EXPERIMENT 5

MOLECULAR SYMMETRY, POINT GROUPS AND CHARACTER TABLES

NOTE: lab write-up consists of submitting answers to the exercises embedded in handout.

INTRODUCTION

Finite symmetries are useful in the study of molecules. They are used in the classification of molecules, simplifying quantum mechanical calculations on molecules, determining the presence of certain molecular properties such as molecular polarity and chirality. It will become apparent how important symmetry considerations are for molecules and orbitals in physical processes such as NMR spectroscopy and x-ray crystallography in molecular structure determination. In this dry lab, we will focus on finite symmetries and groups of finite symmetry operators, using Chapter 11 of Atkins and de Paula[1] as a principle reference. Other books listed in the references are excellent source books as well.[2-4]

The set of all symmetry operations for a molecule form a mathematical structure called a group. In this lab, we will look at group structure, classes of symmetry operations, naming of molecular point groups and physical implications. The latter will include how group structure can predict when a molecule is polar or chiral and how one can explain and understanding orbitals and nodes in a molecule.[5-7]

SYMMETRY ELEMENTS AND OPERATIONS

A symmetry operation transforms a molecule into itself so that the transformed molecule is indistinguishable from the original structure. Also, at least one point in the molecule is always left undisturbed by the transformation. This is the origin of the term, molecular point group. Often, two or more atoms are permuted during the course of the molecular transformation. Since atoms of the same type are indistinguishable, the transformed molecule is indistinguishable from the starting molecule. So, a molecular point group consists of all those symmetry operations that leave a point in the molecule invariant and permute identical atoms.

Symmetry operations come in several flavors: 1) no operation, 2) rotation, 3) reflection, 4) inversion, 5) improper rotation. The operation is denoted by symbols in plain text (E, C_n, etc.), whereas the actual axis or plane referred to in a molecule is denoted by symbols in italics (*E*, *C_n*, etc.).
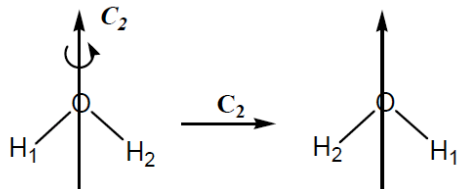
1) **E** The identity transformation

This operation does nothing and is a symmetry element of all molecules. The symbol E is used from the German **Einheit**, meaning unity.
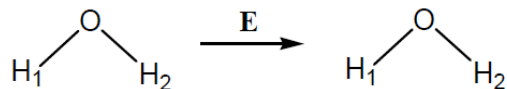
2) C_n The rotation operation

This takes place about a rotation axis. The molecule is rotated by an angle of $2\pi/n$ radians (n is an integer). For a water molecule the rotation is $2\pi/2 = \pi$ radians or 180°:

By convention, a rotation by a positive angle indicates a counterclockwise direction (as above) and a rotation through a negative angle is performed in a clockwise direction. Each rotation of the molecule into itself is an n-fold rotation along the axis.

Some molecules have more than one axis, as in the example below (C_4 and C_2 axes exist):
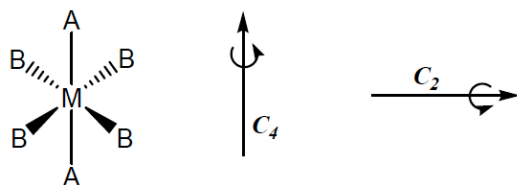
In these cases, the convention dictates that the axis with the higher value of n is called the principal axis (C_4 above).

Some molecules contain more than one operation along an axis. Consider the square planar structure XeF_4 – it has a C_4 axis through the Xe atom that is perpendicular to the plane of the molecule. Carrying out two consecutive 4-fold rotations, i.e. $C_4^2 = C_4C_4$, about a C_4 axis is equivalent to conducting a C_2 rotation about the same axis. Therefore, the C_2 axis is coincident with the C_4 axis. In XeF_4, the C_4 axis is the principal axis of rotation with a C_2 axis coincident to it. In H_2O, the C_2 axis is the principal axis of rotation with no other axes coincident to it.
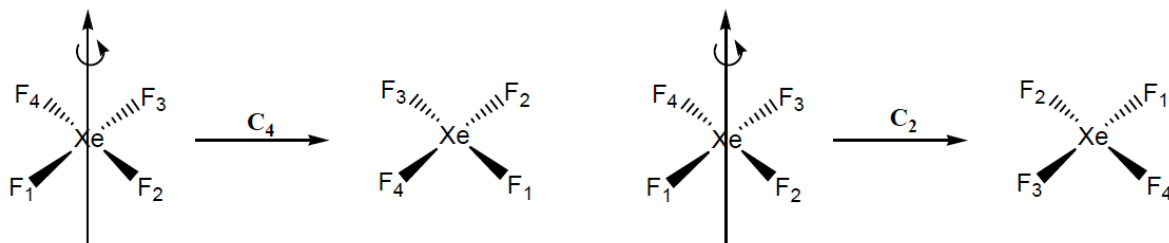
For a diatomic molecule (e.g., HCl), a rotation by any arbitrary angle can be performed about the internuclear axis. Such an axis is called a C_∞ axis and is the principal axis of rotation. It also has a coincident axis.
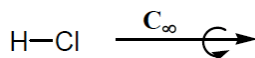
3) σ Reflection through a plane

A reflection takes place in a plane of symmetry, sometimes called a mirror plane (**speigal** is German for mirror). Reflection planes can either contain rotation axes or be

perpendicular to an axis of rotation. When a plane is perpendicular to a principal axis of rotation it is designated by the symbol σ_h and sometimes called the horizontal plane.[1] When a plane contains a principal axis of rotation it is usually denoted by σ_v. That is to say the plane and axis are parallel to one another. This is usually called the vertical plane.[1]
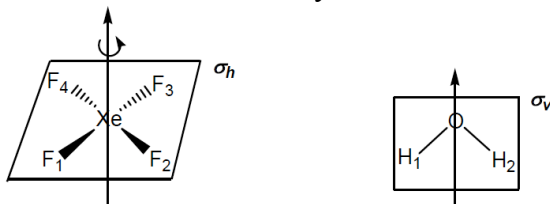
A special case of plane is the dihedral plane, denoted σ_d. In the BF$_3$ molecule below there are three reflection planes, each containing BF$_n$ (only the plane through B-F$_2$ is shown). Each of these planes bisects the angle between the remaining two fluorines in the rotation of the **secondary** C_2 axis (the principal axis here is the C_3 axis through the central boron with the fluorines perpendicular to that axis; only one of the C_2 axes is shown – the one through B-F$_2$ permuting F$_1$ and F$_3$).
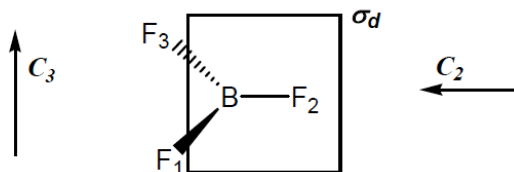
Note that often other criteria are needed to distinguish between σ_v planes and σ_d planes. For example, water has two reflection planes, but both of them are σ_v planes—one as shown above, the other which is perpendicular to it. These σ_v planes are both parallel to the principal axis, which is C_2. There are no other C_2 axes perpendicular to this principal axis that can be bisected by a plane, so neither of these planes can be σ_d. In XeF$_4$, the reflection plane perpendicular to the principal C_4 axis is a σ_h plane. There are four planes that bisect the F$_n$XeF$_m$ angles. There are also secondary and tertiary C_2 axes lying along F$_n$-Xe-F$_m$ and bisecting the F$_n$XeF$_m$ angle respectively. Those planes corresponding to the bisecting C_2 axis are those that are σ_d planes.

4) **i** Inversion through the origin

The inversion operation, denoted i or I, occurs through the centre of inversion, i. A point in the molecule (x, y, z) is taken and transformed to another point (-x, -y, -z). The chemical environments are identical. Water does not posses an inversion centre, whereas XeF$_4$ does.
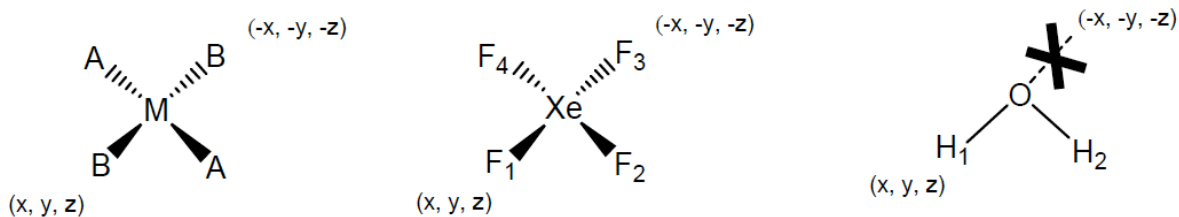
[1] Keep in mind that not all σ_h planes are 'horizontal,' nor are all σ_v planes 'vertical.'

5) S_n Improper rotation

Improper rotation is composed of two successive transformations: 1) an *n*-fold rotation about an axis (using S notation instead of C notation to denote the axis—S_n); 2) a reflection in a plane that is perpendicular to that S_n axis. The *n*-fold rotation does not need to match an actual *n*fold rotation axis in the molecule, as seen in allene below. Here, the *n*-fold rotation is by 90° whereas a rotation axis should be 180° for complete symmetry.

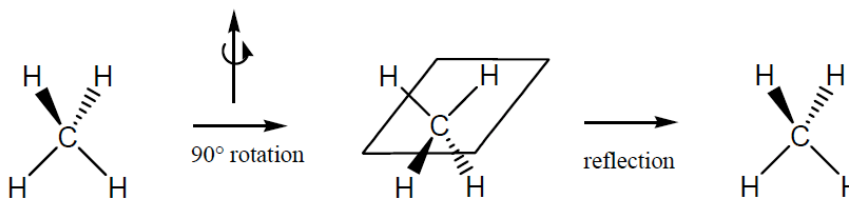90° rotation   reflection
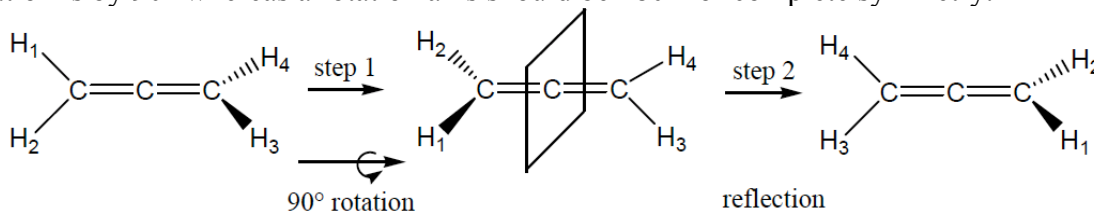
This particular rotation through the three-carbon chain (step 1) yields a representation of the structure that is distinguishable from the original molecule. A reflection through a plane containing the central carbon (step 2) must be carried out to make the two indistinguishable.

