Chapter 3: An Introduction to Group Theory

Many problems in chemistry can be simplified based on the symmetry of molecules and/or the symmetries of atomic and molecular orbitals. Since this course will deal mostly in the mathematical models used to describe molecular motions (rotations and vibration) and the orbitals needed to describe the electronic structure of atoms and molecules, some introduction to the mathematics of symmetry is useful. The concepts discussed in this chapter will be used through the text to demonstrate how symmetry can be used to simplify the descriptions of atomic and molecular behavior.

Overview

Group Theory is the mathematical theory associated with the mathematical properties of groups. In chemistry, group theory is the mathematics of symmetry. A **group** (G) is a set of elements (A, B, etc.) that can be associated through a mathematical operation (sometimes referred to as a **multiplication operation**, eg. A*B) and satisfying the following criteria:

1. The group must have an **identity element** (E) such that for each element A in the group, A*E = E*A = A. (It can be proven that for a given group and multiplication operation, the identity element is unique.)
2. Each element A in the group must have an **inverse** (A^{-1}) that is also a member of the group and that satisfies the criterion $A*A^{-1} = A^{-1}*A = E$. (It can be proven that each element has one and only one inverse.)
3. The group must be **closed** under multiplication. That means that for any pair of elements in the group A and B for which A*B = C, C must also be a member of the group.

Note that the multiplication operation need not be **commutative**. The order of multiplication may matter. There is no guarantee that A*B = B*A. Many groups that satisfy this property are called **abelian** groups.

The set of numbers 1 and –1 form an abelian group under the normal operation of simple multiplication. A simple **group multiplication table** can be constructed for this group.

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

Clearly, the identity element in this group is 1 since multiplication by 1 gives the same number back. Also, both members happen to be their own inverse since

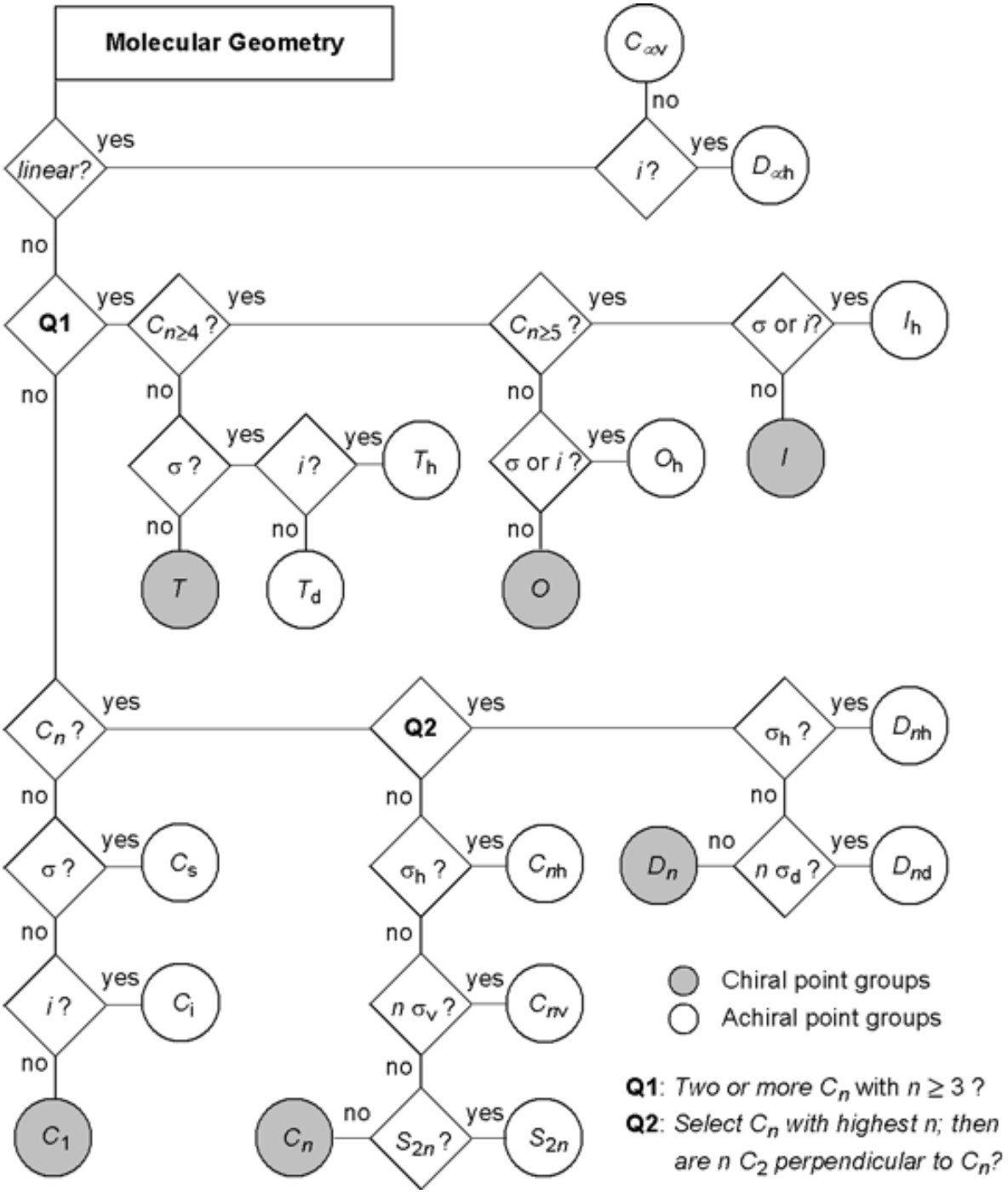
$$1*1 = 1 \qquad \text{and} \qquad (-1)*(-1) = 1$$

Group Theory in Chemistry

In Chemistry, group theory is useful in understanding the ramifications of symmetry within chemical bonding, quantum mechanics and spectroscopy. The group elements we are concerned with are **symmetry operations**.

