is a very good approximation to the true wave function, and

3 The expectation value of the energy calculated with ψ is greater than or equal to L.

Problem 8–18. Suppose ψ_1 and ψ_2 are functions of a single variable, defined by:
$\psi_1 = 1$ if $-\frac{1}{2} \leq x \leq \frac{1}{2}$ and 0 otherwise, and
$\psi_2 = 1$ if $-\frac{1}{4} \leq x \leq 1\frac{1}{4}$ and 0 otherwise.
Sketch graphs of ψ_1 and ψ_2. Are ψ_1 and ψ_2 normalized? What is the overlap (ψ_1, ψ_2)? What is the relationship between the overlap integral and the length of the segment of the real line for which *both* ψ_1 and ψ_2 are nonzero? This illustrates the origin and use of the term overlap in the context of molecular orbital theory.

The variation theorem has been an extremely powerful tool in quantum chemistry. One important technique made possible by the variation theorem is the expression of a wave function in terms of variables, the values of which are selected by *minimizing* the expectation value of the energy.

For example, the Hamiltonian for Be^{3+} is $\mathcal{H} = T - 4/r$. If we assume a normalized wave function of the form $\psi_Z = \sqrt{\frac{Z^3}{\pi}} e^{-Zr}$, the expectation value of the energy, in atomic units, is: $\mathcal{E}(Z) = \frac{1}{2}Z^2 - 4Z$. To find the best approximation to the energy available from this class of trial wave functions, we simply take the minimum value of $\mathcal{E}(Z)$; namely, $\mathcal{E} = -8$ a.u. In this case, the corresponding wave function $\sqrt{\frac{64}{\pi}} e^{-4r}$, is the eigenfunction, and the -8 a.u. is the correct energy. In most practical cases, of course, the wave function corresponding to the minimum expectation value of the energy will not be an exact solution.

A standard type of variable used in the definition of an orbital is a set of linear expansion coefficients. Given the basis functions $\varphi_1, \varphi_2, \dots \varphi_n$, a general trial function $\psi = a_1\varphi_1 + a_2\varphi_2 + \dots + a_n\varphi_n$ contains the coefficients $a_1, \dots a_n$ to be determined by minimizing the expectation value of the energy. The equation that determines the values of these coefficients is a secular equation, identical in form to the equation used to determine normal frequencies and normal modes of vibration. In the electronic structure case, determination of the energy levels associated with the linear combinations of a set of basis functions $\varphi_1, \dots \varphi_n$ requires solution of the secular equation

$$\det(H_{ij} - \mathcal{E}S_{ij}) = 0$$

in which $H_{ij} = (\varphi_i, H\varphi_j)$ and $S_{ij} = (\varphi_i, \varphi_j)$.

The lowest root of this secular equation is greater than or equal to the true ground state energy. If the set of basis functions $\varphi_i, \dots \varphi_j$ is general enough, it can be a good approximation to the ground state energy, and the other eigenvalues approximations to the energies of excited states of the system.

Consider for example the LCAO approximation to the ground state of H$_2^+$. Take as basis functions normalized $1s$ orbitals centered on either nucleus:

$$\varphi_1 = \sqrt{\frac{1}{\pi}} e^{-r_A}, \qquad \varphi_2 = \sqrt{\frac{1}{\pi}} e^{-r_B}$$

Here r_A and r_B are the distances from any point in space to the positions of nuclei A and B.

The molecular wave function ψ is a linear combination $\psi = a\varphi_1 + b\varphi_2$, with coefficients a and b to be determined. Because the calculations are independent of the spin coordinates, we omit them. To set up the secular equation we must evaluate the matrix elements H_{ij} and S_{ij}. Because φ_1 and φ_2 are normalized, $S_{11} = (\varphi_1, \varphi_1) = 1 = S_{22}$. Because the basis functions are really two copies of the same function – only centered at different positions in space – some of the matrix elements are equal: $H_{11} = H_{22}$, $H_{12} = H_{21}$, $S_{11} = S_{22} (= 1)$, and $S_{12} = S_{21}$.

The form of the secular equation is then:

$$\det \begin{pmatrix} H_{11} - \mathcal{E} & H_{12} - \mathcal{E}S_{12} \\ H_{12} - \mathcal{E}S_{12} & H_{11} - \mathcal{E} \end{pmatrix} = 0$$

Expanding the determinant gives a quadratic equation for $\mathcal{E}$, with the solutions:

$$\mathcal{E}_+ = \frac{H_{11} + H_{12}}{1 - S_{12}}, \qquad \mathcal{E}_- = \frac{H_{11} - H_{12}}{1 + S_{12}}$$

If $H_{12} < 0$ and $S_{12} > 0$, $\mathcal{E}_+$ is lower than $\mathcal{E}_-$. $\mathcal{E}_+$ represents the best approximation to the ground state energy available from wave functions of the form $a\varphi_1 + b\varphi_2$.

Because H_{11} represents the binding energy of an isolated Hydrogen atom, the predicted binding energy is $\mathcal{E}_+ - H_{11}$.

Problem 8–19. Verify the solution of the secular equation.

Problem 8–20. At the equilibrium internuclear distance, 2.0 a.u., $H_{11} = 0.9726 a.u.$, $H_{12} = -0.6993 a.u.$, $S_{12} = 0.5865 a.u.$ What is the estimated binding energy in atomic units of H_2^+, in this simple LCAO approximation? What percentage of the total binding energy is predicted? The energy of a Hydrogen atom is $-\frac{1}{2}$ a.u. The actual dissociation energy of H_2^+ is 0.6 a.u.

Chapter 9

SYMMETRY PROPERTIES OF MOLECULAR ORBITALS; CORRELATION DIAGRAMS

9.1 Diatomic molecules

Correlation diagrams (not to be confused with correlation energies) are a technique for predicting the symmetries and relative energies of orbitals in a molecule, by means of a comparison with atomic states. In two limiting cases, the *separated atoms* $(R = \infty)$ and the *united atom* $(R = 0)$, atomic orbitals accurately represent molecular orbitals. Correlation diagrams provide a scheme for interpolating between these two limiting cases.

For example, the LCAO molecular orbitals for H_2 are proportional to sums and differences of atomic orbitals: $1s_A + 1s_B$ and $1s_A - 1s_B$.

Although these orbitals are not exact molecular orbitals, they have the proper symmetry. Therefore it is appropriate to regard them as qualitative representatives of the true molecular orbitals, particularly in predictions of phenomena in which symmetry properties play an important role.

If we imagine the nuclei to be forced together to $R = 0$, the wave function $1s_A + 1s_B$ will approach, as a limit, a charge distribution around the united atom that has neither radial nor angular nodal planes. This limiting charge distribution has the same symmetry as the $1s$ orbital on the united atom, Helium. On the other hand, the combination $1s_A - 1s_B$ has a nodal plane perpendicular to the molecular axis at all internuclear separations. Hence its limit in the united atom has the symmetry properties of a $2p$ orbital. A simple correlation diagram for this case is:

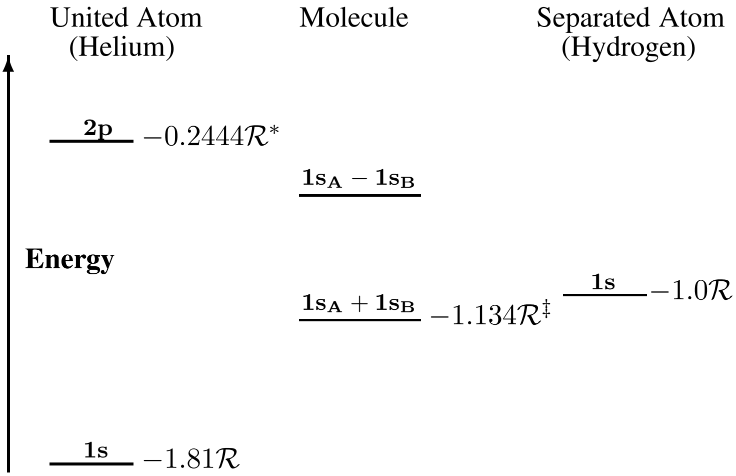


Figure 9.1. Energy level diagram for hydrogen molecule, H_2, and separated atoms H $(R = \infty)$ and He $(R = 0)$. $\mathcal{R}$ = the Rydberg constant = 13.6057 eV = 0.5 a.u. (atomic unit of energy). *Value from ionization potential of He (1s 2p ^{1}P). ‡Value from ionization potential of H_2. The experimental ionization potentials are quite precise; but for systems containing more than one electron their interpretation in terms of orbital energies is an approximation.

The correlation diagram is in effect a graph with internuclear distance R increasing from 0 to ∞ as abscissa, and energy as ordinate. Using experimental values, we can calibrate the graph at $R = 0$, $R =$ the equilibrium internuclear distance, and $R = \infty$.

The diagram suggests, albeit in a crude way, that the $1s_A + 1s_B$ molecular orbital should be bonding, and the $1s_A - 1s_B$ should be antibonding. This leads to the prediction that diatomic molecules containing 2 electrons should be more tightly bound than those containing 1 or 3 electrons, and that examples such as He−He should not be stably bound.

Problem 9–1. The *bond order* of a diatomic molecule is defined as $\frac{1}{2}$[number of electrons in binding orbitals – number of electrons in antibonding orbitals]. Show that the following values are correct:

Number of electrons	1	2	3	4
Bond order	$\frac{1}{2}$	1	$\frac{1}{2}$	0

Relate this to the comment, preceding this problem, about the relative stability of H_2^+, H_2, He_2^+, He_2.