By the same reasoning, the reflection plane perpendicular to the S_n axis need not be an actual reflection plane. In the complex ion $[Co(NCS)_4]^{+2}$, the reflection plane that is being considered for step 2 (after the rotation of step 1) is not a true mirror plane. However, upon the reflection step we see the original structure.
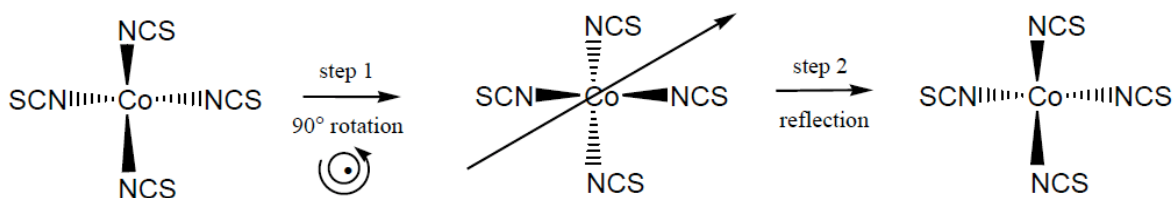
Water does not possess an improper axis of rotation because it does not have a plane of symmetry that is perpendicular to the axis of rotation (it does have vertical reflection planes, but these have no bearing on the S_n operation). The CH_4 molecule, however, has four S_4 axes (one through each CH bond), but no C_4 axis.

90° rotation   reflection

Improper rotation is typically denoted as S_n, as shown below, but it is easier to write out both the rotation and reflection steps as we have done above.
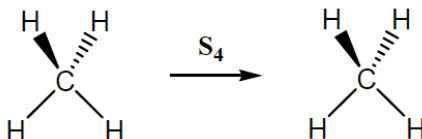
We can know the n value for the S_n operation by the angle used for the rotation step. In CH_4 this is 90°, which is rotation by $2\pi/n$ or 360°/4, so n = 4 and the molecule has S_4 improper rotation. This is also true for $[Co(NCS)_4]^{+2}$ which requires a 90° rotation, so it also has an improper rotation S_4. If a molecule had a 60° rotation this would mean it had S_6 improper rotation (360°/6 = 60°).

A convenient way to determine point groups for molecules is to use a flow chart (Figure 1). Consider ammonia as an example. Is the molecule linear? The answer is **no**. It has only one axis of rotation, a C_3 axis that is the principle axis of rotation. Are there any C_2 axes perpendicular to the principal axis? The answer is **no**. Is there a reflection plane perpendicular to the principal axis? Again, the answer is **no**. Does it contain three σ_v planes containing the C_3 axis? The answer is **yes**. Therefore NH_3 must have C_{3v} symmetry.
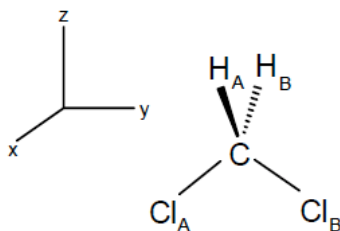
SYMMETRY GROUPS

We use the phrases symmetry groups and molecular point groups synonymously.

A mathematical group, $\mathbf{G} = \{G, \cdot\}$, consists of a set of elements[2] $G = \{E, A, B, C, D, ...\}$ and a binary relation, called group multiplication or group product or simply multiplication or product, denoted by '$\cdot$', which satisfies the following properties:

a. The product of any two elements A and B in the group is another element in the group, i.e., we write $A \cdot B \in G$.

b. If A, B, C are any three elements in the group then $(A \cdot B) \cdot C = A \cdot (B \cdot C)$. Therefore, group multiplication is associative, and frequently, we omit the brackets.

c. There is a unique element E in G such that $E \cdot A = A \cdot E = A$, for every element A in G. The element E is called the identity element.

d. For every element A in G, there is a unique element X in G, such that $X \cdot A = A \cdot X = E$. The element X is referred to as the inverse of A and is denoted A^{-1}. The identity is its own inverse.

The number of elements in a group is called the order of the group. Frequently, this is denoted by the symbol h. It is common to omit the symbol '$\cdot$' when no confusion will arise. Also, when there can be no confusion, we will use the symbol G for the group rather than $\mathbf{G}$.

We can think of the group elements as symmetry operations of a molecule. This means that we can "translate" $A \cdot B$ to: "first we perform the symmetry operation B on the molecule followed by symmetry operation A." The net result of such consecutive action on a molecule is another symmetry operation. Take dichloromethane as an example. The molecular structure and Cartesian axis system are shown below. In this figure, you can think

of the origin of the Cartesian axes as centered on the C atom with the z-axis bisecting the HCH and the ClCCl angles. The x-axis lies in the HCH plane, while the y-axis is in the

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[2] Do not confuse symmetry elements discussed in section 2 with group elements. The set of symmetry elements does not form a group, only the symmetry operations form a group. The term element used in this definition is standard usage in set theory.
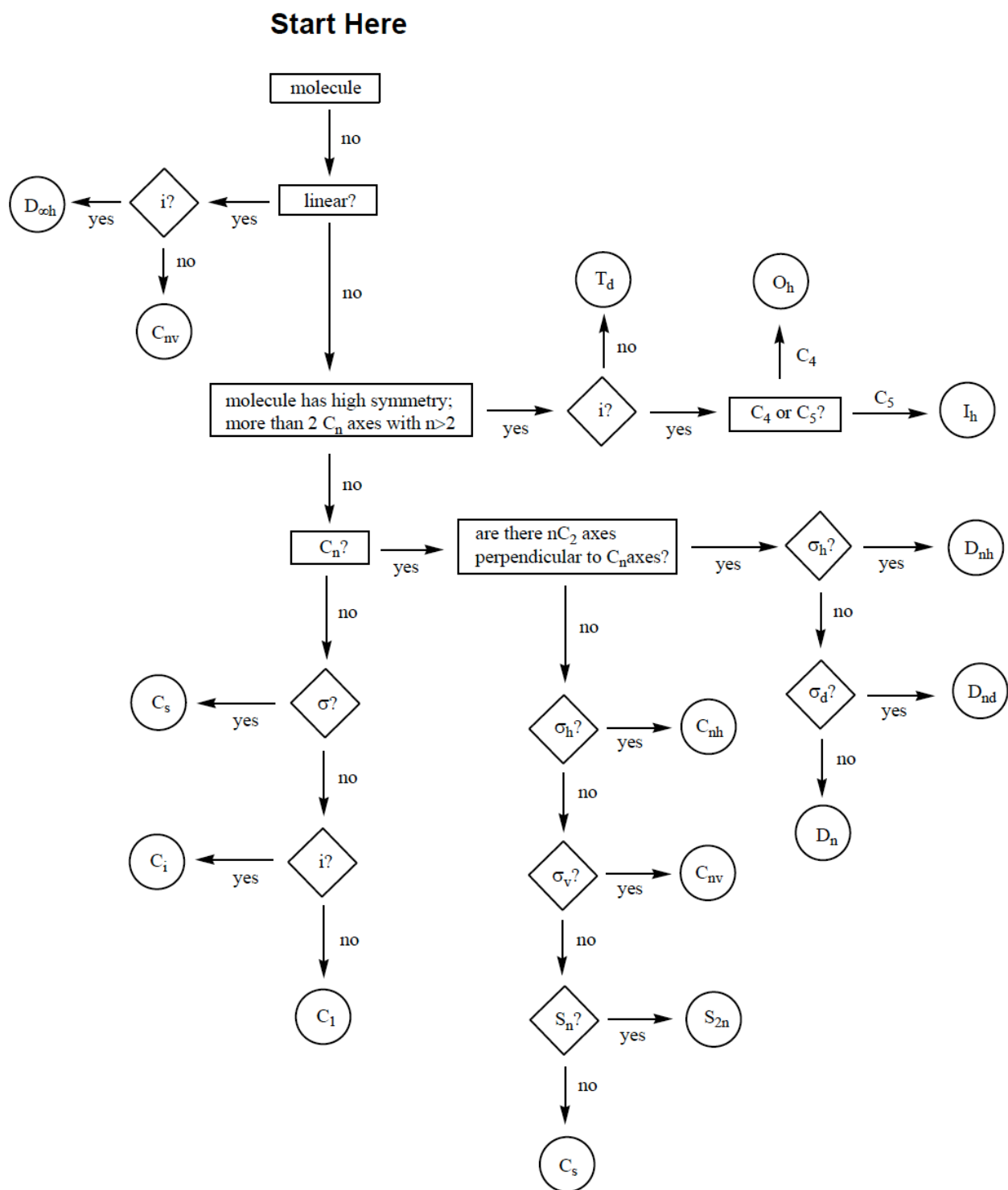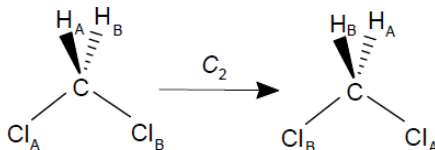
Start Here

Figure 1: Schoenflies flow chart for determining point groups of molecules

ClCCl plane.

The identity operation, E, leaves the molecule unchanged. The C_2 axis lies along the z-axis. The C_2 operation transforms the dichloromethane molecule as so.