Symbol	Operation	Description	Element	Mathematical example
E	identity	This is the "don't do anything to it" operation	E.	E (x,y,z) = (x,y,z)
C_n	Proper rotation	This is an operation in which the object is rotated about an axis by an angle of $2\pi/n$ radians. The axis will be referred to as the "C_n axis".	C_n. The axis with the largest value of n is designated the "principle rotation axis" and the z-axis is always assigned as lying along the **principle rotation axis**.	$C_4(x,y,z) = (y,-x,z)$ $C_2(x,y,z) = (-x,-y,z)$ Etc.
σ	Reflection plane	This operation involves reflection of the object through a mirror plane.	σ_v, σ_d or σ_h. σ_v and σ_d contain the principle rotation axis, whereas σ_h planes are perpendicular to the principle rotation axis.	$\sigma_v(x,y,z) = (-x,y,z)$ (for reflection through the yz plane) $\sigma_h(x,y,z) = (x,y,-z)$ $\sigma_d(x,y,z) = (y,x,z)$
i	Inversion center	This operation involves reflection trough a point.	i. The inversion center (if it exists) will always be located at the center of mass of a molecule.	i(x,y,z) = (-x,-y,-z)
S_n	Improper rotation	This operation involves a rotation	S_n.	

		through a C_n axis followed by reflection by a σ_h plane.		



A symmetry operation is a geometrical manipulation that leaves an object in a geometry that is indistinguishable from that which it had before the manipulation. There are five important types of symmetry operations with which we are concerned. Each type of operation has an associated **symmetry element**. Using standardized notation, these operations and elements can be summarized as follows.

A given molecule may have several of the above symmetry elements. The particular combination will define a group, and that group can be given a named based on the type of symmetry elements it contains. Further, all of the convenient wavefunctions that describe the vibrations, rotations and molecular orbitals of the molecule will be eigenfunctions of the symmetry elements, forcing some very useful mathematical properties upon the wavefunctions.

A case study: the symmetry of a tennis racket

A tennis racquet has all of the same symmetry elements as a water molecule or a formaldehyde molecule. Let's identify these symmetry elements and write out a group multiplication table for the group to which that particular set belongs.

The most obvious symmetry element is always the identity element (E). Every object possesses this symmetry element. Some objects are so asymmetrical that this is the only symmetry element they possess. Certainly, a tennis racquet possesses the symmetry element **E**.

The next most useful element to examine is the reflection plane. An object may or may not possess this type of symmetry. A tennis racquet has two vertical (σ_v) reflection planes. One is in the plane of the strings and the other is perpendicular to the face of the racquet. This happens often that an object has more than one of a given type of symmetry element. For our purposes, we will designate the plane that is perpendicular to the face of the racquet as $\boldsymbol{\sigma_v}$ and the one that is parallel to the face of the racquet as $\boldsymbol{\sigma_v}$**'**.

A tennis racquet possesses neither an inversion center (i) nor an improper rotation axis (S_n). The set of symmetry elements that the object does possess (E, C_2, σ_v and σ_v') define a group that goes by the label C_{2v}. Any object that has these and only these symmetry elements is said to have C_{2v} symmetry. It is easy to demonstrate that the set of symmetry elements that define C_{2v} define a group.

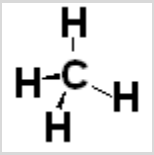
Determining the Point Group for a Molecule: the Schoenflies notation

The first step in determining the point group for a molecule is to determine the structure of the molecule. Once this is done, identify all of the symmetry elements the molecular structure possesses. Once this has been accomplished, you can use the preceding flowchart to determine the correct point group using the **Scheonflies notation** system.

Example: Determine the point group for a methane molecule.

Solution: A methane molecules has tetrahedral symmetry. It contains the following symmetry elements: E, 4 C_3 (one each along a C-H bond) axes, 6 σ planes (one each containing the carbon and a pair of hydrogen atoms), 3 C_2 axes (each on bisecting an HCH bond angle.) It also has 3 S_4 axes (each one co-linear with a C_2 axis.) The molecule belongs to the point group T_d, as can be discerned from the following analysis.

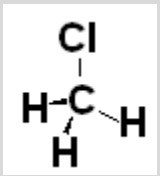
1. Is the molecular Linear? *No*
2. Does the molecule have two or more $C_{n\geq3}$ axes? *Yes*
3. Does the molecule have a $C_{n\geq4}$ axis? *No*
4. Does the molecule have any σ planes? *Yes*
5. Does the molecule have an inversion center? *No*



➔ The molecule belongs to the T_d Point Group.

Example: Determine the point group for CH_3Cl.

Solution: Chloromethane has the same tetrahedral shape as methane, but belongs to the point group C_{3v}. The molecule has the following symmetry elements: E, C_3 (along the C-Cl bond axis) and 3 σ_v planes (each containing the chlorine and carbon atoms plus one hydrogen atom. The classification of the molecule goes as follows:



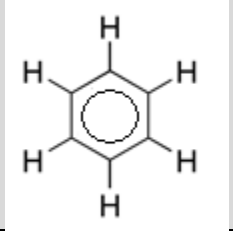
1. Is the molecule linear? *No*
2. Does the molecule have two or more $C_{n\geq3}$ axes? *No*
3. Does the molecule have a C_n axis? *Yes*
4. Are there n C_2 axes perpendicular to the principle axis? *No*
5. Does the molecule have a σ_h plane? *No*
6. Does it have n σ_v planes? *Yes*

➔ The molecule belongs to the C_{3v} point group.

Example: Determine the point group for benzene.

Solution: Benzene has a planar geometry and belongs to the point group D_{6h}. The molecule possesses the following symmetry elements: E, C_6, 6 C_2, 6 σ_v, σ_h and *i*. The classification of the molecule goes as follows:

1. Is the molecule linear? *No*
2. Does the molecule have two or more $C_{n\geq3}$ axes? *No*
3. Does the molecule have a C_n axis? (n = 6 for benzene) *Yes*
4. Are there n C_2 axes perpendicular to the principle axis? *Yes*
5. Does the molecule have a σ_h plane? *Yes*



➔ The molecule belongs to the point group D_{6h}

Example: Classify ethane by its point group.