In fact, the measured dissociation energies of appropriate examples of homonuclear diatomic molecules and molecular ions are: H_2^+, 2.648 e.v.; H_2, 4.476 e.v.; He_2^+, 3.1 e.v.; He_2, only slight attraction in the ground electronic state (binding of van der Waals type, at internuclear separations large compared with typical chemical binding energies.)

Although the correlation diagram does not provide good quantitative values for binding energies, it does accurately reveal the spatial symmetries of the wave functions. Because the orbital $1s_A + 1s_B$ is symmetric with respect to inversion and the orbital $1s_A - 1s_B$ is antisymmetric, the ground states of H_2^+ and H_2 are expected to be spatially symmetric and that of He_2^+ is expected to be antisymmetric. This is observed.

To extend the correlation diagram to second-row diatomics (Figure 9.2), let us consider the possible symmetry species associated with the symmetry group of homonuclear diatomics, $D_{\infty h}$.

$D_{\infty h}$	E	$2C_\phi$	C_2'	i	$2iC_\phi$	iC_2'
$A_{1g}(\Sigma_g^+)$	1	1	1	-1	-1	-1
$A_{1u}(\Sigma_u^-)$	1	1	1	1	1	1
$A_{2g}(\Sigma_g^-)$	1	1	-1	1	1	-1
$A_{2u}(\Sigma_u^+)$	1	1	-1	-1	-1	-1
$E_{1g}(\Pi_g)$	2	$2\cos\phi$	0	2	$2\cos\phi$	0
$E_{1u}(\Pi_u)$	2	$2\cos\phi$	0	-2	$-2\cos\phi$	0
$E_{2g}(\Pi_g)$	2	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0
$E_{2u}(\Pi_u)$	2	$2\cos 2\phi$	0	-2	$-2\cos 2\phi$	0

. . . an infinite number of additional
representations exist

In this character table, we have included the spectroscopic symbol for the symmetry type. A molecular orbital, in distinction to a full many-electron wave function, will be identified by a lower case symmetry species. Thus $1s_{\rm A} + 1s_{\rm B}$ is denoted $\rm a_1$.

Problem 9–2. What is the symmetry species of $1s_{\rm A} + 1s_{\rm B}$? What is the symmetry species of $2p_{\pi{\rm A}} + 2p_{\pi{\rm B}}$?

To generate the correlation diagram, let us assemble the states of the united and separated atoms, and connect them according to the rules:

1 The connected states must have the same symmetry in $D_{\infty h}$ over the whole range of internuclear distances. (Recall that angular momentum states s, p, d, … refer to the symmetries of *atomic states*.)

2 States of the same symmetry will not cross. If it appeared that two such states would cross, at the apparent crossing point a secular equation similar to the one appearing at the end of the previous chapter would split them, raising the energy of one orbital and lowering that of the other, preventing the crossing. In fact the secular equation involving the two orbitals in question would be a part of the full secular equation of the system.

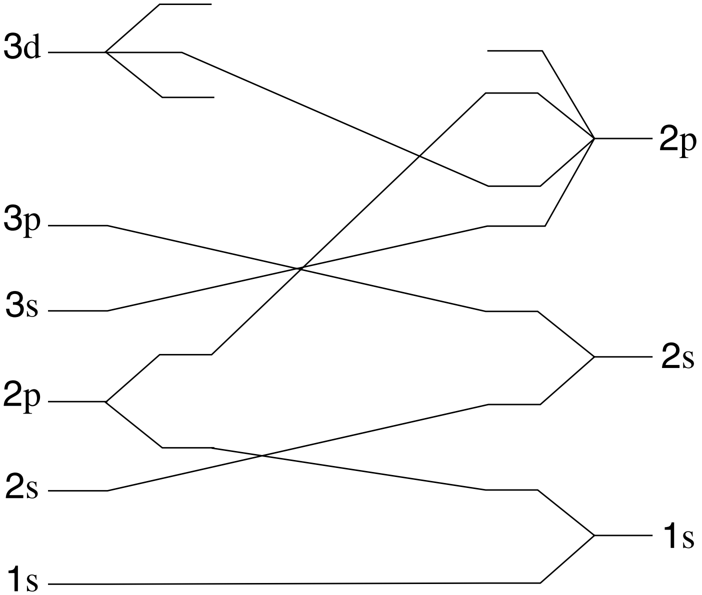


Figure 9.2. Correlation diagram for second-row diatomic molecules. The column on the left shows orbitals for the united atom, those on the right those of the separated atoms.

Problem 9–3. Predict the electron configurations, and the possible symmetry species of the ground states of the second-row diatomics: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, Ne_2.

Problem 9–4. Compute the bond order for these molecules.

9.2 Triatomic molecule – Walsh diagrams

Triatomic molecules are the simplest cases in which there arises a question of predicting the shape. Some triatomic molecules, such as BeH_2, are linear in the ground state; whereas others, such as H_2O, are bent. A correlation technique developed by Walsh permits predictions of whether triatomic molecules and ions should be bent or linear. In this case correlation is made, not between states differing in bond *length* as in the diatomic case, but between states differing in bond *angle*. The Walsh diagrams relate molecular orbitals for the linear – $D_{\infty h}$ – and bent – C_{2v} – geometries.

Walsh analyzed the symmetry species of LCAO molecular orbitals in the linear and bent geometries, and determined how the energies of individual orbitals vary with bond angle. Assuming that orbital energies are approximately additive, this information suffices in most cases to determine the variation with bond angle of the energy of a full electronic configuration. A comparison of the energies of bent and linear structures leads to a prediction of which should be observed.

Walsh diagrams give rules only for the qualitative decision: bent or linear? If a molecule is bent, determination of the exact value of the bond angle requires a detailed calculation.

9.3 Molecular orbitals for the bent AH_2 molecule (C_{2v})

We shall continue to use the standard coordinate system, in which the molecule lies in the yz plane.

The valence orbitals from which the MO's are to be constructed are:

- An s orbital on the central atom: s^A
- Three p orbitals on the central atom: p_x^A, p_y^A, p_z^A
- 1s orbitals on either Hydrogen: s^1, s^2

It is important to appreciate pictorially where the positive and negative parts of the p orbitals are, and which Hydrogen is number 1 and which number 2; as shown in Figure 9.3.

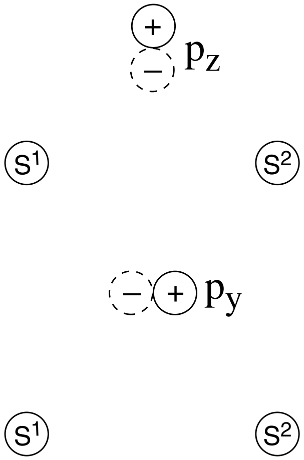


Figure 9.3. Orbital geometry and nomenclature for a bent triatomic molecule. Solid contours indicate regions where the wave function is positive; broken contours indicate regions where the wave function is negative.

To find the symmetry species of the molecular orbitals, we shall construct the representation generated by the six valence orbitals, and reduce it into irreducible components. In the following table, each entry gives the result of applying the operation heading the column, to the orbital at the left of the row.

	E	C_2	σ_v	σ_v'	Symmetry Species
s^A	s^A	s^A	s^A	s^A	a_1
p_x^A	p_x^A	$-p_x^A$	p_x^A	$-p_x^A$	b_1
p_y^A	p_y^A	$-p_y^A$	$-p_y^A$	p_y^A	b_2
p_z^A	p_z^A	p_z^A	p_z^A	p_z^A	a_1
s^1	s^1	s^2	s^2	s^1	$a_1 + b_2$
s^2	s^2	s^1	s^1	s^2	
Γ	6	0	2	4	

Reduction of Γ using the C_{2v} character table shows that:

$$\Gamma = 3A_1 + B_1 + 2B_2$$

in accordance with the last column.

The molecular orbitals of lowest energy that can be formed from these basis orbitals can be described at least roughly as:

φ_1, a bonding orbital, symmetry a_1:	$\varphi_1 = \frac{1}{2}(s^A - p_z^A) + s^1 + s^2$
φ_2, a bonding orbital, symmetry b_2:	$\varphi_2 = p_y^A - s^1 + s^2$
φ_3, a non-bonding orbital, symmetry a_1:	$\varphi_3 = \frac{1}{2}(s^A + p_z^A)$
φ_4, a non-bonding orbital, symmetry b_1:	$\varphi_4 = p_x^A$

Problem 9–5. Verify the entries in the table on p. 88.

Problem 9–6. Verify the reduction $\Gamma = 3A_1 + B_1 + 2B_2$ (p. 88).

Problem 9–7. In his original paper, Walsh started with the following basis:
An s orbital on the central atom: s^A
A p orbital on the central atom, oriented perpendicular to the molecular plane.
Two p orbitals, oriented along the bond directions:

$$p^1 = \frac{1}{\sqrt{2}}(p_y + p_z) \text{ and } p^2 = \frac{1}{\sqrt{2}}(p_y - p_z)$$

The sum and difference of the hydrogen $1s$ orbitals:

$$s^1 + s^2 \text{ and } s^1 - s^2$$

Construct the analog of Figure 9.3 for Walsh's basis set. Show that the representation generated by the new basis has the same components upon reduction as the old representation.

Problem 9–8. Sketch the shapes of the four molecular orbitals φ_1, φ_2, φ_3, φ_4.

Problem 9–9. What other molecular orbitals could be formed from the basis orbitals? Why are they expected to have higher energies?