Carrying out two consecutive C_2 operations is equivalent to the identity transformation. There are two reflection planes in the molecule; both contain the rotation axis. One plane is the plane of the page containing the ClCCl plane. We will label this plane $\sigma'(yz)$. The second plane is perpendicular to the plane of the page; we will label it $\sigma(xz)$. The action of $\sigma'(yz)$ is to give the arrangement of atoms shown, where the two hydrogen atoms have been interchanged, while the two chlorine atoms and carbon are unchanged. $\sigma(xz)$
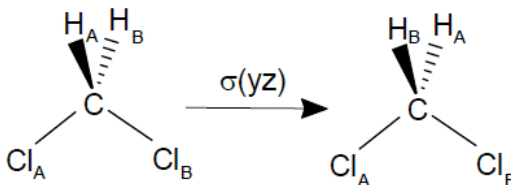
permutes the chlorine atoms, but leaves carbon and the two hydrogen atoms fixed.
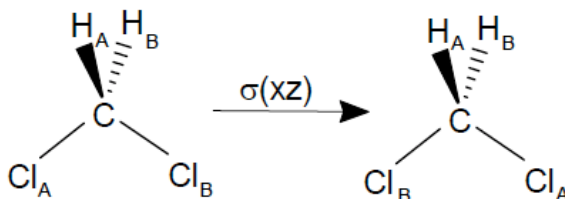
Applying the plane $\sigma(yz)$ twice, i.e., $(\sigma'(yz))^2 = \sigma'(yz)\sigma'(yz) = E$, we get the identity. This means that $\sigma'(yz)$ is its own inverse (see (d) above). Similarly, we find that $(\sigma(xz))^2 = \sigma(xz)\sigma(xz) = E$, and $\sigma(xz)$ is its own inverse. Now, if we carry out a $\sigma(xz)$ reflection first and follow it by a $\sigma'(yz)$ reflection, we get the following.
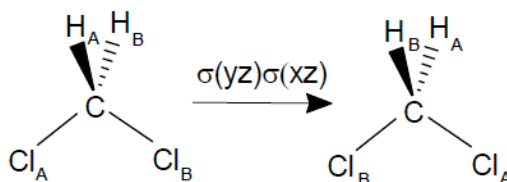
Comparing this diagram to that of a C_2 rotation we see that the result is identical. Therefore, we say that $\sigma'(yz)\sigma(xz) = C_2$. You can show that performing the reflections in reverse order yields the same result. Note that the symmetry elements remain fixed and are not transformed to new positions when the atoms in the molecule move to new positions. What about carrying out a C_2 rotation followed by the reflection $\sigma'(yz)$? Performing these symmetry operations yields the following.
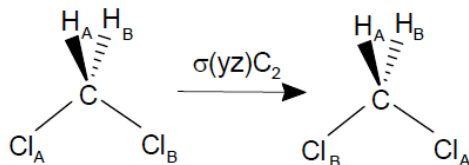
This is equivalent to a σ(xz) operation. You can show that carrying out these operations in reverse order affords the same result. Next, we compute the product σ(xz)C₂.
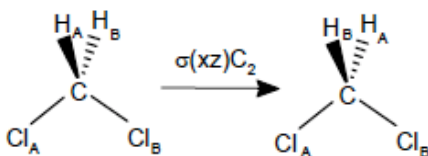
This is identical with a σ′(yz) operation. Again, check that the reverse sequence of operations yields the same result. Using the definition of the group and the products of symmetry operations that we have just uncovered, we can construct a group multiplication table:

C_{2v}	E	C_2	σ(xz)	σ'(yz)
E	E	C_2	σ(xz)	σ'(yz)
C_2	C_2	E	σ'(yz)	σ(xz)
σ(xz)	σ(xz)	σ'(yz)	E	C_2
σ'(yz)	σ'(yz)	σ(xz)	C_2	E

This table contains all the information about the group and its structure. The name of this molecular point group is C_{2v}. There are some observations to make about this table.

a. Notice the inner four-by-four box. In each row and each column, each operation appears once and only once. In other words, each row and each column is a permutation of the others. This is a feature possessed by all group multiplication tables.

b. We can identify smaller groups within the larger one. For example, {E,C₂} is a group. There are two others; what are they? These smaller groups are called subgroups of C_{2v}.

c. In this particular table, we observe that the group product is commutative. This is not necessarily true for other groups.

In the ammonia molecule, the nitrogen atom is the fixed point. The molecule has a C₃ axis of rotation. Note that the both the C₃ and C_3^2 operations occur about the same C₃ axis.
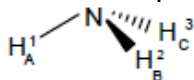
There are three reflection planes; each plane contains an NH bond and bisects the opposing HNH angle. Each plane can be labeled by the number on the hydrogen atom it contains, thus σ₁ is the plane containing H_A^1. This reflection interchanges atoms H_B and H_C, leaving H_A fixed. Note that the numbers remain fixed to their original positions. The symmetry elements
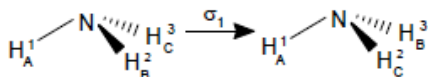
must not shift with the atoms when they are transformed to new positions. In the previous

example, we used labels for the reflection planes that were expressed in terms of the fixed axes external to the molecule. In this example, it is not obvious how to do that. So keep in mind here that the numbers stay fixed and the letters move. You will want to use the double labels whenever it is inconvenient to label axes with references outside the molecule. It is irrelevant whether the numbers stay fixed and the letters move or vice versa. Just be consistent within a given application.

Since $\sigma_1^2 = \sigma_2^2 = \sigma_3^2 = E$, each reflection is its own inverse. Since $C_3^3 = C_3^2 C_3 = C_3 C_3^2 = E$, C_3^2 is the inverse of a C_3 rotation (or C_3 is the inverse of C_3^2). Recall that a C_3 rotation is a 120° rotation in the counterclockwise direction about the rotation axis, while C_3^2 is a 240° counterclockwise rotation. Also, we can interpret a C_3^2 rotation as a -120° rotation (clockwise).

Example A: rotation, $C_3 \times C_3 = C_3^2$, for ammonia:
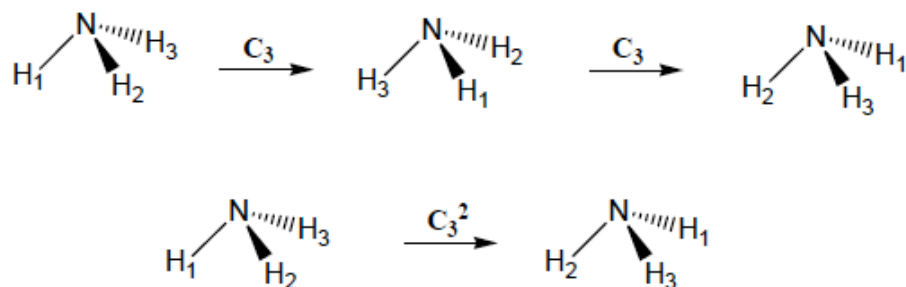
Example B: reflection, $\sigma_3 \times \sigma_2 = C_3$, for ammonia
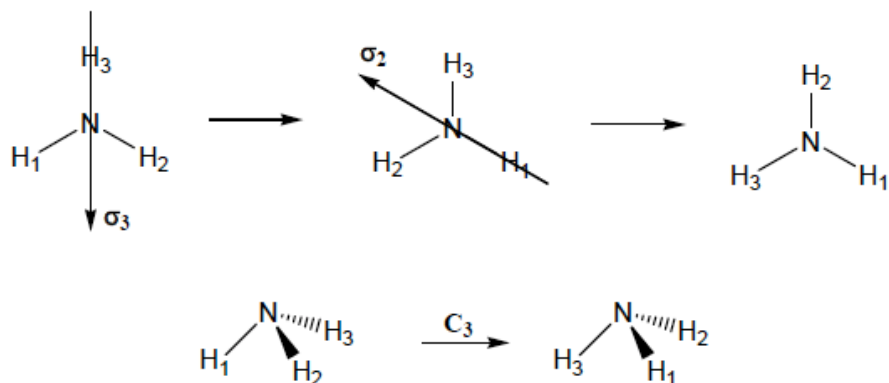
Example C: both operations combined, $C_3 \times \sigma_1 = \sigma_2$, for ammonia
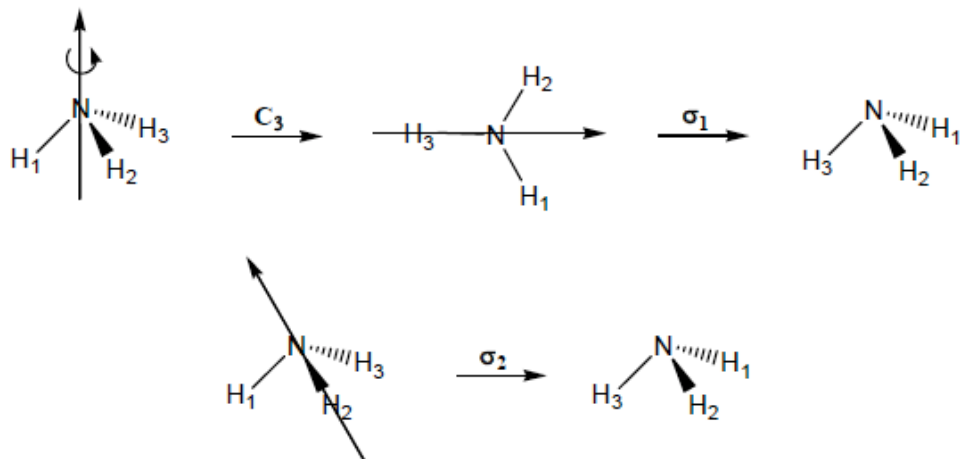
Remember that:
  i. the C_3 axis rotates counterclockwise
  ii. in a multiplication the row across is the first term and the column down is the second term
  iii. each row (column) is a permutation of another row (column)
  iv. no symmetry element can occur more than once in a row or column
  v. labels for reflection planes always correspond to those in the original molecule, despite the numbering system after an operation (see examples B and C)

Given these definitions and considerations, here is the complete group multiplication table:

C_{3v}	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^2	E

Exercise 1: The point group of the BrF_5 molecule is C_{4v}. There are eight symmetry operations in the group. Construct the group multiplication table using the template below. You may use the textbook, models, or other resources to help you. Use the given molecule and numbering system as well as the rules from Exercise 1 and the following hints. Draw out your results as you did before.   (16 marks)