Solution: Ethene has a planar geometry. The molecule possesses the following symmetry elements: E, 3 C_2, 3 σ, and *i*. The classification of the molecule goes as follows:

1. Is the molecule linear? *No*
2. Does the molecule have two or more $C_{n\geq 3}$ axes? *No*
3. Does the molecule have a C_n axis? *Yes (n = 2)*
4. Are there n C_2 axes perpendicular to the principle axis? *Yes*
5. Does the molecule have a σ_h plane? *Yes*

➔ The molecule belongs to the D_{2h} point group.

Example: Classify the isomers of dichloroethene by their point groups.

Solution: Dichloroethene has three isomers. All of them have a planar geometry.

The cis- and gem- isomers have the following symmetry elements: E, C_2, and 2 σ_v. (The 1,1- (or gem-) isomer has the same elements as the cis- isomer.) The classification of the molecule goes as follows:

1. Is the molecule linear? *No*
2. Does the molecule have two or more $C_{n\geq 3}$ axes? *No*
3. Does the molecule have a C_n axis? *Yes (n = 2)*
4. Are there n C_2 axes perpendicular to the principle axis? *No*
5. Does the molecule have a σ_h plane? *No*
6. Does the molecule have n σ_v planes? *Yes*

➔ The cis-isomer belongs to the C_{2v} point group.

The trans-isomer has the following symmetry elements: E, C_2, σ_h, and *i*. The classification of the molecule goes as follows:

1. Is the molecule linear? *No*
2. Does the molecule have two or more $C_{n\geq 3}$ axes? *No*
3. Does the molecule have a C_n axis? *Yes (n = 2)*
4. Are there n C_2 axes perpendicular to the principle axis? *No*
5. Does the molecule have a σ_h plane? *Yes*

➔ The trans-isomer belongs to the C_{2h} point group.

Multiplication Operation for Symmetry Elements

Multiplication is fairly simple when it comes to symmetry operations. One simply applies the operations from right to left. Going back to the tennis racket example, it is fairly simple to visualize each symmetry element. To show this, it is useful to construct a group multiplication table. To do this, it is useful to pick a corner of the object and imagine where it is transported under a pair of sequential operations. Then imagine what operation will affect the same transformation directly. By applying them pairwise, one can generate the group multiplication table:

$\mathbf{C_{2v}}$	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

What should jump right out from this multiplication table is that the group C_{2v} 1) is abelian (actually, this will become clear after the term is defined) and 2) has the property that each element happens to be its own inverse! For some objects (such as a three-legged stool or an ammonia molecule) this will not be the case.

More definitions: Order and Class

An important definition is the **order** of a group. The order (h) is simply the number of symmetry elements in the group. For the C_{2v} point group, the order is h=4.

Another important concept defines the number of **classes** of operations a point group contains. Two operations (A and B) belong to the same class if there is a third operation (C) in the group that relates them by the **similarity transform**

$$C^{-1}AC = B$$

According to this definition, the operations A and B are said to be **complementary**. A complete set of complementary operations within a group defines a **class**. This will be demonstrated later, using the C_{3v} point group operations.

In the case of the C_{2v} point group, no two elements are in the same class. This has some very important ramifications for the point group. A group for which this the case is said to be an **abelian group**. Not all point groups will have this property however.

Representations

A **representation** is any mathematical construct that will reproduce the group multiplication table. In general, there are an infinite number of representations possible for a given group, however, most of them will be related through simple relationships, and thus can be constructed from (or reduced to) other representations. Those that cannot be reduced to linear combinations of other representations are called **irreducible representations**. The irreducible representations are particularly useful as they can be used to predict the mathematical properties of any function that is an eigenfunction of all of the symmetry elements of a group. The number of classes of operations always gives the number of irreducible representations. Each irreducible representation can be labeled as Γ_i.

To construct a representation for a group, one must assign each operation a mathematical element. For the C_{2v} point group, we can get away with using either 1 or –1 for each element. (This is a consequence of each operation belonging to its own class.) The simplest representation can be constructed by assigning each symmetry element as 1. The group multiplication table will hold, as can be seen below.

C_{2v}	**1**	**1**	**1**	**1**
1	1	1	1	1
1	1	1	1	1
1	1	1	1	1
1	1	1	1	1

Note that each product gives a value that corresponds to the correct element. For example, we let $C_2 = 1$ and $\sigma_v = 1$. The product of $C_2 * \sigma_v$ yields σ_v'. And since the value we assigned $\sigma_v' = 1$ . . and 1*1 = 1 . . everything worked. This particular representation seems pretty trivial since it has to work for any multiplication table that can ever be written! In fact, every point group has this type of representation. Since 1 gives all of the elements of this representation, this is called the **totally symmetric representation**.

Another representation (Γ_2) can be constructed in which E and C_2 are represented by a 1 and σ_v and σ_v' are represented by –1. In this case, the multiplication table looks as follows:

C_{2v}	**1**	**1**	**–1**	**–1**
1	1	1	–1	–1
1	1	1	–1	–1
–1	–1	–1	1	1
–1	–1	–1	1	1

It should be clear again (or easily enough verified) that this has the same pattern as the group multiplication table.

Two other representations can be constructed in this manner (with all of the elements given as either 1 or –1). Together with the first representation, these can be summarized as in the following table.

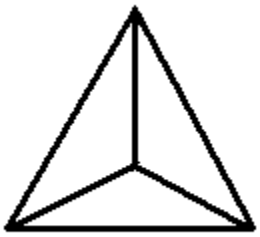
C_{2v}		E	C_2	σ_v	σ_v'
Γ_1	A_1	1	1	1	1
Γ_2	A_2	1	1	-1	-1
Γ_3	B_1	1	-1	1	-1
Γ_4	B_2	1	-1	-1	1

These irreducible representations (Γ_i) go by a standardized set of naming rules. First, the irreducible representations are all singly degenerate (no two-by-two or three-by-three matrices were needed for the representations) so all of the irreducible representations are given the symbol A or B. A is used if the representation is symmetric (1) with respect to the principle rotation axis (C_2) and B if it is antisymmetric (-1) with respect to the principle axis. The subscript is 1 if the representation is symmetric with respect to the σ_v reflection plane, and 2 if the representation is antisymmetric with respect to this plane of reflection. If an irreducible representation requires a set of two-by-two matrices, the representation is designated E, and three-by-three matrix irreducible representations are labeled T.