Problem 9–10. How, qualitatively, might the exact Hartree-Fock orbitals for a bent AH_2 molecule differ these simple LCAO molecular orbitals?

Problem 9–11. Verify the assignments of symmetry species of the basis orbitals.

Problem 9–12. Sketch the shapes of these orbitals.

9.4 Molecular orbitals for the linear AH_2 molecule ($D_{\infty h}$)

In order to be consistent with the bent case, let us call the molecular axis the y axis. The valence orbitals then have the following symmetry species:

s^1	a_{1g}
p_x^A, p_z^A	e_{1u}
p_y^A	a_{2u}
$s^1 + s^2$	a_{1g}
$s^1 - s^2$	a_{2u}

The molecular orbitals of lowest energy that can be formed from these basis orbitals correspond to sums of basis orbitals of the same symmetry species, *containing no nodal planes between the atoms.* These are:

ψ_1, a bonding orbital, symmetry a_{1g}

$$\psi_1 = s^A + s^1 + s^2$$

ψ_2, a bonding orbital, symmetry a_{2u}

$$\psi_2 = p_y^A - s^1 + s^2$$

ψ_3, a two-fold degenerate non-bonding orbital, symmetry e_{1u}

$$\psi_3 = (p_x^A, p_z^A)$$

9.5 Correlation of orbitals between bent and linear geometries

If we imagine a continuous deformation of the nuclear framework from the bent to the linear geometry, we expect that the orbitals will change continuously also.

Orbital φ_1 of the bent molecule will go into orbital ψ_1 of the linear molecule. Notice that this orbital can contain an admixture of p_z^A in the bent case, but not in the linear case.

Orbital φ_2 of the bent molecule will go into ψ_2 of the linear molecule.

Orbital φ_3 and φ_4 of the bent case will go into the doubly-degenerate orbital ψ_3 of the linear case.

Symmetry alone cannot predict the correct order and angular variation of the energy levels. Walsh was able to complete the analysis by a treatment in simple physical terms of the variation of the energies of the orbitals with bond angle. He based his derivations of the energy variations on elementary spectroscopic inferences, and on the principle that the value of the interelectronic repulsion energy in an orbital is reduced if the regions of interacting electron density move apart.

Figure 9.4 shows Walsh's diagram expressing the orbital correlation and suggesting the variation in orbital energy with bond angle.

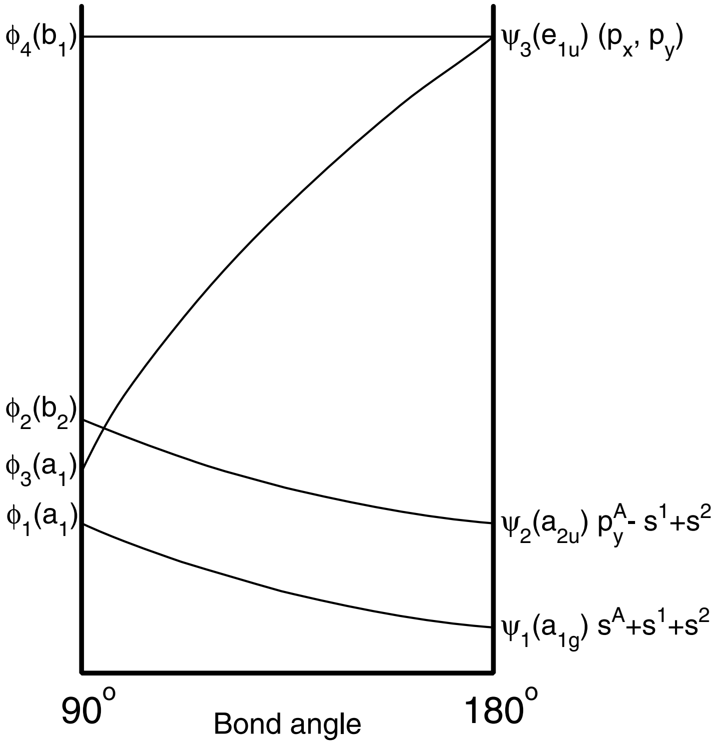


Figure 9.4. Walsh diagram showing correlation of orbitals between bent and linear triatomic molecules, and suggesting variation in orbital energy with bond angle.

The decrease in energy of φ_1 and φ_2 in going over to ψ_1 and ψ_2 respectively, is a result of the reduction of the repulsion energy between the electrons in the internuclear regions, as the molecule becomes more nearly linear.

The increase in energy of φ_3 in going over to ψ_3 can be traced to the excitation energy required to change from s character of φ_3 to fully p character of ψ_3.

The independence of orbital energy for $\varphi_4 \rightarrow \psi_4$ is explicable by the fact the p_x orbital is always perpendicular to the molecular plane, so that its interaction with the rest of the molecule does not depend on bond angle.

The conclusions to be drawn from the correlation diagram in Figure 9–4 are: Molecules with 1–4 valence electrons should in their ground states have electrons occupying only orbitals having energies that decrease with increasing bond angle, and hence should be linear. Molecules with 5–8 valence electrons have electrons occupying the $\varphi_3 - \psi_3$ orbital, the energy of which increases steeply with angle, and hence they should be bent.

Problem 9–13. Verify the correlations of orbitals for C_{2v} and $D_{\infty h}$ geometries.

Problem 9–14. Which of the following molecules should be linear in their ground states? Which would change geometry – linear → bent, or bent → linear – in going to the first excited state?

$$\mathrm{BeH_2},\ \mathrm{HgH_2},\ \mathrm{NH_2},\ \mathrm{CH_2},\ \mathrm{H_2O}.$$

Problem 9–15. Could the same predictions be made from a simple electron repulsion argument? If n pairs of electrons must be accommodated in the valence-shell molecular orbitals, then assume simply that they will be as far apart as possible. Up to four electrons will push each other as far apart as possible, to create linear geometry; more than four must be distributed more densely, so that the angle between the substituents will be less that 180°. Does this simple hypothesis explain everything that Walsh's rules do? Is there any advantage to using Walsh's correlation diagram analysis?

Chapter 10

SPECTROSCOPY AND SELECTION RULES

10.1 Introduction

There are several incentives for determining conditions under which quantities of the form $(\phi_1, \mathcal{O}\psi_2)$ are equal to zero. Here ψ_1 and ψ_2 are wave functions and $\mathcal{O}$ is an operator. In the LCAO (linear combination of atomic orbitals) approximation to molecular orbitals, two basis functions ψ_1 and ψ_2 do not "mix," if $(\psi_1, \mathcal{H}\psi_2) = (\psi_1, \psi_2) = 0$. Thus a criterion for the vanishing of the matrix elements H_{12} and S_{12} can simplify the interpretation and calculation of molecular orbitals.

A number of spectroscopic phenomena also depend on the values of matrix elements. For example, the intensity of a particular line in an absorption or emission spectrum is proportional to the square of a matrix element of the electric dipole operator: $(\psi_1, e\mathbf{r}\ \psi_2)$.

Transitions for which $(\psi_1, e\mathbf{r}\ \psi_2) = 0$ are called *forbidden* transitions.

10.2 The relationship between symmetry properties and the vanishing of matrix elements

An elementary example illustrates the role of symmetry in determining when a matrix element must be equal to zero. Consider the one-dimensional integral:

$$I = \int_{-\infty}^{\infty} (\cos x)\ x\ (\cos 2x)\, dx$$

To prove that $I = 0$, divide the region of integration into two parts: $x \geq 0$ and $x \leq 0$. Then:

$$I = I_- + I_+ = \int_{-\infty}^{0} (\cos x)\ x\ (\cos 2x)\, dx + \int_{0}^{\infty} (\cos x)\ x\ (\cos 2x)\, dx$$

Rewriting I_- by inverting the limits and transforming the variables $x \rightarrow -x$:

$$\begin{aligned} I_- &= \int_0^\infty \cos(-x)(-x)\cos(-2x)\,dx \\ &= -\int_0^\infty (\cos x)\; x\; (\cos 2x)\,dx \end{aligned}$$

because $\cos(-x) = \cos x$. But this shows that

$$I_- = -I_+,$$

and hence that

$$I = I_- + I_+ = 0.$$

Problem 10–1. Show that if f and g are *any* two functions such that $f(-x) = f(x),\ g(-x) = g(x)$, then $I_{fg} = \int_{-\infty}^{\infty} f(x)\cdot x\cdot g(x)\,dx = 0$. Functions such that $f(-x) = f(x)$ are called *even* functions.

Problem 10–2. Show that if f and g are any two functions such that $f(-x) = -f(x), g(-x) = -g(x)$, then $I_{fg} = \int_{-\infty}^{\infty} f(x)\cdot x\cdot g(x)\,dx = 0$. Functions such that $f(-x) = -f(x)$ are called *odd* functions.

Problem 10–3. The $1s$ and $2s$ states of the Hydrogen atom are both spherically symmetric. Show that the transition $1s \rightarrow 2s$ is forbidden.

In more complicated cases, the derivation of selection rules from symmetry requires more formal application of group theory. The fundamental problem is to derive the symmetry properties of a product from the symmetry properties of the factors. For only if the product contains a totally symmetric component can the matrix element have a non-zero value.

10.3 The direct-product representation

If f and g are functions of known symmetry, what is the symmetry of the product $f \cdot g$? The function $f \cdot g$ is defined as $f \cdot g(x) = f(x) \cdot g(x)$.