Hints for constructing the table:
  1. start with the identity row and column
  2. do the rotational axes times rotational axes
  3. remember σ planes times themselves = E
  4. look for patterns in the table and confirm these by drawing out structures

rotations for BF_5
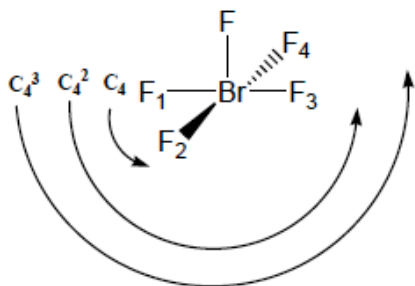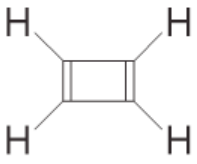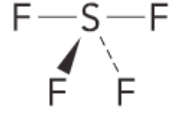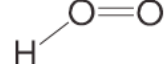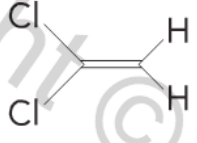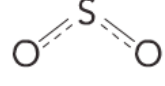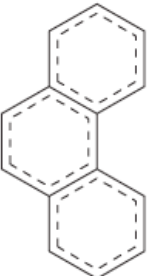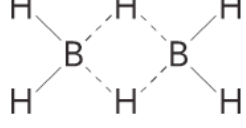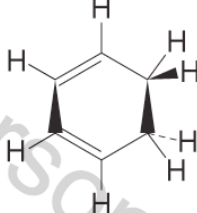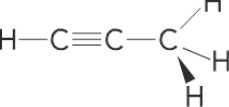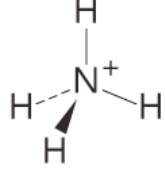
reflection planes for BF_5

C_{4v}	E	C_4	C_4^2	C_4^3	σ_1	σ_2	σ_3	σ_4
E								
C_4								
C_4^2								
C_4^3								
σ_1								
σ_2								
σ_3								
σ_4								

Happily it is not necessary to derive a group multiplication table each time you want to find the point group of a molecule or molecular ion. It is sufficient to determine the presence of only a particular subset of symmetry elements (C_n or σ_x). Once you have discovered the molecular point group, the character table for the point group will give you the remaining group operations. See Atkins and de Paula, Resource Section Part 3 for printed character tables.

Exercise 2: Determine the molecular point groups for the following species. Use the flow chart. It may also help to use a molecular model kit. (10 marks)

PHYSICAL IMPLICATIONS OF SYMMETRY

Chemists use symmetry in a wide variety of ways. In quantum chemistry, symmetry allows us to classify molecular orbitals and state wave functions.[5-7] With this classification, we can simplify calculations of certain matrix elements or expectation values. Often, it is possible to decide when matrix elements or expectation values are zero just on the basis or symmetry alone. In vibrational spectroscopy, frequently, the vibrational modes of a molecule are classified according to their behavior under the symmetry operations of the molecular point group. You are already familiar with polarity and chirality from earlier chemistry courses. Now we will examine these concepts in greater depth with respect to the specific symmetry of a molecule. Relating these concepts to symmetry will help in future chemistry courses.

Polarity: The idea is very simple; a polar molecule has a permanent electric dipole moment, μ, which is a vector quantity. The dipole moment has a specific orientation in the molecule. If a molecule has a rotation axis, then the dipole moment must lie along the rotation axis, since no dipole moment can change under a rotation. Consider water, its dipole moment lies along its C_2 axis:
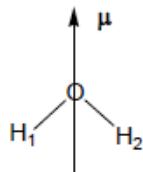
If a molecule possesses a secondary axis or a plane of symmetry perpendicular to the axis of rotation, then it can have no dipole moment. This would mean that μ would have to lie along all such rotation axes (both principal and secondary) and all mirror planes. This cannot happen and for such molecules $\mu = 0$.

Look at the example of XeF_4, it has both principal and secondary axes which are perpendicular to each other. The individual dipole moments along each Xe-F bond cancel each other out and the result is no dipole moment, $\mu = 0$.
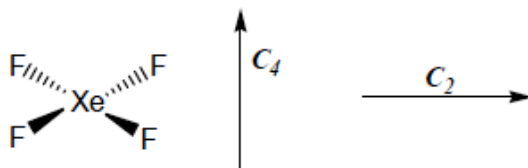
Along similar lines of reasoning, if a molecule has a centre of inversion, then it can have no permanent dipole moment. A dipole moment would change sign under inversion and that is not physically possible. Another way of looking at this is that with a centre of inversion, the dipole moment would have to be a point, and that is not possible for a vector quantity. Note that molecules from the point groups T_d, O_h, and I_h will not have dipoles.

Chirality: If a molecule is chiral, it is optically active. A molecule is chiral when mirror images of the molecule cannot be superposed (to place one geometric figure over another so that all like parts coincide.). For a molecule to exhibit chirality, it must have no improper axes of rotation. Note that $S_2 = i$ (an inversion) and $S_1 = \sigma$ (a reflection). Thus, if a molecule

possesses reflection planes or an inversion centre, it cannot be chiral. Molecules from the point groups D_{nd}, D_{nh}, T_d, and O_h are not chiral.

Exercise 3: From the set of molecules given for Exercise 2, use symmetry to identify the molecules (1) with permanent electric dipole moments and (2) that are chiral.   (10 marks)

Symmetry operations have many implications where orbitals in a molecule are concerned and can be approached in the same way as atoms in a molecule. For example, atomic orbitals move with the operations in the same way as atoms:
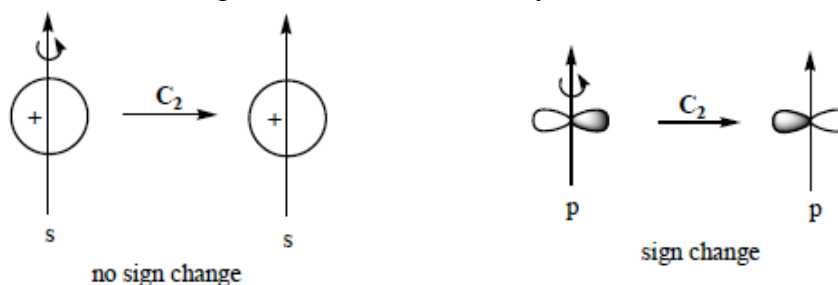
Note the sign changes for the different orbitals under the C_2 operation; the s orbital does not change whereas the p orbital does.

Bonding can be described in terms of electron distribution within an orbital of a molecule. This is represented with molecular orbitals (MO) that are the result of a linear combination of atomic orbitals (LCAO). An energy diagram of this is drawn as shown:
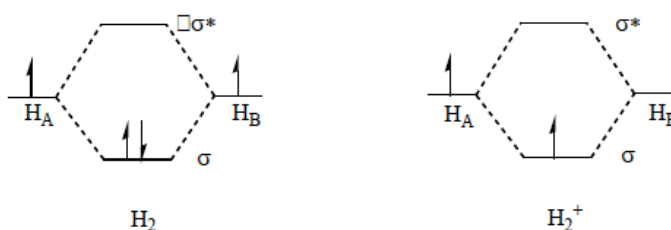
Notice the differences in the MO diagrams for the diatomic molecule H_2 and its molecular ion, H_2^+. The electron density for each of these is described by writing the wave equation as a linear combination of two 1s atomic orbitals, one on each of the two hydrogen atoms. Labeling the hydrogen atoms as H_A and H_B, the bonding σ combination can be written as

$$\psi_b = \frac{1}{\sqrt{2(1+S)}}(1S_A + 1S_B)$$

while the anti-bonding σ^* combination can be expressed as

$$\psi_a = \frac{1}{\sqrt{2(1-S)}}(1S_A - 1S_B)$$

where the $1S_A$ and $1S_B$ orbitals are centred on hydrogen atoms A and B, respectively, and S is the overlap integral between $1S_A$ and $1S_B$. In the bonding molecular orbital, σ, electron density is built up in the inter-nuclear region (as seen in the diagram where the electrons have been placed). In the anti-bonding orbital, σ^*, electron density is removed from the inter-nuclear region.

This approach to describing the electron distribution in molecules is called molecular orbital (MO) theory. Expressing the MO as a linear combination of atomic orbitals is called the LCAO-MO method. For all complex molecules or molecular ions, LCAO-MO theory

provides a good model for understanding bonding.

TRANSFORMATIONS

As seen, the atoms in a molecule were permuted when the molecule was subjected to symmetry operations. Now, we shall associate with each atom some object or collection of objects and see what happens to these objects under a symmetry transformation. Examples of these objects include coordinate systems and atomic orbitals. These are the most common objects to be associated with atoms in molecules. Our approach will differ slightly from that given in Atkins and de Paula.[1]

Let us attach a coordinate system to each atom in SO_2 as shown,
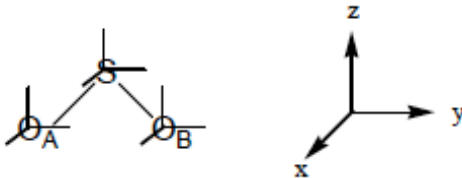
where x_S is the x-axis associated with sulfur, x_A the x-axis associated with oxygen atom A, and x_B is the x-axis associated with oxygen atom B and similarly for the y-axes and z-axes. The entire molecule lies in the yz-plane.