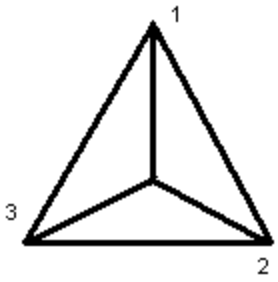
We'll discuss more on the difference between a reducible and irreducible representation later. First, lets work through a slightly more difficult point group. The C_{3v} point group is not abelian and requires matrices for some of the irreducible representations.

The Symmetry of a Triangular Pyramid: a more complex point group

An example of a point group that requires two-by-two matrix elements for the irreducible representations is the C_{3v} point group. This point group (which describes the symmetry elements of an ammonia molecule or a pyramid with an equilateral triangular base) consists of the symmetry elements E, C_3, C_3' (or C_3^2), σ_v, σ_v' and σ_v".



In the figure to the left, the C_3 axis runs perpendicular to the base of the pyramid (you are looking straight down on the top of the pyramid) and the C_3 operation might correspond to a clockwise rotation of the figure about that axis. The C_3' axis is the same as the C_3 axis, but the C_3' operation corresponds to a *counter*clockwise rotation by $2\pi/3$ radians. Note that this operation is equivalent to performing the C_3 operation twice (hence the alternative notation of C_3^2.) The σ_v, σ_v' and σ_v" elements are reflection planes that lie perpendicular



to the base, but each containing one edge of the pyramid. The reader is left to imagine the identity element.

If the corners of the base of the pyramid are labeled for convenience, the effect of each symmetry operation can be represented as follows.

$$\begin{aligned} E \;\; * (1,2,3) &= (1,2,3) \\ C_3 \; * (1,2,3) &= (3,1,2) \\ C_3^2 * (1,2,3) &= (2,3,1) \end{aligned} \qquad \begin{aligned} \sigma_v \; * (1,2,3) &= (1,3,2) \\ \sigma_v' * (1,2,3) &= (3,2,1) \\ \sigma_v'' * (1,2,3) &= (2,1,3) \end{aligned}$$

Following these permutations, it is possible to construct the group multiplication table. The group multiplication table for this group (C_{3v}) looks as follows:

C_{3v}	**E**	**C_3**	**C_3^2**	**σ_v**	**σ_v'**	**σ_v''**
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3
σ_v''	σ_v''	σ_v	σ_v'	C_3	C_3^2	E

From this information, it is possible to separate the operations into classes. Note, for example that $(\sigma_v)^{-1} = \sigma_v$ and $(\sigma_v')^{-1} = \sigma_v'$ and $(\sigma_v'')^{-1} = \sigma_v''$. Using these relationships, the similarity transforms of C_3 involving these operations all yield C_3^2.

$$\begin{aligned} (\sigma_v)^{-1} * C_3 * \sigma_v &= (\sigma_v * C_3) * \sigma_v = \sigma_v'' * \sigma_v \;\; = C_3^2 \\ (\sigma_v')^{-1} * C_3 * \sigma_v' &= (\sigma_v' * C_3) * \sigma_v' = \sigma_v * \sigma_v' \;\; = C_3^2 \\ (\sigma_v'')^{-1} * C_3 * \sigma_v'' &= (\sigma_v'' * C_3) * \sigma_v'' = \sigma_v' * \sigma_v'' \;\; = C_3^2 \end{aligned}$$

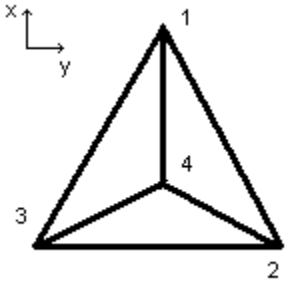
Similarly, the similarity transforms on C_3^2 using these operations all yield C_3.

$$\begin{aligned} (\sigma_v)^{-1} * C_3^2 * \sigma_v &= (\sigma_v * C_3^2) * \sigma_v = \sigma_v' * \sigma_v \;\; = C_3 \\ (\sigma_v')^{-1} * C_3^2 * \sigma_v' &= (\sigma_v' * C_3^2) * \sigma_v' = \sigma_v'' * \sigma_v' \;\; = C_3 \\ (\sigma_v'')^{-1} * C_3^2 * \sigma_v'' &= (\sigma_v'' * C_3^2) * \sigma_v'' = \sigma_v * \sigma_v'' \;\; = C_3 \end{aligned}$$

This is sufficient to indicate that the operations C_3 and C_3^2 belong to the same class. However, to show that these are the only two operations in this class. Consider the similarity transforms based on the operators E, C_3 and C_3^2 on C_3:

$$\begin{aligned} (E)^{-1} * C_3 * E &= (E * C_3) * E = E * C_3 \;\; = C_3 \\ (C_3)^{-1} * C_3 * C_3 &= (C_3^2 * C_3) * C_3 = E * C_3 \;\; = C_3 \\ (C_3^2)^{-1} * C_3 * C_3^2 &= (C_3 * C_3) * C_3^2 = C_3^2 * C_3^2 \;\; = C_3 \end{aligned}$$

The fact that the result of a similarity transform on either C_3 or C_3^2 never results in σ_v, σ_v' or σ_v", is a consequence of the proper rotation operations belonging to a different class than the reflection planes. In fact, there are three classes of operations for this point group. This implies that there are three irreducible representations for this point group.



Another useful approach is to use matrix operators to affect the changes to the object caused by the symmetry operation. The choice of matrix operators depends on the basis set of functions being used to model the system. In this case, we will use position vectors of the corners of the bas of the pyramid. Other choices of basis might be the atomic orbitals on the atoms in a molecule. This is a very convenient choice when the task of constructing symmetry-adapted linear combinations of atomic orbitals for the purpose of modeling molecular orbitals. But I digress . . .

Consider the position vectors of the corners of the base of our trigonal pyramid. They can be specified by indicating the (x, y, z) coordinates if the origin is located in the plane of the base along the axis where all of the symmetry elements intersect.