It is easy to determine the symmetry of the product if the symmetry species of f and g are both one-dimensional. If f and g both transform according to one-dimensional representations Γ_f and Γ_g of a symmetry group, the group operation A takes f into $\Gamma_f(A)\cdot f = \chi_f(A)\cdot f$, and g into $\Gamma_g(A)\cdot g = \chi_g(A)\cdot g$. The product $f \cdot g$ is transformed into $\chi_f(A) \cdot \chi_g(A) \cdot f \cdot g$. The product $f \cdot g$ is a basis for another one-dimensional representation of the group, Γ_{fg}, the characters of which are the products of those of the representations Γ_f and Γ_g. That is:

$$\chi_{fg}(A) = \chi_f(A) \cdot \chi_g(A)$$

The representation Γ_{fg} is the *direct product* of the representations Γ_f and Γ_g.

Problem 10–4. If f transforms as A_2 in C_{2v} and g transforms as B_1, what is the symmetry species in C_{2v} of the product $f \cdot g$?

To verify that the product formula for characters holds even for functions that transform according to representations of higher dimensions, suppose that the functions $f_1, f_2 \ldots f_n$ and $g_1, g_2 \ldots g_n$ form bases for $n-$ and $m-$dimensional representations of a group. Thus under any group operation A, each f_i is transformed into a linear combination of all the $f_k, k = 1, \ldots n$; and similarly each g_j is transformed into a linear combination of all the $g_l, l = 1, \ldots n$.

$$A \cdot f_i = \sum_{k=1}^{n} \left[\Gamma_f(A)\right]_{ik} f_k$$

$$A \cdot g_j = \sum_{\ell=1}^{m} \left[\Gamma_g(A)\right]_{j\ell} g_\ell$$

Combining these equations, the product $f_i g_j$ will be transformed into a linear combination of the $m \times n$ functions $f_k g_\ell, k = 1, \ldots n; \ell = 1, \ldots m$.

$$A f_i g_j = A f_i \cdot A g_j = \sum_{k=1,n}^{n} \sum_{\ell=1}^{m} \left[\Gamma_f(A)\right]_{ik} \left[\Gamma_g(A)\right]_{j\ell} f_k g_l$$

The set of products $f_k g_\ell$ forms a basis for a representation called the *direct product* of the representations Γ_f and Γ_g.

$$\Gamma_{fg} = \Gamma_f \otimes \Gamma_g$$

Note that if Γ_f is $n-$dimensional and Γ_g is $m-$dimensional, Γ_{fg} is $m \times n-$ dimensional.

The diagonal elements in a direct-product matrix Γ_{fg} are those giving the coefficient of a particular term $f_i g_j$ in the linear combination expressing $A(f_i g_j)$. This element of $\Gamma_{fg}(A)$ is equal to

$$\left[\Gamma_f(A)\right]_{ii} \left[\Gamma_g(A)\right]_{jj} .$$

The trace of the direct product matrix is:

$$\sum_{ij} [\Gamma_f(A)]_{ii} \, [\Gamma_g(A)]_{jj}$$

equal to:

$$\chi_{fg}(A) = \chi_f(A) \cdot \chi_g(A).$$

The direct product representation is usually reducible, unless both component representations are one-dimensional. For instance, in a group such as D_{3h}, in which no irreducible representation has dimension higher than two, the direct product of E_1 and E_2 will be four-dimensional, and thus it *must* be reducible.

Problem 10–5. In a homonuclear diatomic molecule, taking the molecular axis as z, the pair of LCAO–MO's $\psi_1 = 2p_{xA} + 2p_{xB}$ and $\psi_2 = 2p_{yA} + 2p_{yB}$ forms a basis for a degenerate irreducible representation of $D_{\infty h}$, as does the pair $\psi_3 = 2p_{xA} - 2p_{xB}$ and $\psi_4 = 2p_{xA} - 2p_{xB}$. Identify the symmetry species of these wave functions. Write down the four-by-four matrices for the direct product representation by examining the effect of the group elements on the products $\psi_1\psi_3$, $\psi_1\psi_4$, $\psi_2\psi_3$, and $\psi_2\psi_4$. Verify that the characters of the direct product representation are the products of the characters of the individual representations.

Extension of this analysis to the product of *three* factors, in order to treat objects of the form $(\phi_i,\ \mathcal{O}\psi_j)$, in which $\mathcal{O}$ is a linear operator, gives the result that:

$$\begin{array}{ccccccc}
\Gamma_{(\psi_i,\mathcal{O}\psi_j)} & = & \Gamma_{\psi_i} & \otimes & \Gamma_{\mathcal{O}} & \otimes & \Gamma_{\psi_j} \\
\Gamma_{(\psi_i,\mathcal{O}\psi_j)} & = & \Gamma_{\psi_i} & \otimes & \Gamma_{\mathcal{O}} & \otimes & \Gamma_{\psi_j} \\
\chi_{(\psi_i,\mathcal{O}\psi_j)} & = & \chi_{\psi_i} & \cdot & \chi_{\mathcal{O}} & \cdot & \chi_{\psi_j}
\end{array}$$

For example, in C_{2v}, if ψ_i has symmetry species A_2 and ψ_j has symmetry species B_2; then, recalling that x has symmetry species B_1 also; the product $\psi_i x \psi_j$ transforms according to a representation Γ with characters:

E	C_2	σ_v	σ_v'
1	1	−1	−1

Thus $\Gamma_{(\psi_1, x\psi_2)} = \Gamma_{A_2} \otimes \Gamma_{B_1} \otimes \Gamma_{B_1} = \Gamma_{A_2}$

Problem 10–6. In D_{3h}, if ψ_i has symmetry species E′, ψ_j has symmetry species E″, and z has symmetry species A_2'', what is the set of characters corresponding to the direct product representation for $(\psi_i, z\psi_j)$? Of what irreducible representations is it composed?

In order to apply the direct product representation to the derivation of selection rules, recognize that a matrix element of the form $(\psi_i, \mathcal{O}\psi_j)$ will be equal to zero for symmetry reasons if there is even one symmetry operation that takes the integrand into its negative. The argument follows exactly the course of that of section 10.2. Thus the matrix element will vanish unless the direct product representation is totally symmetric (A_1), or *contains* A_1 upon reduction.

The main applications of this result are:

(1) Simplification of secular equations. Because the Hamiltonian is totally symmetric – that is, for a molecule of C_{2v} symmetry such as H_2O, of symmetry species A_1 – the matrix elements $H_{ij} = (\psi_i, \mathcal{H}\psi_j)$ as well as the overlap integrals $S_{ij} = (\psi_i, \psi_j)$ will be equal to zero unless the direct product representation $\Gamma_{\psi_i} \otimes \Gamma_{\psi_j}$ contains A_1. This is the basis for the assertion that "states of different symmetry do not mix."

(2) Selection rules. A transition between states ψ_i and ψ_j associated with light absorption or emission will be forbidden if $(\psi_i, e\mathbf{r}\ \psi_j) = 0$.

10.4 Selection rules in spectroscopy

For light to induce a transition between energy levels of an atom or molecule, it is necessary that the frequency of the light and the energy difference between the levels satisfy, at least approximately, the Planck relationship:

$$\Delta E = h\nu$$

But even if the light is of the proper frequency, the intrinsic probabilities of transitions are highly variable. The experimentally observed intensity of a transition is proportional to the square of a matrix element:

$$|(\psi_0, e\mathbf{r}\ \psi_1)|^2$$

Thus the intensity depends on the detailed size, shape and symmetry of the wave functions, and can even be zero in the case of a forbidden transition.

The mechanism by which light causes an atom or molecule to undergo a transition can be described in terms of the eigenfunctions of a Hamiltonian. If

ψ_0 and ψ_1 are eigenfunctions of a Hamiltonian $\mathcal{H}$, an atom or molecule in state ψ_0 or ψ_1 would remain in that state indefinitely, if undisturbed.

The effect of the light is to alter the Hamiltonian, by addition of an additional potential term, V. In general, ψ_0 and ψ_1 will no longer be eigenfunctions of the new Hamiltonian $\mathcal{H}+V$. However, it the term V is very small – that is, the light is just "tickling" the molecule – the states ψ_0 and ψ_1 may still be *approximate* eigenfunctions. A reasonable expression for the molecular wave function is a linear combination of the form $a\psi_0 + b\psi_1$, with a and b determined by a secular equation. If ψ_0 and ψ_1 mix only slightly, the perturbed state can be characterized as a superposition of ψ_0 with a small amount of ψ_1. That is, the population of atoms or molecules under illumination may be regarded as predominantly in the state ψ_0, with a small admixture of the state ψ_1.

The predominant term in the perturbing potential V is of the form $e\mathbf{r}$, equal to the electric dipole moment operator. This is the origin of the selection rule that: if $(\psi_0, e\mathbf{r}\ \psi_1) = 0$, the perturbed secular equation will not mix the states ψ_0 and ψ_1, so that the transition $\psi_0 \rightarrow \psi_1$ will not occur.

Within this basic general framework, molecules exhibit a variety of spectroscopic phenomena. Energies of transitions between electronic states are typically in the range $10^{-19} - 10^{-17}$ joule/molecule. These transitions are observed in absorption and emission spectra in the visible and ultraviolet region. They are also responsible for the phenomena of circular dichroism and optical rotatory dispersion, (see section 10.4) in which the interaction between light and a molecule alters the state of polarization of the light. Energies of transition between vibrational energy levels are typically of order of magnitude 10^{-20} joule/molecule. These transitions are observed in infrared absorption and Raman spectra.