Like H_2O, the SO_2 molecule belongs to the C_{2v} molecular point group and the symmetry operations are, E, C_2, σ_v, σ_v':

E   identity operation
C_2 180° rotation along z-axis, in this case, through the centre of the S atom bisecting the O-S-O angle
σ_v reflection plane along the C_2 axis in the xy plane
σ_v' reflection plane perpendicular to the C_2 axis in the yz plane

Consider what happens to the axes attached to each atom under each of the group operations. Of course, the identity operation E leaves each axis system unchanged. Observe the axes on each atom through the $\sigma_v'(yz)$ operation (we start with this operation rather than C_2 for simplicity as we will see later on):
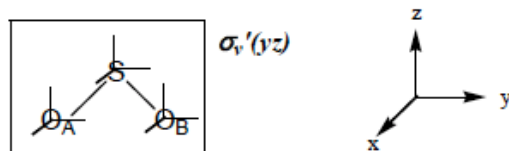
x axis   changes sign for any atom through this reflection plane; this is because the plane bisects the axis (think of a traditional Cartesian coordinate system with zero at the centre of each atom and positive and negative values on each side of the axis)
y axis   does NOT change sign
z axis   does NOT change sign

These observations can be written out as such:

$$\sigma_v'(yz)\ x_S = -x_S \qquad \sigma_v'(yz)\ y_S = y_S \qquad \sigma_v'(yz)\ z_S = z_S$$
$$\sigma_v'(yz)\ x_S = -x_S \qquad \sigma_v'(yz)\ y_A = y_B \qquad \sigma_v'(yz)\ z_A = z_B$$
$$\sigma_v'(yz)\ x_S = -x_S \qquad \sigma_v'(yz)\ y_B = y_A \qquad \sigma_v'(yz)\ z_B = z_A$$

We could represent all the coordinates as a 9-component vector and each transformation as a 9×9 matrix. That is cumbersome and by noticing that x-axes always transform into x-axes, y-axes into y-axes, and z-axes into z-axes, it is possible to represent the transformation as the matrix product of the x, y, z row vector times three 3×3 matrices. Thus we write for the σv'(yz) reflection:

$$\sigma_v'(yz)\ (x_S,\ x_A,\ x_B) = (x_S,\ x_A,\ x_B) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\sigma_v'(yz)\ (y_S,\ y_A,\ y_B) = (y_S,\ y_A,\ y_B) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v'(yz)\ (z_S,\ z_A,\ z_B) = (z_S,\ z_A,\ z_B) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Each line in the matrix represents the value of the sign as well as the position in space of the axis. Consider the C_2 rotation operation:
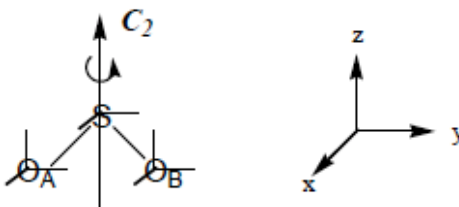
x axis changes sign for any atom through this rotation because the axis now points in the opposite direction relative to the C_2 axis

y axis also changes sign because the axis points in the opposite direction relative to the C_2 axis

z axis does NOT change sign; axis on any atom is unchanged by this operation

Results of the C_2 operation on all the axes is written out as such:

$$C_2 x_S = -x_S \qquad C_2 y_S = -y_S \qquad C_2 z_S = z_S$$
$$C_2 x_A = -x_B \qquad C_2 y_A = -y_B \qquad C_2 z_A = z_B$$
$$C_2 x_B = -x_A \qquad C_2 y_B = -y_A \qquad C_2 z_B = z_A$$

Results for the matrices corresponding to these axes:

$$C_2\ (x_S,\ x_A,\ x_B) = (x_S,\ x_B,\ x_A) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$C_2\ (y_S,\ y_A,\ y_B) = (y_S,\ y_B,\ y_A) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$C_2 \, (z_S, z_A, z_B) = (z_S, z_B, z_A) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

All lines of the matrix show negative values for the x- and y-axes through the rotation; however, the second and third lines show that x_A and x_B change positions. The oxygen A atom rotates into the position of the oxygen B atom and vice versa. Thus the values in a line of the matrix show the position (+ or -) of the axis as well as the position of the atom in space (A or B). We can write out the results for the other reflection plane, $\boldsymbol{\sigma_v(xz)}$ in the same way:

$$\sigma_v \, (xz) \, (x_S, x_A, x_B) = (x_S, x_B, x_A) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\sigma_v \, (xz) \, (y_S, y_A, y_B) = (y_S, y_B, y_A) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$\sigma_v \, (xz) \, (z_S, z_A, z_B) = (z_S, z_B, z_A) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$
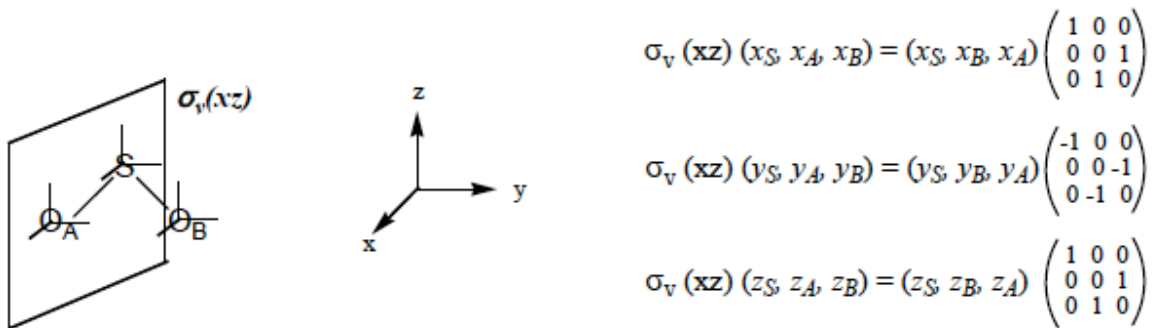
The exchange of position of the oxygen atoms occurs for the reflection operation through this plane as it did under the C_2 operation. The identity transformation, E, is simply represented by the identity matrix for each axis (we will not write this out). Considering all the transformations from the symmetry operations for the x-axis (x_S, x_A, x_B), we have the four matrices representing all four operations, which are written out as follows:

$$\mathbf{D}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{D}(C_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \quad \mathbf{D}(\sigma_v(xz)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad \mathbf{D}(\sigma_v{'}(yz)) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

These four distinct matrices are said to form a (reducible) representation of the group C_{2v}. In fact, the matrices mimic the group operations; taking products of these matrices would allow us to reconstruct the group multiplication table (as seen earlier). The four matrices representing the transformations of the y-axis (y_S, y_A, y_B) and the z-axis (z_S, z_A, z_B) also form (reducible) representations. For (y_S, y_A, y_B), we have

$$\mathbf{D}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{D}(C_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \quad \mathbf{D}(\sigma_v(xz)) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \quad \mathbf{D}(\sigma_v{'}(yz)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

In this case, notice that not all of the matrices are distinct compared to the matrices for the x-axis. $\mathbf{D}(E)$ is the same as $\mathbf{D}(\sigma_v{'}(yz))$ and $\mathbf{D}(C_2)$ is the same as $\mathbf{D}(\sigma_v(xz))$ for the x-axis. The x-axis representation is said to be faithful, but the y-axis is not. Observe that the representation constructed from (z_S, z_A, z_B) is not faithful either:

$$\mathbf{D}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{D}(C_2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad \mathbf{D}(\sigma_v(xz)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad \mathbf{D}(\sigma_v{'}(yz)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The dimensions of these representations are equal to the dimension of the matrices (3×3) and also to the number of objects that are used to construct the representation (three axes: x, y, and z).

Every set of objects on the atoms (coordinate system or orbital) produces a matrix

representation. If we were to place atomic p orbital functions on each atom, we would construct a set of matrices like those computed in Atkins and de Paula (Chapter 11), with σ_v (A&dP) = $\sigma_v(xz)$ (ours). Their matrix for the transformation of the three p_x orbitals is the same as our matrix for the transformation of (x_S, x_A, x_B). Think about why this is the case.

Exercise 4: Find the matrix representations for the p_y and p_z orbitals on SO_2. Write these as shown in the example above for the x-, y-, and z-axes (the results above are the matrix representations for the p_x orbital on SO_2). You will have 12 matrices for each orbital (p_y, p_z) with x-, y-, and z-axes for a total of 24 matrices. Label the sets of matrices as faithful or not faithful. (12 marks)

It is possible to have many different matrix representations; the larger the group the larger the number of matrices in each representation. It is often easier to work with a more invariant quantity—the trace of the matrix. The trace is the sum of the diagonal elements of a matrix, **D**:

$$\chi(R) = Tr\mathbf{D}(R) = \sum_{j=1}^{d} D_{jj}(R) \tag{3.1}$$

where d is the dimension of the representation and $D_{jj}(R)$ is the jj-th diagonal element of the matrix $\mathbf{D}(R)$. The symbol χ is frequently used in two senses. First, when written as $\chi(R)$, it means the trace of the matrix representing the transformation corresponding to the symmetry operation R ($\chi(C_2)$ for example). Secondly, when it is written alone as χ, it means the set of all traces for all symmetry operations in the group. It is often called the character of the representation when used in the latter sense. Even so, people will speak of $\chi(R)$ as the character of the individual operation R. For example, for the representation defined by (x_S, x_A, x_B), we have

Table 1: Reducible representation for x-axis

C_{2v}	E	C_2	σ_v (xz)	σ_v'(yz)
Γ	3	-1	1	-3

where Γ is a symbol denoting the (reducible) representation. It is represented by the set of traces for each symmetry operation, i.e., the character. So, we would write:

$$\chi(E) = Tr\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 3 \quad \chi(C_2) = Tr\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} = -1 \quad \chi(\sigma_v(xz)) = Tr\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = 1 \quad \chi(\sigma_v'(yz)) = Tr\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = -3$$

Another advantage of working with characters is that the **traces of matrices representing elements in the same class are identical**. This is no advantage here since each element is in a class by itself (each symmetry operation is distinct). However, for larger groups, this can simplify calculations to a considerable extent. Consider ammonia from earlier, which included symmetry operations include C_3 and C_3^2. These are considered to

belong to the same class and the same applies to all three σ operations as well. We need only to find the trace for one element of each of these classes—two traces total as opposed to five.

　　　Looking again at the matrix representation for (x_S, x_A, x_B), we observe that there is still some structure that we have not made use of. The matrices are of block diagonal form:

$$\mathbf{D(E)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Since no transformation in the group interchanges x_S with either x_A or x_B, we can actually look at x_S separately (the upper left hand box). The matrix representation for x_S is a 1×1 matrix representation:

$$\mathbf{D}(E) = 1, \ \mathbf{D}(C_2) = -1, \ \mathbf{D}(\sigma_v(xz)) = 1, \ \mathbf{D}(\sigma_v'(yz)) = -1$$

This is labeled $\mathbf{\Gamma_1}$ and leaves us with x_A and x_B, the matrices for which can be written in 2×2 form (lower right hand box):

$$\mathbf{D(E)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \mathbf{D(C_2)} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \quad \mathbf{D(\sigma_v(xz))} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \mathbf{D(\sigma_v'(xz))} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\text{trace } (\Gamma_2) = 2 \qquad\qquad = 0 \qquad\qquad = 0 \qquad\qquad = -2$$

These are the traces for x_A and x_B and are called $\mathbf{\Gamma_2}$. We say that we have reduced the 3×3 matrix representation to a 1-dimensional representation and a 2-dimensional matrix representation. We refer to the 3×3 matrix representation as a reducible representation. The 1-dimensional representation cannot be reduced further and it is said to be an irreducible representation. Note that the traces for the 2×2 matrices can be further reduced; this is then a reducible representation for x_A and x_B.