Corner	x	y	z
1	0	$1/\sqrt{3}$	0
2	1/2	$-1/2\sqrt{3}$	0
3	-1/2	$-1/2\sqrt{3}$	0
4	0	0	h

Only corners 1, 2 and 3 will be important since none of the symmetry elements moves the fourth corner! Assuming unit length for the base edges and a height of h for the pyramid, the following table gives the (x, y, z) coordinates for each of the four corners.

From the previous discussion, we have already determined the effects of each of the symmetry operations.

E * (1,2,3)	= (1,2,3)	σ_v * (1,2,3)	= (1,3,2)
C_3 * (1,2,3)	= (3,1,2)	σ_v' * (1,2,3)	= (3,2,1)
C_3^2 * (1,2,3)	= (2,3,1)	σ_v" * (1,2,3)	= (2,1,3)

The task now is to construct matrix representations for each of the symmetry operations that will affect the above stated changes when matrix multiplication is used as the operation.

The identity element is easy. It will be the 3x3 identity matrix given by $E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

This is easily confirmed since $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$

for any choice of x, y and z. The other operations are a little trickier, but not too hard. It can be shown that the matrix that affects a rotation of α radians about the z-axis is given by

$$\begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

So that the resultant of this operation is given by

$$\begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x\cos\alpha - y\sin\alpha \\ x\sin\alpha + y\cos\alpha \\ z \end{pmatrix}$$

For a rotation of $2\pi/3$ radians, it is useful to note the following.

$$\cos(2\pi/3) = -1/2$$
$$\sin(2\pi/3) = \sqrt{3}/2$$

So the transformation of corner 1 of the pyramid is accomplished as follows for the C_3 operation.

$$\begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 1/\sqrt{3} \\ 0 \end{pmatrix} = \begin{pmatrix} -1/2 \\ -1/2\sqrt{3} \\ 0 \end{pmatrix}$$

The operation has transformed corner 1 into corner 3. It is also easily shown that the operator matrix also transforms corner 2 into corner 1, and corner 3 into corner 2. This is just as expected according to the expression shown above:

$$C_3 * (1, 2, 3) = (3, 1, 2)$$

Additionally, the matrix must satisfy the multiplication table relationship of $C_3 * C_3 = C_3^2$.

$$\begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This is the rotation matrix for a rotation of $-2\pi/3$ radians. Hence, the product worked out as expected since the C_3^2 operation is equivalent to the rotation of $-2\pi/3$ radians.

The matrix representations for the σ_v planes can be worked out by one of two methods. One is to set up the matrix equation for how a point is transformed. The other is by using the group multiplication table to generate a matrix as the product of two other operations in the group for which the matrix has already been established.

To demonstrate these methods, recall from above that the σ_v operation exchanges corners 2 and 3. The matrix for this operation must satisfy the following expression:

$$\begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix}\begin{pmatrix} 1/2 \\ -1/2\sqrt{3} \\ 0 \end{pmatrix} = \begin{pmatrix} -1/2 \\ -1/2\sqrt{3} \\ 0 \end{pmatrix}$$

The matrix that will affect this transformation is:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Now, using the group multiplication table, we can generate σ_v' and σ_v" by the relationships

$$\sigma_v * C_3^2 = \sigma_v'$$
$$\sigma_v * C_3 = \sigma_v''$$

or

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma_v'$$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma_v''$$

The set of matrices can now be used as a representation of the group. However, these matrices can be seen as a reproducible representation of the group since they are in block-diagonal form.

$$E=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} \qquad C_3=\begin{pmatrix}-1/2&-\sqrt{3}/2&0\\\sqrt{3}/2&-1/2&0\\0&0&1\end{pmatrix} \qquad C_3^2=\begin{pmatrix}-1/2&\sqrt{3}/2&0\\-\sqrt{3}/2&-1/2&0\\0&0&1\end{pmatrix}$$

$$\sigma_v=\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix} \qquad \sigma_v'=\begin{pmatrix}1/2&-\sqrt{3}/2&0\\-\sqrt{3}/2&-1/2&0\\0&0&1\end{pmatrix} \qquad \sigma_v''=\begin{pmatrix}1/2&\sqrt{3}/2&0\\\sqrt{3}/2&-1/2&0\\0&0&1\end{pmatrix}$$

This representation can be broken down into two simpler representations. The first consists only of the lower right block of each of the matrices above. This yields the totally symmetric representation. The other is a representation of 2x2 matrices that are made from the upper left block of each of the matrices above. There is one other irreducible representation for the C_{3v} point group. It is given in the table below without derivation, but it is easy to demonstrate that it satisfies the group multiplication table.

C_{3v}		**E**	**C_3**	**C_3^2**
Γ_1	A_1	1	1	1
Γ_2	A_2	1	1	1
Γ_3	E	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1/2&\sqrt{3}/2\\-\sqrt{3}/2&-1/2\end{pmatrix}$	$\begin{pmatrix}-1/2&-\sqrt{3}/2\\\sqrt{3}/2&-1/2\end{pmatrix}$

C_{3v}		**σ_v**	**σ_v'**	**σ_v"**
Γ_1	A_1	1	1	1
Γ_2	A_2	-1	-1	-1
Γ_3	E	$\begin{pmatrix}-1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1/2&\sqrt{3}/2\\\sqrt{3}/2&-1/2\end{pmatrix}$	$\begin{pmatrix}1/2&-\sqrt{3}/2\\-\sqrt{3}/2&-1/2\end{pmatrix}$

The "Great Orthogonality Theorem"

One thing that is important about irreducible representations is that they are orthogonal. This is the property that makes group theory so very useful in chemistry, because orthogonality makes integrals zero. It's always easier to do the integrals when orthogonality tells us the result will be zero before doing any complicated math!