10.4.1 Electronic transitions

The measure of the intensity of an electronic absorption or emission spectrum is the oscillator strength, a dimensionless quantity:

$$f_{ij} = \frac{8\pi^2 mc}{3he^2} |(\psi_i, e\mathbf{r}\ \psi_j)|^2$$

The electric dipole operator $e\mathbf{r}$ is a vector, with components (ex, ey, ez). Thus if

$$(\psi_i, x\psi_j) = (\psi_i, y\psi_j) = (\psi_i, z\psi_j) = 0,$$

the transition is forbidden, and will not appear in the spectrum. If only one or two components are non-zero, the transition will be allowed, but only for light of proper polarization. For example, if $(\psi_i, x\psi_j) = 0$ but $(\psi_i, y\psi_j) \neq 0$ and $(\psi_i, z\psi_j) \neq 0$, we would say that the transition is polarized along y and z

axes. Directions of polarizations are detectable in spectra of *oriented* samples.

An *optically active* transition is one that causes the plane of polarization of a light wave to rotate upon passage through a sample. The rotational strength of a transition will be zero if the following quantity is zero:

$$(\psi_i, e\mathbf{r}\,\psi_j)\cdot(\psi_j, \boldsymbol{\mu}\,\psi_i)$$

in which the vector $\boldsymbol{\mu}$ is the *magnetic* dipole moment operator. The components of $\boldsymbol{\mu}$ have the same symmetry properties as the rotations R_x, R_y and R_z; so that the selection rule for optical activity states that a transition will be optically inactive if:

$$\begin{aligned}(\psi_i, x\psi_j)\cdot(\psi_j, R_x\psi_i) &= 0\\(\psi_i, y\psi_j)\cdot(\psi_j, R_y\psi_i) &= 0\\(\psi_i, z\psi_j)\cdot(\psi_j, R_z\psi_i) &= 0\end{aligned}$$

Problem 10–7. Formaldehyde, CH_2O, has C_{2v} symmetry. The ground state has symmetry species A_1, and low-lying excited states have symmetry species A_2, B_2, and A_1. To which excited states are transitions allowed? What are the directions of polarization of the allowed transitions?

Problem 10–8. Pyrimidine:

has C_{2v} symmetry. The ground state has symmetry species A_1, and low-lying excited states have symmetry species A_2, B_1 and B_2. Are any of the transitions from ground states to excited states optically active?

Problem 10–9. Consider two pyrimidine molecules, located in space so that the planes of both molecules are parallel to the $y - z$ plane, such that a translation along the $x-$axis by 3.4 Å and a rotation by 36° around the $x-$axis will bring the two into coincidence. (This geometry is an extremely rough model for part of one strand of a DNA double helix).

continues...

(a) Verify that the symmetry group of the combined molecules is C_2. Label the two molecules A and B, and denote the eigenfunctions of the two in isolation by $\psi_0(\mathrm{A}), \psi_0(\mathrm{B}), \psi_1(\mathrm{A}), \psi_1(\mathrm{B}), etc.$ Then if the wave functions of A and B do not overlap, and the interaction is very weak, approximate ground and excited state wave functions for the combined system of potential spectroscopic importance are:
Ground state: $\psi_0(\mathrm{A}) \cdot \psi_0(\mathrm{B})$
Excited states: $\psi_0(\mathrm{A}) \cdot \psi_i(\mathrm{B}) \pm \psi_i(\mathrm{A}) \cdot \psi_0(\mathrm{B}), i = 1, 2, 3,$
where ψ_1, ψ_2, and ψ_3, are the low-lying excited states of symmetry species A_2, B_2 and A_1 (see previous problem).
(b) What are the symmetry species of these states in C_2? Do any transitions forbidden in the monomer become allowed in the dimer?
(c) Which transitions in the dimer are optically active?

Problem 10–10. (a) Can a transition that is forbidden for absorption be optically active? (b) Can a transition for which $(\psi_i, e\mathbf{r}\,\psi_j) \neq 0$ and $(\psi_j, \boldsymbol{\mu}\,\psi_i) \neq 0$ be optically inactive? Explain your answers.

Problem 10–11. If a molecule has a center of symmetry or a plane of symmetry, no electronic transition can be optically active. Verify this for the groups $C_{1h}, S_2 = C_i$, and D_{2h}, by considering the various combinations of symmetry species for ground and excited states. Can you see why the statement will always be true? Can you prove it?

10.4.2 Vibrational transitions

Infrared and Raman spectra arise from transitions between energy levels in which the vibrational energy of the molecule is changing. Infrared spectra correspond to absorption of light, coupled with excitation of normal modes of vibration, with no change in electronic state. Raman spectra arise from transitions involving both electronic and vibrational energy: absorption of light coupled with electronic excitation is followed by emission of a photon with a frequency change corresponding to gain or loss of energy to vibrational modes.

A normal mode of vibration is said to be “infrared active” if the fundamental transition, in which the mode is excited by one quantum of vibrational energy, is *allowed.* Initial and final states are described by vibrational wave functions, of which the ground state wave function has A_1 symmetry and the excited state has the same symmetry as the normal mode. Thus the fundamental transition to a mode of symmetry species Γ will be allowed if any of the following direct products contains the totally symmetric representation A_1 :

$$\mathrm{A}_1 \otimes x \otimes \Gamma \qquad \mathrm{A}_1 \otimes y \otimes \Gamma \qquad \mathrm{A}_1 \otimes z \otimes \Gamma$$

The Raman effect depends on a change in the *polarizability* of the molecule, upon deformation by a vibration.

The polarizability of a molecule measures the dipole moment induced by an electric field (induced in response to an applied electric field). In a typical process of scattering of light by a molecule, a periodically varying electric field in the light wave induces a periodically varying dipole moment in a molecule. Usually the induced dipole moment has the same frequency, and therefore the scattered radiation, emitted by this oscillating dipole, has this frequency too. But if there is a *change* in the polarizability upon vibrational distortion, then the induced dipole moment has a component that varies with the vibrational frequency. The periodic variation of the induced dipole will include "beat" frequencies in which the frequency of the emitted light differs from the exciting frequencies by a multiple of the vibrational frequency. This gives rise to the Raman effect.

The polarizability tensor of a molecule related the components of the induced dipole moment of the molecule to the components of the electric field doing the inducing. It therefore has 9 components, α_{xx}, α_{xy}, etc., only 6 of which are independent. The theory of the Raman effect shows that a vibrational transition, from the totally symmetric ground state to an excited state of symmetry species Γ, will be Raman active if at least one of the following direct products contains the totally symmetric representation:

$$\begin{array}{ccccc}
\mathrm{A}_1 & \otimes & x^2 & \otimes & \Gamma \\
\mathrm{A}_1 & \otimes & y^2 & \otimes & \Gamma \\
\mathrm{A}_1 & \otimes & z^2 & \otimes & \Gamma \\
\mathrm{A}_1 & \otimes & xy & \otimes & \Gamma \\
\mathrm{A}_1 & \otimes & xz & \otimes & \Gamma \\
\mathrm{A}_1 & \otimes & yz & \otimes & \Gamma
\end{array}$$

Problem 10–12. Which normal modes of H_2O are infrared active? Which are Raman active?

Problem 10–13. Which normal modes of CH_3 are infrared active? Which are Raman active?

Problem 10–14. If a molecule has a center of symmetry, no vibrational mode can be active in *both* the infrared and Raman. Verify this for the groups D_{2h} and $D_{\infty h}$, by considering all possible symmetry species of the normal modes. Can you see why the statement will always be true? Can you prove it?

Chapter 11

MOLECULAR ORBITAL THEORY OF PLANAR CONJUGATED MOLECULES

11.1 Introduction

These simple molecular orbital pictures provide useful descriptions of the structures and spectroscopic properties of planar conjugated molecules such as benzene and naphthalene, and heterocyclic species such as pyridine. Heats of combustion or hydrogenation reflect the resonance stabilization of the ground states of these systems. Spectroscopic properties in the visible and near-ultra-violet depend on the nature and distribution of low-lying excited electronic states. The success of the simple molecular orbital description in rationalizing these experimental data speaks for the importance of symmetry in determining the basic characteristics of the molecular energy levels.

In this section we shall first treat the simple molecular orbital description of pyridine. Each molecular energy level corresponds to a configuration, specified by the occupancy of individual molecular orbitals. Each molecular orbital has the symmetry species of an irreducible representation of the symmetry group, C_{2v}. The spatial symmetry of the overall molecular wave function is the direct product of the symmetry species of the occupied orbitals.

The distribution of the molecular orbitals can be derived from the patterns of symmetry of the atomic orbitals from which the molecular orbitals are constructed. The orbitals occupied by valence electrons form a basis for a representation of the symmetry group of the molecule. Linear combination of these basis orbitals into molecular orbitals of definite symmetry species is equivalent to reduction of this representation. Therefore analysis of the character vector of the valence-orbital representation reveals the numbers of molecular orbitals of each symmetry. A sum of basis orbitals of a proper symmetry type is called a *symmetry-adapted linear combination.*

We shall introduce the technique of *projection operators* to determine the appropriate expansion coefficients for symmetry-adapted molecular orbitals. Projection by operators is a generalization of the resolution of an ordinary 3–vector into x, y and z components. The result of applying symmetry projection operators to a function is the expression of this function as a sum of components each of which transforms according to an irreducible representation of the appropriate symmetry group.