The original 3×3 matrix can be reduced down or decomposed into 1×1 and 2×2 matrices.

Table 2: x_S, x_A, x_B

C_{2v}	E	C_2	σ_v (xz)	σ_v'(xz)
Γ_1	1	-1	1	-1
Γ_2	2	0	0	-2

Exercise 5: The above example just showed a decomposition of the matrices to obtain the representations for the x-axis. Using the templates below, repeat this analysis for the representations based on (y_S, y_A, y_B) and (z_S, z_A, z_B) to obtain the "character tables" analogous to Tables 1 and 2 (hint – use your results for the p_y and p_z orbitals from Exercise 4 and start by finding the trace of each matrix and work from there). You will need to write out the 2×2 matrices and traces on a separate sheet of paper. (12 Marks)

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ				
Γ_1				
Γ_2				

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ				
Γ_1				
Γ_2				

We can find all the irreducible representations of a point group in this way. The number of irreducible representations is equal to the number of classes. For C_{2v}, there are four classes, one for each symmetry operation, so there must be four irreducible representations. The characters for each of these irreducible representations can also be determined. These have been found for all molecular point groups and have been compiled into tables called character tables.

CHARACTER TABLES

Atkins and de Paula provide the character tables for most of the important molecular point groups in Resource Section Part 3. The five tables for the point groups C_n (n = 2, 3, 4, 5, 6) are listed there and in many other texts (see references). We shall examine the character tables for the two point groups C_{2v} and C_{3v} and our comments easily generalize to other point groups.

This is the character table for the C_{2v} point group:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h = 4$	
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 top row in the table gives the name of the point group, followed by the symmetry operations arranged according to classes. For C_{2v}, each symmetry operation is in a class by itself. The next four rows and the first five columns give the name and character for the irreducible representations. There are four irreducible representations (equal to the number of classes of symmetry operations)—A_1, A_2, B_1, B_2. The A and B notation is used to signify the character under the principal rotation (in this case C_2), A if the character is +1, B if it is −1.

Each irreducible representation is 1-dimensional since the trace of the matrix for the identity operation is 1. (If the trace were 2, then the representation would be 2-dimensional, if 3, then the representation would be 3-dimensional; 2- and 3-dimensional representations are not irreducible.) The sum of the squares of the values of the irreducible representations for each class must be equal to the order of the group (h), in this case, $1^2 + 1^2 + 1^2 + 1^2 = 4$ for the class represented by E. In the last two columns, functions at the fixed point are listed according to which irreducible representation they transform. For example, x transforms as the B_1 irreducible representation, as does a p_x orbital. The product xy transforms as A_2 and therefore so does a d_{xy} orbital. The terms R_x, R_y, and R_z refer to operators such as angular momentum operators - think of $\hat{L}_x$ as an example of R_x.

      If we compare Γ_1 (also χ_1) for the transformation of x_S in Table 2 with the irreducible representations in the character table for C_{2v}, we see that it corresponds to B_1. That is because the S atom is at the fixed point of the point group. We say that x_S forms a basis for the representation B_1. The same is not true for x_A and x_B; they form a basis for a 2-dimensional reducible representation (recall the 2×2 matrices above). The character, Γ_2 (or χ_2), for this representation is given in Table 2 as well.

      Given the character of a reducible representation, there is a formula that connects the number of occurrences of an irreducible representation in the reducible representation. Let Γ denote a reducible representation and Γ' an irreducible representation of a point group. If $c_{\Gamma'}$ is the number of times the irreducible representation Γ' appears in the reducible representation, Γ, then

$$c_{\Gamma'} = \frac{1}{h} \sum g(C) \chi^{(\Gamma')}(C) \chi(C) \qquad (3.2)$$

where h is the number of symmetry operations in the group (4 in this case), g(C) is the number of symmetry operations in the class of operations **C** (here this is 1, but for ammonia it would be either 2 or 3 because there are two symmetry operations in the C_3 class and three in the class of σ). The term, $\chi^{(\Gamma')}(C)$, is the character of the irreducible representation Γ' (from the character table). Finally, $\chi(C)$ is the character for the reducible representation for the class of operations C (this is Γ_2, the actual values in Table 2). Recall that all symmetry operations in a class (C_n or σ) have the same character.

      Considering the class of symmetry operations and referring to the character table for C_{2v} for the character of each irreducible representation, and Table 2 for the character of each reducible representation, we can write out the equations:

$$
\begin{array}{cccc}
\text{E} & \text{C}_2 & \sigma_v\,(xz) & \sigma_v{'}(yz) \\
\end{array}
$$

$c_{A1} = ¼[(1)(1)(2) + (1)(1)(0) + (1)(1)(0) + (1)(1)(-2)] = 0$
$c_{A2} = ¼[(1)(1)(2) + (1)(1)(0) + (1)(-1)(0) + (1)(-1)(-2)] = 1$
$c_{B1} = ¼[(1)(1)(2) + (1)(-1)(0) + (1)(1)(0) + (1)(-1)(-2)] = 1$
$c_{A2} = ¼[(1)(1)(2) + (1)(-1)(0) + (1)(-1)(0) + (1)(1)(-2)] = 0$

We have shown that the reducible representation Γ_2 decomposes into the irreducible representations A_2 and B_1. Frequently, we denote this fact by writing, $\Gamma_2 = A_2 \oplus B_1$. Also, we can decompose the original 3-dimensional reducible representation into, $A_2 \oplus 2B_1$.

      We will use the character table for C_{3v} as an example of how to determine the basis functions for these irreducible representations:

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y)(R_x, R_y)$	(x^2-y^2, xy) (xz, yz)

We can see upon examination of the character table that there are three irreducible representations and three classes. Two of the irreducible representations, A_1 and A_2, are 1-dimensional (both +1 as they do not change sign under the rotation operation) and the third, **E**, is 2-dimensional. (Do not confuse the identity operation, E, and the label, **E,** which designates 2-dimensional representations. Other dimensions can exist and are labeled T for 3-dimensional and F for 4-dimensional, but we will not investigate these here.) The sum of the squares of the values (dimensions) of the three irreducible representations is 6 (E—$[1^2 + 1^2 + 2^2]$, or 2 C_3—$2[1^2 + 1^2 + (-1)^2]$, or 3 σ_v—$3[1^2 + (-1)^2 + (0)^2]$). This is the order of the group, h. Suppose that we have been given the following reducible representation:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	5	2	-1

Then, decomposing the reducible representation into irreducible representations according to Equation 2, we get:

$$E \qquad\qquad 2C_3 \qquad\qquad 3\sigma_v$$
$$c_{A1} = 1/6[(1)(1)(5) + (2)(1)(2) + (3)(1)(-1)] = 1$$
$$c_{A2} = 1/6[(1)(1)(5) + (2)(1)(2) + (3)(-1)(-1)] = 2$$
$$c_E = 1/6[(1)(2)(5) + (2)(-1)(2) + (3)(0)(-1)] = 1$$

and so we would write $\Gamma = A_1 \oplus 2A_2 \oplus E$ for the decomposition.

Exercise 6: Decompose the reducible representations for p_x and p_y obtained in Exercise 5 (Γ_2 from the Tables) into their irreducible components by using equation 2, as was shown in the above ammonia C_{3v} decomposition. Filling out the templates given will help keep track of your values. From the decomposition determine the basis functions for these irreducible representations of C_{2v} (i.e. A_1, A_2, B_1, or B_2) and then draw the p_y and p_z orbitals on the oxygen atoms that correspond to these bases. (Note that we have ignored the s orbitals on both the S and the two O atoms. A full treatment would include them.)   (20 marks)

p_y decomposition

$$E \qquad\qquad C_2 \qquad\qquad \sigma_v\,(xz) \qquad\qquad \sigma_v{'}(yz)$$
$c_{A1} = \frac{1}{4}[(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )] = $
$c_{A2} = \frac{1}{4}[(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )] = $
$c_{B1} = \frac{1}{4}[(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )] = $
$c_{B2} = \frac{1}{4}[(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )] = $

p_z decomposition

$$
\begin{array}{cccc}
& E & C_2 & \sigma_v\,(xz) & \sigma_v{}'(yz) \\
c_{A1} = \tfrac{1}{4}[(\ )(\ )(\ ) & +(\ )(\ )(\ ) & +(\ )(\ )(\ ) & +(\ )(\ )(\ )] = \\
c_{A2} = \tfrac{1}{4}[(\ )(\ )(\ ) & +(\ )(\ )(\ ) & +(\ )(\ )(\ ) & +(\ )(\ )(\ )] = \\
c_{B1} = \tfrac{1}{4}[(\ )(\ )(\ ) & +(\ )(\ )(\ ) & +(\ )(\ )(\ ) & +(\ )(\ )(\ )] = \\
c_{B2} = \tfrac{1}{4}[(\ )(\ )(\ ) & +(\ )(\ )(\ ) & +(\ )(\ )(\ ) & +(\ )(\ )(\ )] = \\
\end{array}
$$

MOLECULAR ORBITALS

We want to be able to write down the basis for the reducible representations in terms of the basis for the irreducible representations. For example, in the C_{2v} case, we have been working with the reducible representation Γ_2, which has the basis (x_A, x_B). This representation decomposes into $A_2 \oplus B_1$ as we have seen $(\Gamma_2 = A_2 + B_1)$. What are the bases for A_2 and B_1 in terms of x_A and x_B? Atkins and de Paula[1] gives a description of the procedure in Chapter11 and we shall follow this method. The technique is called building symmetry-adapted linear combinations (SALC) of atomic orbitals. It works quite well for 1-dimensional representations but care must be exercised when applying it to 2- and 3-dimensional representations. (Atkins and de Paula illustrates this in their discussion) The steps given in the textbook are repeated here with corresponding results:

1. Construct a table showing the effect of each symmetry operation on each orbital (or any function for that matter) of the original basis (see Table 3a below).
2. To generate the combination of a specified symmetry species, take each column in turn and:
   i. Multiply each member of the column by the character of the corresponding operation (Table 3b, 3c).
   ii. Add together all orbitals in each column with the factors as determined in (i)
   iii. Divide the sum by the order of the group (total number of symmetry operations, h)

Atkins and de Paula use ammonia (C_{3v}) as an example. Here, we shall work with Γ_2 for a C_{2v} molecule, where we work with p_x orbitals rather than the x-axis (recall that these transform equivalently). Following the instructions in step 1, we set up the table:

Table 3a: Transformations for p_x orbitals

Operation	Original Basis	
	p_{xA}	p_{xB}
E	p_{xA}	p_{xB}
C_2	$-p_{xB}$	$-p_{xA}$
$\sigma_v(xz)$	p_{xB}	p_{xA}
$\sigma_v{}'(yz)$	$-p_{xA}$	$-p_{xB}$

Notice the operation of C_2 on p_{xA} yields $-p_{xB}$ and the same is true for this operation on p_{xB} (the result is $-p_{xA}$) because the atoms in these points swap positions.