The **Great Orthogonality Theorem** (GOT) can be stated:

$$\sum_R \left[\Gamma_i(R)_{mn}\right]\left[\Gamma_j(R)_{m'n'}\right]^* = \frac{h}{\sqrt{l_i l_j}}\delta_{ij}\delta_{mm'}\delta_{nn'}$$

(Any theorem with that many subscripts must have something truly useful to say!) In this notation, $\Gamma_i(R)_{mn}$ indicates the row m, column n element of the i^{th} irreducible representation for symmetry operation R. The m and n are needed since not all irreducible representations are made up of just 1 and –1. Many irreducible representations need to use matrices to represent each symmetry element. For these cases, l_i gives the dimension of the matrices used in the Γ_i. In our example of the C_{2v} point group, all irreducible representations have $l = 1$, so the GOT can be stated more simply (for this point group specifically) as

$$\sum_R \left[\Gamma_i(R)\right]\left[\Gamma_j(R)\right]^* = h\delta_{ij}$$

Consider applying this statement to the A_2 and B_1 irreducible representations (Γ_2 and Γ_3) for the C_{2v} point group.

$$\begin{aligned}\sum_R \left[\Gamma_2(R)\right]\left[\Gamma_3(R)\right]^* &= \Gamma_2(E)\Gamma_3(E) + \Gamma_2(C_2)\Gamma_3(C_2) + \Gamma_2(\sigma_v)\Gamma_3(\sigma_v) + \Gamma_2(\sigma_v')\Gamma_3(\sigma_v') \\ &= (1)(1) + (1)(-1) + (-1)(1) + (-1)(-1) \\ &= 1 - 1 - 1 + 1 \\ &= 0\end{aligned}$$

Similarly, considering using the GOT on just Γ_4 (the B_2 irreproducible representation) yields the following

$$\begin{aligned}\sum_R \left[\Gamma_4(R)\right]\left[\Gamma_4(R)\right]^* &= \Gamma_4(E)\Gamma_4(E) + \Gamma_4(C_2)\Gamma_4(C_2) + \Gamma_4(\sigma_v)\Gamma_4(\sigma_v) + \Gamma_4(\sigma_v')\Gamma_4(\sigma_v') \\ &= (1)(1) + (-1)(-1) + (-1)(-1) + (1)(1) \\ &= 1 + 1 + 1 + 1 \\ &= 4\end{aligned}$$

Recall that the order of the group (h) is 4 because there are four symmetry elements in the group.

In the case of the C_{3v} point group, there is a 2x2 matrix representation. Consider the upper right member of each of the Γ_3 (E) matrices (row 1, column 2) and apply the GOT to these elements along with the elements of Γ_1 (A_1).

$$\begin{aligned}\sum_R \left[\Gamma_1(R)\right]\left[\Gamma_3(R)_{12}\right] &= (1)(0) + (1)(\sqrt{3}/2) + (1)(-\sqrt{3}/2) + (1)(0) + (1)(-\sqrt{3}/2) + (1)(\sqrt{3}/2) \\ &= 0\end{aligned}$$

Similarly, applying the GOT to the row 1, column 1 elements of Γ_3 (E) we see

$$\sum_R [\Gamma_3(R)_{11}][\Gamma_3(R)_{11}] = (1)^2 + (-1/2)^2 + (-1/2)^2 + (-1)^2 + (1/2)^2 + (1/2)^2$$
$$= 3$$
$$= 6/2$$
$$= h/l_3$$

Now tell me . . isn't that truly a ***Great* Orthogonality Theorem**? (Now how much would you pay?) Once we introduce the concept of *character*, we will restate the GOT in terms of class characters.

Character and Character Tables

Most summaries of group theory do not give the full matrix specifications for each irreducible representation in each important point group. Rather, a very useful quantity is defined, called the **character**. An important property that elements of the same class will share is that they have the same character. As such, it is only necessary to show the character once for each class of operations in the group.

The character of an element is given by the sum of the diagonal elements of the matrix used to represent the symmetry operation.

$$\chi_i(R) = \sum_m \Gamma_i(R)_{mm}$$

C_{3v}	E	C_3	σ_v
A_1	1	1	1
A_2	1	1	-1
E	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \cos(2\pi/3) & -\sin(2\pi/3) \\ \sin(2\pi/3) & \cos(2\pi/3) \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

To evaluate the characters of each of the classes within each irreproducible representation, we need only generate a representation for one operation within each class. The three irreducible representations for some characteristic operators in each class can be expressed as follows:

Using the expressions above, the character table for the C_{3v} group can be expressed as

C_{3v}	E	2 C_3	3 σ_v
A_1	1	1	1
A_2	1	1	-1

E	2	-1	0

Note that the character of the identity element is always given as the dimension of the matrices used in the irreducible representation.

$$\chi_i(E) = l_i$$

The GOT can be expressed in terms of characters.

$$\sum_R \chi_i(R)\chi_j(R) = h\delta_{ij}$$

This statement has a number of important and useful properties and consequences. One relationship deals with the sum of the squares of the characters of the identity elements.

$$\sum_i [\chi_i(E)]^2 = h$$

These expressions can be used to find and verify the characters for other point groups. For example, consider the partial character table for the point group C_{4v}.

A typical kind of exam or quiz question might be to fill in the missing values. In this case, all of the values are missing! So let's tackle the problem based on what we know from definitions, and complete the problem by using of the GOT.

C_{4v}	E	2 C_4	C_2	2 σ_v	2 σ_d
A_1					
A_2					
B_1					
B_2					
E					

First off, the order of the group is h = 8. Second, every group has a totally symmetric representation. This is the A_1 representation and has members that are all 1. Let's fill that in (using red for clarity.)

C_{4v}	E	2 C_4	C_2	2 σ_v	2 σ_d
A_1	1	1	1	1	1
A_2					
B_1					
B_2					
E					

Additionally, we can fill in the column for the identity element. All of the A and B representations are singly degenerate, and the E representation is doubly degenerate. So using the expression

$$\sum_i [\chi_i(E)]^2 = h$$

That yields the following (shown in red):

C_{4v}	E	2 C_4	C_2	2 σ_v	2 σ_d
A_1	1	1	1	1	1
A_2	1				
B_1	1				
B_2	1				
E	2				

And it clearly satisfies

$$\sum_i [\chi_i(E)]^2 = (1)^2 + (1)^1 + (1)^2 + (1)^1 + (2)^2$$
$$= 8 = h$$

Now using the definition that A representations have a character of 1 for the (are symmetric with respect to) the principle rotation axis and B representations have a character of –1 for (or are antisymmetric with respect to) the principle axis rotation. Thus, we can fill in

C_{4v}	E	2 C_4	C_2	2 σ_v	2 σ_d
A_1	1	1	1	1	1
A_2	1	1			
B_1	1	-1			
B_2	1	-1			
E	2	?			