11.2 The LCAO–MO description of pyridine

Pyridine, symmetry group C_{2v}, has six electrons in a $2p_\pi$ system delocalized around the ring, and two lone-pair electrons in an orbital localized at the Nitrogen atom. The $1s$ electrons, as well as the electrons in orbitals describing the σ bonds, need not be considered explicitly in describing the resonance stabilization and low-lying excited states of pyridine. The simple molecular orbital description has the following characteristic assumptions:

(1) The electronic wave functions are adequately described as antisymmetrized products of symmetry-adapted linear combinations of atomic orbitals.

(2) Excitations are adequately described in terms of altered orbital occupancies.

Problem 11–1. Consider three levels of approximation: (a) Exact many-electron wave function, (b) Hartree-Fock wave function, (including all electrons), (c) Simple LCAO–MO valence electron wave function. For each of the following molecular properties, would you expect the Hartree-Fock approximation to give a correct prediction (to within $\sim 1\%$ in the cases of quantitative predictions)? Would you expect the LCAO–MO approximation to give a correct prediction?

1. Symmetry of the ground state wave function.
2. Energy of the ground state.
3. Excitation energies to excited states.
4. Possible symmetries of excited states.
5. The relative energies of excited states identified by assignments of orbital occupancies.
6. Allowed or forbidden character of transitions.
7. Polarization of transitions.
8. Oscillator strength of transitions.

The molecular orbitals for pyridine will be illustrated by the following type of contour diagram:

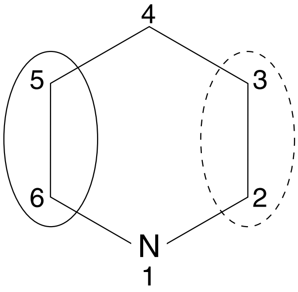


Figure 11.1. Typical contour diagram for a molecular orbital of pyridine, viewed perpendicular to the molecular plane.

This molecular orbital, designated π_3, has a positive value above carbon atoms 5 and 6, indicated by the solid contour; negative value above carbon atoms 3 and 2, indicated by the dashed contour, and has a nodal plane including atom 4 and the nitrogen atom. The contours are those that might be drawn in a plane parallel to the molecular plane, 1 Å above it.

Figure 11.2 shows a side view of the molecular orbital, with contours drawn in a plane perpendicular to the molecular plane and perpendicular to the C_2 axis.

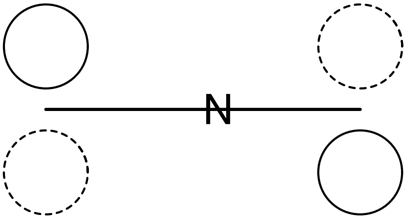


Figure 11.2. Typical contour diagram for a molecular orbital of pyridine, viewed parallel to the molecular plane.

The operations of C_{2v} have the following effects on the orbital:

$$\begin{aligned} E\pi_3 &= \pi_3 \\ C_2\pi_3 &= \pi_3 \\ \sigma_v\pi_3 &= -\pi_3 \\ \sigma'_v\pi_3 &= -\pi_3 \end{aligned}$$

Thus π_3 transforms according to symmetry species a_2.

Problem 11–2. Each atomic p_π orbital is antisymmetric with respect to reflection in the molecular plane. What limitations does this fact place on the possible symmetry species, in C_{2v}, of the molecular orbitals describing the π system?

The full complement of ground and low-lying pyridine molecular orbitals is as follows:

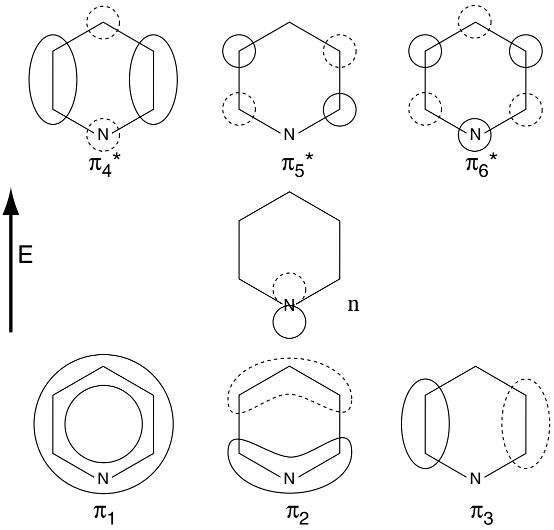


Figure 11.3. Molecular orbitals for pyridine.

The orbitals are numbered in order of increasing energy, as determined from a secular equation. π_1 is the ground state; the others are excited states. Antibonding orbitals are flagged with an asterisk. Note that the lone-pair orbital n is neither bonding nor antibonding, but *non-bonding*.

Problem 11–3. Verify the transformation properties and symmetry species of the pyridine molecular orbitals.

Problem 11–4. Determine and sketch the nodal structure of the pyridine molecular orbitals.

Problem 11–5. Denoting the p_π orbital on the i^{th} atom by p_i, π_3 is proportional to the linear combination $p_4 + p_5 - p_2 - p_3$. What linear combinations correspond to the other π orbitals?

Problem 11–6. The following rules are a generally reliable guide to relative order of energy levels:

1 There are an equal number of bonding and antibonding orbitals.

2 The larger the number of nodal planes, the higher the energy.

3 The electronegativity of Nitrogen is greater than that of Carbon; therefore a molecular orbital that includes the Nitrogen p orbital is lower in energy than the analogous orbital in benzene.

Are these rules sufficient to determine the relative energies of the molecular orbitals?

Problem 11–7. Verify the symmetry species of the first excited state, and the polarization of the transition to it from the ground state.

Problem 11–8. Predict the symmetry species of other low-lying excited states of pyridine, determine whether transitions to or from the ground state are allowed or forbidden, and determine the polarizations of the allowed transitions.

11.3 Distribution of molecular orbitals among symmetry species

The determination of molecular orbitals in terms of symmetry-adapted linear combinations of atomic orbitals is analogous to the determination of normal vibrational modes by forming symmetry-adapted linear combinations of displacements. Both calculations are in reality the reduction of a representation generated by a known basis. In the vibrational case the representation Γ_{tot} is generated by a vector of displacements. In the molecular orbital case, the representation Γ_{AO} is generated by a set of atomic orbitals.

The characters of the representation Γ_{AO} generated by the six p_π orbitals and the non-bonding orbital of pyridine are:

$$\begin{aligned} \chi(E) &= 7 \\ \chi(C_2) &= -1 \\ \chi(\sigma_v) &= 3 \\ \chi(\sigma_v') &= -5 \end{aligned}$$

It is then easy to compute that $\Gamma_{AO} = \mathrm{A}_1 + 2\mathrm{A}_2 + 4\mathrm{B}_1$.

Problem 11–9. Show that

$$\begin{aligned} E(p_2) &= p_2 \\ C_2(p_2) &= -p_5 \\ \sigma_v(p_2) &= p_5 \\ \sigma_v'(p_2) &= -p_2 \end{aligned}$$

Problem 11–10. Verify that $\Gamma_{AO} = (\, 7 \quad -1 \qquad 3 \quad -5 \,)$.

Problem 11–11. Verify that $\Gamma_{AO} = \mathrm{A}_1 + 2\mathrm{A}_2 + 4\mathrm{B}_1$, and show that it corresponds to the molecular orbitals shown in Figure 11.3.

11.4 The Hückel approximation

The Hückel approximation is defined by a set of simplications to the form of the Hamiltonian in the LCAO–MO description of planar conjugated molecules. Although the Hückel approximations are quite severe, nevertheless they produce results that rationalize qualitatively the resonance energies and spectra of these molecules.

In the Hückel approximation for hydrocarbons, matrix elements of the Hamiltonian in a basis of p atomic orbitals (ϕ_i = a p_z orbital on atom i) are expressed in terms of two parameters α and β :

$H_{ii} = \alpha$

$H_{ij} = \beta$ if orbitals i and j are centered on *neighboring* carbon atoms, else $H_{ij} = 0$.

$S_{ii} = 1$ (This is merely the normalization condition.)

$S_{ij} = 0$, *even* in the case of orbitals on nearest-neighbor atoms

Note that α and β are *negative* numbers.

For example, the Hückel approximation to the secular equation for benzene is:

$$\det\begin{pmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{pmatrix} = 0$$

Problem 11–12. Write the Hückel approximation to the secular equation for naphthalene.

Problem 11–13. Write down and solve the Hückel approximation to the secular equation for the π system of ethylene. Noting that the energy of two electrons on non-interacting carbon atoms is 2α, show that the binding energy of the two π electrons is -2β.

Solution of the secular equation for benzene gives the following energy levels and eigenfunctions:

Level	Energy	Molecular orbital
E_6	$\alpha - 2\beta$	$\frac{1}{\sqrt{6}}(\psi_1 - \psi_2 + \psi_3 - \psi_4 + \psi_5 - \psi_6)$
E_5	$\alpha - \beta$	$\frac{1}{2}(\psi_1 - \psi_2 + \psi_4 - \psi_5)$
E_4	$\alpha - \beta$	$\frac{1}{\sqrt{12}}(\psi_1 + \psi_2 - 2\psi_3 + \psi_4 + \psi_5 - 2\psi_6)$
E_3	$\alpha + \beta$	$\frac{1}{2}(\psi_1 + \psi_2 - \psi_4 - \psi_5)$
E_2	$\alpha + \beta$	$\frac{1}{\sqrt{12}}(\psi_1 - \psi_2 - 2\psi_3 - \psi_4 + \psi_5 + 2\psi_6)$
E_1	$\alpha + 2\beta$	$\frac{1}{\sqrt{6}}(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6)$

There are six electrons in the π system, filling the first three orbitals. The total energy of the configuration is:

$$\begin{aligned} 2E_1 + 2E_2 + 2E_3 &= (\alpha + 2\beta) + 2(\alpha + \beta) + 2(\alpha + \beta) \\ &= 6\alpha + 8\beta \end{aligned}$$

The corresponding energy of three ethylene molecules is $3\left[2(\alpha+\beta)\right] = 6\alpha + 6\beta$. Therefore the resonance stabilization energy of benzene is 2β.