Step 2 follows by using the A_2 irreducible representation (1, 1, -1, -1) to obtain results for the first column, p_{xA} (2(i) through 2(iii)):

Table 3b: Transformations for p_x orbitals

Operation	Original Basis (step 2 i)	
	p_{xA} (A_2)	p_{xB} (A_2)
E	p_{xA} (+1)	p_{xB} (+1)
C_2	$-p_{xB}$ (+1)	$-p_{xA}$ (+1)
$\sigma_v(xz)$	p_{xB} (-1)	p_{xA} (-1)
$\sigma_v'(yz)$	$-p_{xA}$ (-1)	$-p_{xB}$ (-1)

$\frac{1}{4}\left[(p_{xA})(+1) + (-p_{xB})(+1) + (p_{xB})(-1) + (-p_{xA})(-1)\right] = \frac{1}{4}\left(P_{xA} - P_{xB} - P_{xB} + P_{xA}\right) = \frac{1}{2}\left(P_{xA} - P_{xB}\right).$

The process is repeated for the second column (p_{xB}) still using A_2 irreducible representation,

$\frac{1}{4}\left[(p_{xB})(+1) + (-p_{xA})(+1) + (p_{xA})(-1) + (-p_{xB})(-1)\right] = \frac{1}{4}\left(P_{xB} - P_{xA} - P_{xA} + P_{xB}\right) = \frac{1}{2}\left(P_{xB} - P_{xA}\right).$

These two functions differ by a minus sign, which is unimportant. If we apply each operation in turn to this linear combination, we generate the character for the A_2 irreducible representation.

The same process can be applied to B_1 for each column resulting in the following,

Table 3c: Transformations for p_x orbitals

Operation	Original Basis (step 2 i)	
	p_{xA} (B_1)	p_{xB} (B_1)
E	p_{xA} (+1)	p_{xB} (+1)
C_2	$-p_{xB}$ (-1)	$-p_{xA}$ (-1)
$\sigma_v(xz)$	p_{xB} (+1)	p_{xA} (+1)
$\sigma_v'(yz)$	$-p_{xA}$ (-1)	$-p_{xB}$ (-1)

For p_{xA}, $\frac{1}{4}\left[(1)(p_{xA}) + (-1)(-p_{xB}) + (1)(p_{xB}) + (-1)(-p_{xA})\right] =$

$$\frac{1}{4}\left(P_{xA} + P_{xB} + P_{xB} + P_{xA}\right) = \frac{1}{2}\left(P_{xA} + P_{xB}\right)$$

For p_{xB}, $\frac{1}{4}\left[(1)(p_{xB}) + (-1)(-p_{xA}) + (1)(p_{xA}) + (-1)(-p_{xB})\right] =$

$$\frac{1}{4}\left(P_{xB} + P_{xA} + P_{xA} + P_{xB}\right) = \frac{1}{2}\left(P_{xB} + P_{xA}\right)$$

These results are identical. Again, applying each symmetry operation in turn to this function, we obtain the character for the B_1 irreducible representation.

The significance of this process is founded on the following principle: ***Only linear combinations of atomic orbitals transforming according to the same irreducible***

representation can have nonzero overlap. In the above example, only p_{xS} and $\frac{1}{2}(p_{xA} + p_{xB})$ orbitals transform according to B_1. They can be combined in two possible ways

$$|a|p_{xS} + |b|(p_{xA} + p_{xB}), \tag{3.3}$$

$$|a'|p_{xS} - |b'|(p_{xA} + p_{xB}), \tag{3.4}$$

where a and b are constants. Absolute magnitudes are shown so that the signs may be indicated explicitly. The first combination represents a bonding π molecular orbital, the second, an anti-bonding π^* molecular orbital. The bonding orbital combination in Equation 3 is shown in Figure 2a. There is one nodal plane, the plane of the molecule (yz), and delocalization of electrons is possible throughout the π-network. The entire molecular orbital will transform as the B_1 representation. The anti-bonding combination in Equation 4 is portrayed in Figure 2b. There are now three nodal planes, one in the molecular plane (yz) and one between each SO bond. This orbital also transforms according to the B_1 representation.

(a)   (b)

Figure 2: The (a) bonding and (b) anti-bonding π-molecular orbitals of SO_2.

In the SO_2 molecule, all molecular orbitals can be classified in terms of the irreducible representations of the point group C_{2v}. We have discovered the symmetry of the π MO and π^* MO only. The actual numerical values of the coefficients, a and b (from Equations 3 and 4), must be determined by solving the Schrodinger equation within some approximate scheme.

Once the MOs have been obtained, an energy diagram can be constructed and electrons placed in each MO according to the Pauli exclusion principle. Not all of the MOs are used in this process. The last MO to be filled is called the highest occupied MO or HOMO. The next orbital in the energy sequence, which is left unfilled, is called the lowest unoccupied MO or LUMO. Usually, in simple molecules, if a π-orbital is present, it corresponds to the HOMO and the π^* to the LUMO.

Exercise 7: The point group of ethene, C_2H_4, is D_{2h}. The coordinate axes and the molecular structure are shown in Figure 3. Assume all bond angles are 120°. We intend to construct symmetry adapted linear combinations (SALCs) of atomic valence orbitals to describe the bonding in ethene. NOTE: there are three parts to this exercise, **a**, **b**, and **c**.   (30 marks)
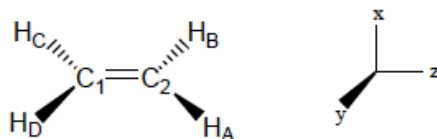

Figure 3: Molecular structure and coordinate system for ethene, C_2H_4.

Table 4: Character table for D$_{2h}$ group

D$_{2h}$	E	C$_2$ (z)	C$_2$ (y)	C$_2$ (x)	I	σ(xy)	σ(xz)	σ(yz)	
A$_g$	1	1	1	1	1	1	1	1	
B$_{1g}$	1	1	-1	-1	1	1	-1	-1	
B$_{2g}$	1	-1	1	-1	1	-1	1	-1	
B$_{3g}$	1	-1	-1	1	1	-1	-1	1	
A$_u$	1	1	1	1	-1	-1	-1	-1	
B$_{1u}$	1	1	-1	-1	-1	-1	1	1	z
B$_{2u}$	1	-1	1	-1	-1	1	-1	1	y
B$_{3u}$	1	-1	-1	1	-1	1	1	-1	x

The point group D$_{2h}$ consists of eight symmetry operations: the identity operation, E, a 2-fold rotation about the z-axis, C$_2$(z), a 2-fold rotation about the y-axis, C$_2$(y), a 2-fold rotation about the x-axis, C$_2$(x), a centre of inversion, i, a reflection in the xy plane, σ(xy), a reflection in the xz plane, σ(xz), and a reflection in the yz plane, σ(yz). The basis on each hydrogen is a 1s orbital and these are denoted (s$_A$, s$_B$, s$_C$, s$_D$). On each carbon there is one 2s and three 2p orbitals denoted (s$_1$, s$_2$) and (p$_{x1}$, p$_{x2}$), (p$_{y1}$, p$_{y2}$), and (p$_{z1}$, p$_{z2}$), respectively.

(a) Calculate the character for the **reducible** representations for each type of orbital on ethene (remember that reducible representations will have values greater than 1), then decompose these reducible representations into their **irreducible** components. To do this apply each operation to the orbital listed (H$_{sA}$ for example) and fill in the template below. Then use Equation 2, as you did in Exercise 3 for SO$_2$, to obtain the irreducible representations. This method of determining reducible representations differs from the previous method as it does not involve matrices. Use the labeling system in Figure 3! Other labeling systems will give different (but not necessarily incorrect) results.

Hint—look at the number of atoms for a particular orbital. For example, there are four H atoms in total, so perform the operation on one and then multipy by 4 (Γ$_{Hs}$ for the operation E is 1×4 = 4, so place the value 4 in the table). Also, there are two C atoms and so the character for these orbitals is multiplied by 2 (Γ$_{2sC}$ for the operation E is 1×2 = 2). The same strategy is used for the 2 p orbitals for coordinates x, y, and z.

Table 5: Reducible representations for ethane

	E	C$_2$ (z)	C$_2$ (y)	C$_2$ (x)	i	σ (xy)	σ (xz)	σ (yz)
Γ$_{Hs}$								
Γ$_{2sC}$								
Γ$_{2px}$								
Γ$_{2py}$								
Γ$_{2pz}$								

Use the following set up for all basis sets from the character table for determining irreducible representations:

$$c_{A_g} = 1/8[(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )] = \boxed{}$$

with column headers: E, $C_2(z)$, $C_2(y)$, $C_2(x)$, i, $\sigma(xy)$, $\sigma(xz)$, $\sigma(yz)$

(b) Building SALCs: step 1 from Atkins rules above has been done for you in Tables 6 through 10.