But should we do about the character of the C_4 operation under the irreducible doubly degenerate representation E? One solution comes from another important consequence of the GOT. This can be stated as

$$\sum_i \chi_i(R_m)\chi_i(R_n) = h\delta_{mn}$$

Using this relationship, we can solve for the character of the C_4 operation under the E irreducible representation.

$$\sum_i \chi_i(E)\chi_i(C_4) = \sum_i \chi_i(E)[2\chi_i(C_4)]$$
$$= 2(1)(1) + 2(1)(1) + 2(1)(-1) + 2(1)(-1) + 2(2)x = 0$$

The only value of x that will satisfy this expression is $x = 0$. We can enter this value and also apply the definitions that the A_1 and B_1 representations are symmetric with respect to the σ_v operation and the A_2 and B_2 representations are antisymmetric with respect to σ_v.

C_{4v}	E	2 C_4	C_2	2 σ_v	2 σ_d
A_1	1	1	1	1	1
A_2	1	1		-1	
B_1	1	-1		1	
B_2	1	-1		-1	
E	2	0		?	

Again, the question mark can be removed as above.

$$\sum_i \chi_i(E)\chi_i(\sigma_v) = \sum_i \chi_i(E)[2\chi_i(\sigma_v)]$$
$$= 2(1)(1) + 2(1)(-1) + 2(1)(1) + 2(1)(-1) + 2(2)x = 0$$

Once again, as luck would have it, the only value of x that satisfies the equation is $x = 0$. Now, we can apply the GOT to the representations for A_1, and A_2 to generate an equation with two unknowns to determine the characters of C_2 and σ_d for representations A_2 and B_1. We can solve it because we know x and y can only be 1 or –1. (These are the only values possible for singly degenerate representations.)

$$\sum_R \chi_i(R)\chi_j(R) = \chi_1(E)\chi_2(E) + 2\chi_1(C_4)\chi_2(C_4) + \cdots$$
$$= (1)(1) + 2(1)(1) + (1)x + 2(1)(-1) + 2(1)y = 0$$
$$= 1 + x + 2y = 0$$

C_{4v}	E	2 C_4	C_2	2 σ_v	2 σ_d
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1		1	
B_2	1	-1		-1	
E	2	0		0	

The only combination that works is $x = 1$ and $y = -1$. The character table now looks as follows:

Completion of the rest of the character table is left as an exercise.

Direct Products

The intensity of a transition in the spectrum of a molecule is proportional to the magnitude squared of the transition moment matrix element.

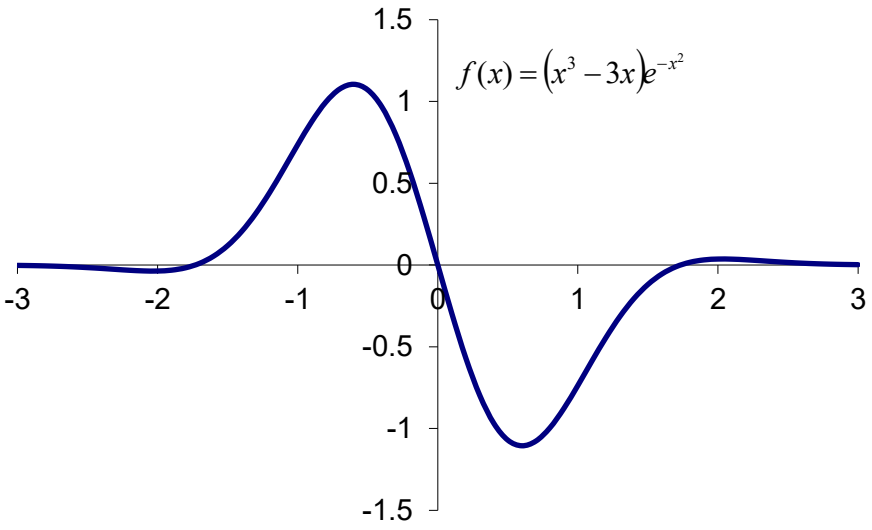
$$\text{Intensity} \propto \left| \int (\psi')^* \, \vec{\mu} (\psi'') d\tau \right|^2$$

By knowing the symmetry of each part of the integrand, the symmetry of the product can be determined as the **direct product** of the symmetries of each part $(\psi')^*$, (ψ'') and μ. This is helpful, since the integrand must not be antisymmetric with respect to any symmetry elements or the integral will vanish by symmetry. Before exploring that concept, let's look at the concept of direct products.

This is a concept many people have seen, in that the integral of an odd function over a symmetric interval, is zero. Recall what it means to be an "odd function" or an "even function.

Symmetry	definition	Integreals
Even	f(-x) = f(x)	$\int_{-a}^{a} f(x)dx = 2\int_{0}^{a} f(x)dx$
Odd	f(-x) = -f(x)	$\int_{-a}^{a} f(x)dx = 0$

Consider the function $f(x) = \left(x^3 - 3x\right)e^{-x^2}$. A graph of this function looks as follows:



One notes that the area under the curve on the side of the function for which $x > 0$ has exactly the same magnitude but opposite sign of the area under the other side of the graph. Mathematically,

$$\int_{-a}^{a} f(x)dx = \int_{-a}^{0} f(x)dx + \int_{0}^{a} f(x)dx$$
$$= -\int_{0}^{a} f(x)dx + \int_{0}^{a} f(x)dx$$
$$= 0$$

It is also interesting to note that the function *f(x)* can be expressed as the product of two functions, one of which is an odd function ($x^3 - 3x$) and the other which is an even function (e^{-x^2}). The result is an odd function. By determining the symmetry of the function as a product of the eigenvalues of the functions with respect to the inversion operator, as discussed below, one can derive a similar result.