Problem 11–14. Verify that these molecular orbitals for benzene are eigenfunctions of the Hückel Hamiltonian, with the given eigenvalues.

Problem 11–15. Verify that the molecular orbitals are orthogonal, within the framework of the Hückel approximation.

Problem 11–16. Why do the results of the last two problems guarantee that the Hamiltonian, expressed in terms of the given molecular orbitals, will be diagonal?

Problem 11–17. What is the resonance stabilization energy of cyclobutadiene, according to Hückel theory? Express your answer in terms of β.

11.5 Projection operators

Projection operators are a technique for constructing linear combinations of basis functions that transform according to irreducible representations of a group. Projection operators can be used to form molecular orbitals from a basis set of atomic orbitals, or to form normal modes of vibration from a basis of displacement vectors. With projection operators we can revisit a number of topics considered previously but which can now be treated in a uniform way.

Decomposition of a function into its components of different symmetry types by means of projection operators is analogous to decomposition of an ordinary 3–vector into its components along x, y, and z axes. The projection along the x–axis of a general vector $v = (X, Y, Z)$ is $v_x = X\hat{x}$, in which $\hat{x}$ is a unit vector in the x direction. Note that the result of applying a projection operator to a vector is a *vector,* not a scalar. The equation could be written in terms of an inner product: $v_x = \hat{x}(\hat{x} \cdot v)$. Generalization of this formula defines a *vector projection operator* $\mathcal{P}_x$ such that $\mathcal{P}_x$ operating on any vector v gives the $x-$component of v as the result:

$$\begin{aligned} \mathcal{P}_x v &= \hat{x}(\hat{x} \cdot v) \\ \mathcal{P}_x &= \hat{x}(\hat{x} \cdot \end{aligned}$$

These vector projection operators are simple in form and function because the components of the vector appear explicitly in the notation for a vector.

Problem 11–18. What are the operators for projection of a vector along the y and z directions?

Problem 11–19. Define the operator for projection of a 3–vector along a direction in the $x-y$ plane pointing at an angle of $45°$ between the x and y axes. What is the projection along this direction of the vector (15, 20, 25)?

Problem 11–20. What is the projection operator that selects from a 3–vector the component lying in the $x-y$ plane?

Vector projection operators act by cancelling out all components of a vector except the one it is designed to select. The decomposition of a function in an analogous way requires expression of the function as a sum of components each of a proper symmetry species. For example, it is possible to write any function of three variables as a sum of components that are symmetric or antisymmetric with respect to inversion:

$$\begin{aligned} F(x,y,z) = & \frac{1}{2}\left[F(x,y,z)+F(-x,-y,-z)\right] \\ & +\frac{1}{2}\left[F(x,y,z)-F(-x,-y,-z)\right] \end{aligned}$$

The *even* component of F is $F_+ = \frac{1}{2}\left[F(x,y,z)+F(-x,-y,-z)\right]$.
The *odd* component of F is $F_- = \frac{1}{2}\left[F(x,y,z)-F(-x,-y,-z)\right]$.

Problem 11–21. Verify that $F_+(x,y,z) = F_+(-x,-y,-z)$ and that $F_-(x,y,z) = -F_-(-x,-y,-z)$.

Problem 11–22. What are the even and odd components of the function $F(x,y,z) = x^2 + y^2 z + xz^2$.

We can define a projection operator to select the even or odd component of $F(x,y,z)$, using symmetry operators. Define the effect of a spatial symmetry operator on a function by letting the operator transform the variables in the *argument* of the function and then evaluating the function. Recall, for example, that the effect of a C_2 around the z axis on a vector $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ is: $C_2 \begin{pmatrix} x \\ y \\ z \end{pmatrix} =$

$\begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$. Then the effect on a function F of a rotation by 180° around the $z-$axis is:

$$C_2\left[F(x,y,z)\right] = F\left[C_2(x,y,z)\right] = F(-x,-y,z).$$

In this notation, $F(-x,-y,-z)$ is simply the *inversion* of $F(x,y,z)$:

$$iF(x,y,z) = F(-x,-y,-z)$$

Problem 11–23. If $F(x,y,z) = x^2 + y^2 z + xz^2$, write the results of applying the operators of the group C_{2v} on F, using the usual coordinate system, in which the axis of rotation is along z, σ_v refers to the x–z plane and σ_v' refers to the $y - z$ plane.

The projection operator that selects the even component of a function F is:

$$\begin{aligned} \mathcal{P}_+ F(x,y,z) &= \frac{1}{2}\left[F(x,y,z) + F(-x,-y,-z)\right] \\ &= \frac{1}{2}\left[F(x,y,z) + iF(x,y,z)\right] \end{aligned}$$

that is:

$$\mathcal{P}_+ = \frac{1}{2}\left[E + i\,\right]$$

Similarly, the projection operator that selects the *odd* component of F is:

$$\mathcal{P}_- = \frac{1}{2}\left[E - i\,\right]$$

Separating the even and odd components of the function F, by means of the projection operators $\mathcal{P}_+$ and $\mathcal{P}_-$ produces functions that transform according to irreducible representations A$_g$ and A$_u$ of the group C_i, which consists of symmetry elements E and i. An analogous technique could be used to construct functions symmetric and antisymmetric with respect to a mirror plane or a dyad.

Problem 11–24. Write the function of problem 11-22, $F(x, y, z) = x^2 + y^2 z + xz^2$ as the sum of two functions symmetric and antisymmetric with respect to σ_v (reflection in the x–z plane). Write a projection operator that would project out the component of a function symmetric with respect to σ_v.

It is no accident that the coefficients of the *operators* E and i in the projection operators are the same as the character vectors in the table of irreducible representations of C_i :

C_i	E	i
A_g	$+\mathbf{1}$	$+\mathbf{1}$
A_u	$+\mathbf{1}$	$-\mathbf{1}$

$$\mathcal{P}_{A_g} = \mathcal{P}_{+} = \tfrac{1}{2}\,[+\mathbf{1}\,E \quad +\mathbf{1}\,i]$$
$$\mathcal{P}_{A_u} = \mathcal{P}_{-} = \tfrac{1}{2}\,[+\mathbf{1}\,E \quad -\mathbf{1}\,i]$$

The characters of the target representation define the form of the projection operator. The normalizing factor $\frac{1}{2}$ is the reciprocal of the number of elements in the group. To verify that, in C_{2v}, any function of the form:

$$\mathcal{P}_{A_2} F(x, y, z) = \frac{1}{4}\left[F + C_2 F - \sigma_v F - \sigma_v' F\right]$$

does indeed transform as A_2, refer to the group multiplication table:

$$\begin{aligned}
E(\mathcal{P}_{A_2} F) &= \frac{1}{4}\left[EF + EC_2 F - E\sigma_v F - \sigma_v' F\right] \\
&= \frac{1}{4}\left[F + C_2 F - \sigma_v F - \sigma_v' F\right] \\
&= \mathcal{P}_{A_2} F
\end{aligned}$$

$$\begin{aligned}
C_2(\mathcal{P}_{A_2} F) &= \frac{1}{4}\left[C_2 F + C_2^2 F - C_2 \sigma_v F - \sigma_v' F\right] \\
&= \frac{1}{4}\left[C_2 F + EF - \sigma_v' F - \sigma_v F\right] \\
&= \mathcal{P}_{A_2} F
\end{aligned}$$

$$\begin{aligned}
\sigma_v(\mathcal{P}_{A_2} F) &= \frac{1}{4}\left[\sigma_v F + \sigma_v C_2 F - \sigma_v^2 F - \sigma_v \sigma_v' F\right] \\
&= \frac{1}{4}\left[\sigma_v F + \sigma_v F - EF - C_2 F\right] \\
&= -\mathcal{P}_{A_2} F
\end{aligned}$$

$$\begin{aligned}\sigma_v'(\mathcal{P}_{A_2}F) &= \frac{1}{4}\left[\sigma_v'F + \sigma_v'C_2F - \sigma_v'\sigma_vF - \sigma_v'^2F\right] \\ &= \frac{1}{4}\left[\sigma_v'F + \sigma_vF - C_2F - EF\right] \\ &= -\mathcal{P}_{A_2}F\end{aligned}$$

This example suggests the general definition of the *character* projection operator, $\mathcal{P}_\Gamma$, to project out that component of a function which transforms according to irreducible representation Γ : (The group operations are denoted by $O_j, j = 1, \ldots h$. h is the number of elements of the group.)

$$\mathcal{P}_\Gamma = \frac{1}{h}\sum_{j=1}^{h}\chi_\Gamma(O_j)O_j$$

Problem 11–25. Project out the irreducible representations in C_{2v} of the function of problem 11–22. Verify that they transform properly.

Problem 11–26. From the vector of general displacements of the three atoms of the water molecule, project out the unique normal mode of B_2 symmetry.

11.6 General properties of projection operators

Let us look more closely at the analogy between vector projection operators and character projection operators, and list some of the more important properties that they share.