Table 6: *Transformations for Hydrogen 1s orbitals*

operation	Original basis			
	s_A	s_B	s_C	s_D
E	s_A	s_B	s_C	s_D
$C_2(z)$	s_B	s_A	s_D	s_C
$C_2(y)$	s_D	s_C	s_B	s_A
$C_2(x)$	s_C	s_D	s_A	s_B
i	s_C	s_D	s_A	s_B
$\sigma(xy)$	s_D	s_C	s_B	s_A
$\sigma(xz)$	s_B	s_A	s_D	s_C
$\sigma(yz)$	s_A	s_B	s_C	s_D

Table 7: *Transformation of carbon 2s orbitals*

operation	Original basis	
	s_1	s_2
E	s_1	s_2
$C_2(z)$	s_1	s_2
$C_2(y)$	s_2	s_1
$C_2(x)$	s_2	s_1
i	s_2	s_1
$\sigma(xy)$	s_2	s_1
$\sigma(xz)$	s_1	s_2
$\sigma(yz)$	s_1	s_2

Table 8: *Transformation of carbon $2p_x$ orbitals*

operation	Original basis	
	p_{x1}	p_{x2}
E	p_{x1}	p_{x2}
$C_2(z)$	$-p_{x1}$	$-p_{x2}$
$C_2(y)$	$-p_{x2}$	$-p_{x1}$
$C_2(x)$	p_{x2}	p_{x1}
i	$-p_{x2}$	$-p_{x1}$
$\sigma(xy)$	p_{x2}	p_{x1}
$\sigma(xz)$	p_{x1}	p_{x2}
$\sigma(yz)$	$-p_{x1}$	$-p_{x2}$

Table 9: Transformation of carbon 2p_y orbitals

| operation | Original basis | |
	p_{y1}	p_{y2}
E	p_{y1}	p_{y2}
C_2 (z)	$-p_{y1}$	$-p_{y2}$
C_2 (y)	p_{y2}	p_{y1}
C_2 (x)	$-p_{y2}$	$-p_{y1}$
i	$-p_{y2}$	$-p_{y1}$
$\sigma(xy)$	p_{y2}	p_{y1}
$\sigma(xz)$	$-p_{y1}$	$-p_{y2}$
$\sigma(yz)$	p_{y1}	p_{y2}

Table 10: Transformation of carbon 2p_z orbitals

| operation | Original basis | |
	p_{z1}	p_{z2}
E	p_{z1}	p_{z2}
C_2 (z)	p_{z1}	p_{z2}
C_2 (y)	$-p_{z2}$	$-p_{z1}$
C_2 (x)	$-p_{z2}$	$-p_{z1}$
i	$-p_{z2}$	$-p_{z1}$
$\sigma(xy)$	$-p_{z2}$	$-p_{z1}$
$\sigma(xz)$	p_{z1}	p_{z2}
$\sigma(yz)$	p_{z1}	p_{z2}

Using these tables choose the one which corresponds to a particular set of orbitals and determine the bases for each irreducible representation for that set of orbitals. For example, in part **(a)** you found Γ_{Hs} had a certain number of irreducible representations; one of the tables corresponds to the H_s orbitals. Apply the characters from the D_{2h} character table that correspond to the irreducible components you obtained in **(a)** and follow step 2 from the Atkins and de Paula rules. This will show the orbital symmetry for each basis set. Draw out the orbital symmetries that match the irreducible representations.

(c) Create a table of symmetry types and their bases. Place the orbitals you drew out in **(b)** into the appropriate boxes of the table below. Label the drawings as σ, σ^*, π, and π^*. When appropriate calculations are performed, the π MO corresponds to the HOMO and the π^* to the LUMO. Label the HOMO and LUMO of the π to π^* transition.

A_g 1s_H orbital looks something like this:
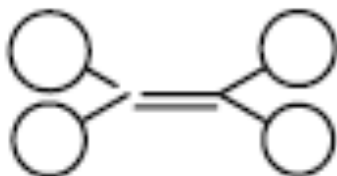
A_g 2s$_C$ orbital looks something like this (σ):
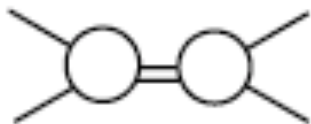
Note that not all the boxes will be filled.

	1s$_H$	2s$_C$	2p$_x$	2p$_y$	2p$_z$
A_g					
B_{1g}					
B_{2g}					
B_{3g}					
A_u					
B_{1u}					
B_{2u}					
B_{3u}					

EXPECTATION VALUES AND MATRIX ELEMENTS

One application of group theory that is important is in the calculation of matrix elements for selection rules and expectation values.

Direct product representations

We denote the direct product of two irreducible (reducible) representations by $\Gamma \times \Gamma'$. The character of the direct product representation is obtained by multiplying the characters of each irreducible representation. For example, for the group C_{2v}, if we take the direct product of the A_2 and B_1 representations we get the following:

C_{2v}	E	C2	σ_v (xz)	σ_v'(yz)
A_2	1	1	-1	-1
B_1	1	-1	1	-1
$A_2 \times B_1$	1	-1	-1	1

Comparing the character of this 1-dimensional representation to the others in the C_{2v} character table we see that $A_2 \times B_1 = B_2$. This is general; the direct product of two or more 1-dimensional representations always yields a 1-dimensional representation. The direct product of two or more 2- or 3-dimensional representations usually yields a reducible representation that can then be decomposed into a sum of irreducible representations according to methods we detailed above.

Molecular states

When we determine the molecular state for a system we take the direct product of the irreducible representations of each MO that each electron occupies. For closed shells (no unpaired electrons), the resulting state is usually the totally symmetric state, A_1, in the case of C_{2v}. The full designation is $^1A_1$ since for a closed subshell, the ground state is always a spin singlet.

Excited states are usually obtained by exciting one or more electrons into empty (virtual) orbitals. For example, in our SO_2 example, suppose an electron is excited from the π-orbital (B_1) to the π* orbital (B_1). Then, the state of the molecule would be $B_1 \times B_1 = A_1$, the totally symmetric representation. Both the ground and excited states would then be A_1. The resulting excited state may be either a singlet or triplet spin state, $^1A_1$ or $^3A_1$.

Exercise 8: The ground state of ethene is ^1A_g. Given the symmetries of the π and π* orbitals of ethene in Exercise 7(c), find the symmetry species of the excited state formed by exciting an electron from the π orbital to the π* orbital. Will the state be a singlet or a triplet or are both possible? (Hint—use direct product)   (5 marks)

Note that the direct product of any representation with itself always contains the totally symmetric representation. As used here, the term "contains" means that the direct product is either equal to the totally symmetric representation or it decomposes into a sum of representations at least one of which is the totally symmetric representation. This property is important for what comes next.

Matrix elements and expectation values

Let O be some operator, then a matrix element involving the operator O is written

$$\int \Psi^* \hat{O} \Phi d\tau \tag{3.5}$$

Then, when $\Psi = \Phi$, the matrix element is equivalent to an expectation value, if the state Ψ is normalized. Since they represent physically observable quantities, non-zero matrix elements must remain unchanged after any symmetry operation. Let Ψ transform as the irreducible representation Γ_Ψ, O as the Γ_O irreducible representation, and Φ as the Γ_Φ irreducible

representation. Now, compute the direct product representation

$$\Gamma_\Psi \Gamma_O \Gamma_\Phi \tag{3.6}$$

If this new representation contains the totally symmetric representation, then the integral will be nonzero.

As an example, we shall consider the dipole moment operator, written as $\vec{\mu} = -e\vec{r}$ where $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$. This operator appears not only in expectation values but also in matrix elements that determine the probability of whether a particular transition between states will occur.

Let us show that the dipole moment of SO_2 can be nonzero. Let the ground state wave function be Ψ, and it transforms as A_1 of C_{2v}. We have

$$\langle \mu \rangle = -e\left[\int \Psi^* x\Psi d\tau + \int \Psi^* y\Psi d\tau + \int \Psi^* z\Psi d\tau\right] \tag{3.7}$$

For the dipole moment to be nonzero, at least one of these integrals must be nonzero. Referring to the C_{2v} character table, we see that x, y, and z, transform as B_1, B_2, and A_1, respectively. Since $\Gamma_\Psi = A_1$ ($\Gamma_{\Psi^*} = \Gamma_\Psi$), we have for the first integral,

$$\Gamma_\Psi \Gamma_x \Gamma_\Psi = A_1 B_1 A_1 = B_1 \tag{3.8}$$

which is not the totally symmetric representation. Hence, the first integral must be zero. Also, we can show that the second integral is zero since it transforms as B_2,

$$\Gamma_\Psi \Gamma_y \Gamma_\Psi = A_1 B_2 A_1 = B_2 \tag{3.9}$$

For the third integral, we see that

$$\Gamma_\Psi \Gamma_z \Gamma_\Psi = A_1 A_1 A_1 = A_1 \tag{3.10}$$

and hence it may be nonzero. This is consistent with the dipole moment having to have a nonzero component in the z-direction since that corresponds to the C_2 rotation axis.

Let Ψ be the ground state function and Φ be the wave function for some excited state and suppose that the spin multiplicity of both the ground and excited states are the same ($\Delta S=0$). Then, a transition between these states has nonzero probability if at least one of the matrix elements,

$$\int \Psi^* x\Phi d\tau; \int \Psi^* y\Phi d\tau; \int \Psi^* z\Phi d\tau \tag{3.11}$$

is nonzero. This is because the band intensity is proportional to the square of the modulus of these three integrals. For the integrals to be nonzero, the direct product representation in Equation 6 must contain the totally symmetric representation. For SO_2, we have already discussed the case of forming an excited state $^1A_1$ from the π and π* orbitals. Is a transition from the ground state to this excited state allowed? The answer is yes, since $\Gamma_\Psi \Gamma_z \Gamma_\Phi$ contains the A_1 representation.

Exercise 9: Using the result from Exercise 8, show whether a transition from the π to π* orbital is allowed or forbidden in ethene. Set up a calculation according to Equation 6 and pay attention to x, y, and z components from the D_{2h} character table. (5   marks)

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7. I. N. Levine, *Physical Chemistry*, 5th ed. Boston: McGraw Hill, 2002, pp. 804-16.

USEFUL WEBSITES

http://radchem.nevada.edu/chem431/lecture_4__molecular_symmetry.htm (lecture notes)

Collection of character tables online:
http://www.mpip-mainz.mpg.de/~gelessus/group.html
http://mathworld.wolfram.com/CharacterTable.html

Slides laying out examples of setting up decompositions:
http://mutuslab.cs.uwindsor.ca/macdonald/250-LectureNotes/Fall2002/Bonding-Notes5.pdf

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2. Lloyd-William, P., Giralt, E. *J. Chem. Educ.* 2003, **80**, 1178 (Td symmetry)
3. McKay, S. E., Boone, S. R. *J. Chem. Educ.* 2001, **78**, 1487 (symmetry with common objects)
4. Flint, E. B. *J. Chem. Educ.* 2011, **88**, 907 (Symmetry and 3-D models)