The even/odd symmetry is an example of inversion symmetry. Recall that the inversion operator (in one dimension) affects a change of sign on *x*.

$$\hat{i}f(x) = f(-x)$$

"Even" and "odd" functions are eigenfunctions of this operator, and have eigenvalues of either +1 or –1. For the function used in the previous example,

$$f(x) = g(x)h(x)$$

where

$$g(x) = x^3 - 3x \qquad \text{and} \qquad h(x) = e^{-x^2}$$

Here, g(x) is an odd function and h(x) is an even function. The product is an odd function. This property is summarized for any $f(x) = g(x)h(x)$, in the following table.

g(x)	h(x)	f(x)	*i*g(x)=__g(x)	*i*h(x)=__h(x)	*i*f(x)=__f(x)
even	even	even	1	1	1
even	odd	odd	1	-1	-1
odd	odd	even	-1	-1	1

Note that the eigenvalue (+1 or –1) is simply the character of the inversion operation for the irreducible representation by which the function transforms! In a similar manner, any function that can be expressed as a product of functions (like the integrand in the transition moment matrix element) can be determined as the direct product of the irreducible representations by which each part of the product transforms.

Consider the point group C_{2v} as an example. Recall the character table for this point group.

C_{2v}	E	C_2	σ_v	σ_v'			
A_1	1	1	1	1	z		x^2-y^2, z^2
A_2	1	1	-1	-1		R_z	xy
B_1	1	-1	1	-1	x	R_y	xz
B_2	1	-1	-1	1	y	R_x	yz

The direct product of irreducible representations can by the definition

$$\chi_{prod}(R) = \chi_i(R) \otimes \chi_j(R)$$

So for the direct product of B_1 and B_2, the following table can be used.

C_{2v}	E	C_2	σ_v	σ_v'
B_1	1	-1	1	-1
B_2	1	-1	-1	1
$B_1 \otimes B_2$	1	1	-1	-1

The product is actually the irreducible representation given by A_2! As it turns out, the direct product will always yield a set of characters that is either an irreducible representation of the group, or can be expressed as a sum of irreducible representations. This suggests that a multiplication table can be constructed. An example (for the C_{2v} point group) is given below.

Studying this table reveals some useful generalizations. Two things in particular jump from the page. These are summarized in the following tables.

	A	B
A	A	B
B	B	A

	1	2
1	1	2
2	2	1

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

This pattern might seem obvious to some. It stems from the idea that

*symmetric*symmetric = symmetric*
*symmetric*antisymmetric = antisymmetric*
*antisymmetric*antisymmetric = symmetric*

Noting that A indicates that an irreducible representation is *symmetric* with respect to the C_2 operation and B indicates that an irreducible representation is *antisymmetric* . . and that the

subscript 1 indicates that an irreducible representation is *symmetric* with respect to the σ_v operation, and that a subscript 2 indicates that an irreducible representation is *antisymmetric* . . the rest seems to follow! Some point groups have irreducible representations use subscripts g/u or primes and double primes. The g/u subscript indicates symmetry with respect to the inversion (*i*) operator, and the prime/double prime indicates symmetry with respect to a σ plane (generally the plane of the molecule for planar molecules).

This method works well for singly degenerate representations. But what does one do for products involving doubly degenerate representations? As an example, consider the C_{3v} point group.

C_{3v}	E	2 C_3	3 σ_v		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x, y)	(R_x, R_y)

Consider the direct product of A_2 and E.

C_{3v}	E	2 C_3	3 σ_v
A_2	1	1	-1
E	2	-1	0
$A_2 \otimes E$	2	-1	0

This product is clearly just the E representation. Now one other example – Consider the product E⊗E.

C_{3v}	E	2 C_3	3 σ_v
E	2	-1	0
E	2	-1	0
E⊗E	4	1	0

To find the irreducible representations that comprise this reducible representation, we proceed in the same manner as determining the number of vibrational modes belonging to each symmetry.

$$N_{A_1} = \frac{1}{6}\left[(1)(4) + 2(1)(1) + 3(1)(0)\right] = 1$$

$$N_{A_2} = \frac{1}{6}\left[(1)(4) + 2(1)(1) + 3(-1)(0)\right] = 1$$

$$N_{E} = \frac{1}{6}\left[(2)(4) + 2(-1)(1) + 3(0)(0)\right] = 1$$

This allows us to build a table of direct products. Notice that the direct product always has the total dimensionality that is given by the product of the dimensions.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	A_1+ A_2+E

The concepts developed in this chapter will be used extensively in the discussions of vibrational, rotational and electronic degrees of freedom in atoms and molecules.

Vocabulary and Concepts

Problems

1. Find the symmetry elements and point groups for the following molecules
    a. SF_4
    b. $CHCl_3$
    c. Pyridine
    d. Naphthalene
    e. ICl_5
    f. PCl_5

2. Consider diazine, which has three isomers. Determine which isomer(s) has/have C_{2v} symmetry and which has/have D_{2h} symmetry.

3. Complete the following character table.

	E	2 A	2 B	C	3 D	3 F
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1

B_1			1			
B_2	1	-1	1	-1	-1	1
E_1			1			
E_2			-1			

4. Complete the following direct product table.

C_{4h}	A_g	B_g	E_g	A_u	B_u	E_u
A_g	A_g	B_g	E_g	A_u	B_u	E_u
B_g	B_g					
E_g	E_g		$A_g+B_g+E_g$			$A_u+B_u+E_u$
A_u	A_u			A_g		
B_u	B_u					
E_u	E_u					

5. Consider the following group multiplication table. Separate the operations into classes.

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	E	F	C	D
B	B	E	A	D	F	C
C	C	D	F	E	A	B
D	D	F	C	B	E	A
F	F	C	D	A	B	E

6. Demonstrate that the A_2, B_1, B_2 and E irreducible representations are orthogonal to the A_1 irreducible representation under the point group C_{4v}.

7. A point group has 8 operations which fall into five classes. How many irreducible representations will it have? How many will be singly degenerate? How many will be doubly degenerate?