A *vector projection operator* acts upon a vector to produce the component of the vector in a specified direction:

$$\mathcal{P}_x v = \hat{x}(\hat{x}\cdot v)$$

A *character projection operator* acts upon a function to produce the component of the function of a specified symmetry type:

$$\mathcal{P}_\Gamma F = \frac{1}{h}\sum_{j=1}^{h}\chi_\Gamma(O_j)O_jF$$

The elements of the analogy are the correspondences between the character vector $\chi_\Gamma(O_j), j = 1, \ldots h$, and the basis vector $\hat{x}$, and between the sum $\frac{1}{h}\sum_{j=1}^{h}\chi_\Gamma(O_j)O_jF$ and the dot product $\hat{x}\cdot v = \sum_i x_iv_i$.

The following important properties of projection operators are most easily visualized in terms of vectors, but are true for the character projection operators as well:

(1) After projection of a component of a vector, reapplication of the same projection operator has no effect.

For example:
$$\begin{aligned}\mathcal{P}_{\hat{x}}(X,Y,Z) &= (X,0,0)\\ \mathcal{P}_{\hat{x}}^2(X,Y,Z) &= \mathcal{P}_{\hat{x}}(X,0,0)=(X,0,0)\end{aligned}$$

In general:
$$\begin{aligned}\mathcal{P}_{\hat{x}}v &= \hat{x}(v\cdot\hat{x})\\ \mathcal{P}_{\hat{x}}(\mathcal{P}_{\hat{x}}v) &= (v\cdot\hat{x})\mathcal{P}_{\hat{x}}\\ &= (v\cdot\hat{x})(\hat{x}\cdot\hat{x})\hat{x}=\hat{x}(v\cdot\hat{x})\end{aligned}$$

The corresponding fact for character projection operators is that

$$\mathcal{P}_\Gamma^2=\mathcal{P}_\Gamma.$$

Problem 11–27. Referring to problem 11–25, reapply the character projection operator $\mathcal{P}_{B_2}$ to the component of symmetry species B_2 and verify that this operation has no effect.

(2) If $\hat{v}$ and $\hat{w}$ are orthogonal, then projection along $\hat{v}$ followed by projection along $\hat{w}$ produces zero.

For example:
$$\begin{aligned}\mathcal{P}_{\hat{x}}(X,Y,Z) &= (X,0,0)\\ \mathcal{P}_{\hat{y}}\mathcal{P}_{\hat{x}}(X,Y,Z) &= \mathcal{P}_{\hat{y}}(X,0,0)=(0,0,0)\end{aligned}$$
or:
$$\mathcal{P}_{\hat{x}}\mathcal{P}_{\hat{y}} = 0$$

The corresponding fact for character projections is that $\mathcal{P}_{\Gamma_1}\cdot\mathcal{P}_{\Gamma_2}=0$.

Problem 11–28. Prove the statement $\mathcal{P}_{\Gamma_1}\cdot\mathcal{P}_{\Gamma_2}=0$ from the orthogonality properties of the character vectors.

Wave functions that satisfy the Pauli principle

Wave functions for electrons must change sign upon interchange of the electrons:

$$\Psi(1,2)=-\Psi(2,1)$$

(Here arguments 1 and 2 stand for the space and spin coordinates of the two electrons.) If the two-electron wave function $\Psi(1,2)$ is constructed from products of one-electron wave functions: $\psi_A(1)\psi_B(2)$ and $\psi_A(2)\psi_B(1)$, we can form symmetric and antisymmetric linear combinations:

$$\begin{array}{ll} \text{Symmetric:} & \psi_A(1)\psi_B(2) + \phi_A(2)\psi_B(1) \\ \text{Antisymmetric:} & \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1) \end{array}$$

We can express the formulation of these combination in terms of a projection operator: Let P_{12} = the permutation operator, defined by $P_{12}\Psi(1,2) = \Psi(2,1)$. The the operators that project out symmetric and antisymmetric states are:

$$\begin{aligned} \mathcal{P}_{symmetric} &= \frac{1}{2}\left[1 + P_{12}\right] \\ \mathcal{P}_{antisymmetric} &= \frac{1}{2}\left[1 - P_{12}\right] \end{aligned}$$

Problem 11–29. (a) Let $\Psi_+(1,2) = \mathcal{P}_{symmetric}\psi_A(1)\psi_B(2)$. Verify that $\Psi_+(2,1) = \Psi_+(1,2)$.
(b) Let $\Psi_-(1,2) = \mathcal{P}_{antisymmetric}\psi_A(1)\psi_B(2)$. Verify that $\Psi_-(2,1) = -\Psi_-(1,2)$.

Problem 11–30. Show that $\mathcal{P}_{antisymmetric}\psi_A(1)\psi_B(2)$ can be written as the determinant of the matrix: $\begin{pmatrix} \psi_A(1) & \psi_B(1) \\ \psi_A(2) & \psi_B(2) \end{pmatrix}$

General applications of projection operators

We have now developed the analogy between the decomposition of a vector into components along coordinate axes, and the decomposition of a set of objects into symmetry-adapted combinations.

- In the derivation of normal modes of vibration we started with a set of displacements of individual atoms. By determining the reducible representation Γ_{tot} and decomposing it, we calculated the number of normal modes of each symmetry species. We could determine what these modes are by solving a secular equation. We could alternatively have used projection operators to determine the symmetry-adapted combinations.
- In the derivation of molecular orbitals we started with individual p_π orbitals and created symmetry-adapted linear combinations by solving a secular

equation. Again, we could have decomposed Γ_{tot} to determine the number of different types of symmetry species and used projection operators to generate them. At worst, it would be necessary to solve a secular equation to find the eigenfunctions that are combinations of projected combinations of the *same* symmetry species.

- Projection operators produce wave functions antisymmetric upon electron exchange required to satisfy the Pauli principle.

With the power of computers that are currently available, it is not necessary to split the secular equation "by hand" just to reduce it to manageable proportions. It is worth realizing however, that both approaches – solving a large secular equation, and projecting out symmetry-adapted linear combinations – are both doing very similar things. Each, in its own way, finds combinations of the starting set of objects that are orthogonal, partly but not necessarily exclusively by virtue of having different symmetries.

Conclusion

Symmetry is the natural language of the fundamental laws of physics. Group theory is its grammar.

In this book we have emphasized the applications of group theory to calculations of properties of molecules, focusing on developing a working knowledge of useful tools for analysis and prediction of structures and spectra.

For readers who wish to pursue the subject, and to learn about a greater variety of applications, here are some of the books that I have enjoyed reading, and can recommend:

I. Stewart and M. Golubitsky, *Fearful Symmetry.* (Oxford, Blackwell Publishers, 1992).

> A popular but serious treatment of the concept of symmetry and its implications, applied to many topics, some of them from everyday life, such as the possible geometries of quilting patterns, and the analysis of the gaits of animals.

H. Weyl, *Symmetry* (Princeton, NJ, Princeton University Press, 1983).

> A discussion of symmetry in nature, art, science and mathematics, coupled with a non-technical discussion of the mathematics of symmetry. Originally prepared as a set of public lectures at the end of a distinguished career by a master. Still an interesting read.

I. Hargittai & M. Hargittai, *Symmetry through the Eyes of a Chemist* (New York, VCH Publishers, 1987).

> The personal touch. Biographical portrayals of the experience of discovery, recorded as far as possible in interviews with participating scientists and their colleagues (but not omitting a few "must-haves" such as Kepler and Pasteur). Topics involve some aspect of symmetry in chemistry and biology, physics to a much lesser degree. The emphasis is: How did the discovery come to be made? The point of view is that a scientific discovery is an act by a human being, working in a particular intellectual climate and in the context of an institutional framework.

I. Hargittai, Ed., *Symmetry: Unifying Human Understanding.* (New York, Pergamon Press, 1986).

A collection of sixty-five articles, encompassing all aspects of symmetry from chemistry and physics to art, literature and dance. Were any argument required to demonstrate the pervasive nature of symmetry not only in the laws governing the physical world but also human endeavor, this book would be a clincher.

E.M. Loebl (ed.), Group Theory and its Applications, Vol. II. (New York, Academic Press, 1971).

Part of a three-volume set covering applications of group theory to physics. The articles by McIntosh and by Wulfman are well worth reading. They contain relatively short and self-contained presentations of material about symmetries of atomic and molecular systems that is difficult to find elsewhere in comparably accessible form.

F.J. Budden, The Fascination of Groups, (Cambridge, U.K., Cambridge University Press, 1972).

An introduction to the mathematics of group theory for the non-mathematician. If you want to learn formal group theory but are uncomfortable with much of the mathematical literature, this book deserves your consideration. It does not treat matrix representations of groups or character tables in any significant detail, however.

The following references are to three classic originals – first published in the 1930's – and a standard modern treatment. The older books are primarily concerned with the electronic structure of atoms. Tinkham's book includes treatment of molecules and solids.

H. Weyl, *The Theory of Groups and Quantum Mechanics* (tr. H.P. Robertson) (New York, Dover Publications, 1984)

E. P. Wigner, *Group theory and its Application to the Quantum Mechanics of Atomic Spectra* (tr. J.J. Griffin) (New York, Academic Press, 1959).

B. L. van der Waerden *Group theory and quantum mechanics* (Berlin-New York, Springer-Verlag, 1974).

M. Tinkham, *Group Theory and Quantum Mechanics.* (New York, McGraw-Hill Book Co., 1964).

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