Symmetry

Michaelmas Term 2024

Contents

1 Introduction

You will already be familiar with the concept of symmetry in an everyday sense. If we say something is 'symmetric', we usually mean it has mirror symmetry, or 'left-right' symmetry, and would look the same if viewed in a mirror. Symmetry is also very important in chemistry. Some molecules are clearly 'more symmetric' than others, but what consequences does this have, if any? The aim of this course is to provide a systematic treatment of symmetry in chemical systems within the mathematical framework known as group theory (the reason for the name will become apparent later on). Once we have classified the symmetry of a molecule, group theory provides a powerful set of tools that provide us with considerable insight into many of its chemical and physical properties. Some applications of group theory that will be covered in this course include:

1. Predicting whether a given molecule will be chiral, or polar.
2. Examining chemical bonding and visualising molecular orbitals.
3. Predicting whether a molecule may absorb light of a given polarisation, and which spectroscopic transitions may be excited if it does.
4. Investigating the vibrational motions of the molecule.

You will meet some of these topics again in later courses (notably Bonding in Molecules, various Spectroscopy courses and the Supplementary Quantum Mechanics and Crystallography courses if you choose to follow either of those). However, they will be introduced here to give you a fairly broad introduction to the capabilities and applications of group theory once we have worked through the basic principles and 'machinery' of the theory.

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2 Symmetry operations and symmetry elements

A symmetry operation is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. It will also look the same if we reflect it through either of two mirror planes, as shown in Figure 1.

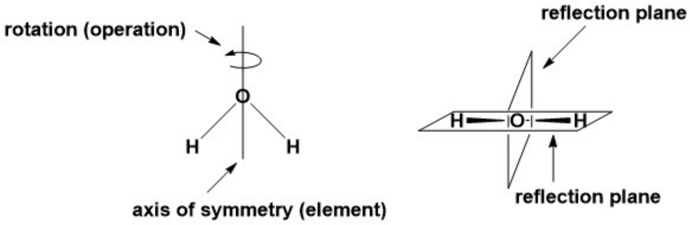
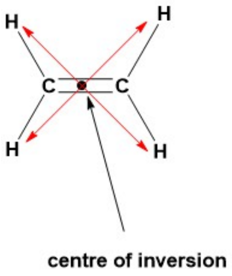


Figure 1: Symmetry elements and operations for H_2O

Each symmetry *operation* has a corresponding symmetry *element*, which is the axis, plane, line or point with respect to which the symmetry *operation* is carried out. The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a symmetry axis; in a reflection the points that remain unchanged make up a plane of symmetry.

The symmetry elements that a molecule may possess are:

1. E - the identity. The identity operation consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule has at least this element.
2. C_n - an n-fold axis of rotation. Rotation by $360°/n$ leaves the molecule unchanged. The H_2O molecule above has a C_2 axis. Some molecules have more than one C_n axis, in which case the one with the highest value of n is called the principal axis. Note that by convention rotations are *counterclockwise* about the axis.
3. σ - a plane of symmetry. Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labelled σ_v, while one perpendicular to the axis is called a horizontal mirror plane and is labelled σ_h. A vertical mirror plane that bisects the angle between two C_2 axes is called a dihedral mirror plane, σ_d.
4. i - a centre of symmetry. Inversion through the centre of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the centre of inversion and out to the same distance on the other side of the molecule. An example of a molecule with a centre of inversion is shown below.



5. S_n - an n-fold improper rotation axis (also called a rotary-reflection axis). The rotary reflection operation consists of rotating through an angle $360°/n$ about the axis, followed by reflecting in a plane perpendicular to the axis. Note that S_1 is the same as reflection and S_2 is the same as inversion.

The identity E and rotations C_n are symmetry operations that could actually be carried out on a molecule. For this reason they are called proper symmetry operations. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed improper symmetry operations.

A note on axis definitions: Conventionally, when imposing a set of cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

2.1 Classification of molecules – point groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called *point groups* (due to the fact that there is at least one *point* in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labelling symmetry groups, called the Schoenflies and Hermann-Mauguin (or International) systems. The symmetry of individual molecules is usually described using the Schoenflies notation, and we shall be using this notation for the remainder of the course.* Note: Some of the point groups share their names with symmetry operations, so be careful you don't mix up the two. For example, C_3 is used to label an operation (a rotation of 120°), but also the C_3 point group (which contains only the E and C_3 operations). It is usually clear from the context which one is being referred to.

Common molecular point groups are listed below.

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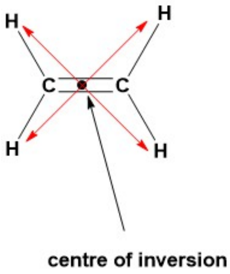
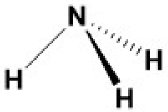
*Though the Hermann-Mauguin system can be used to label point groups, it is usually used in the discussion of crystal symmetry. In crystals, in addition to the symmetry elements described above, translational symmetry elements are very important. Translational symmetry operations leave no point unchanged, with the consequence that crystal symmetry is described in terms of space groups rather than point groups.

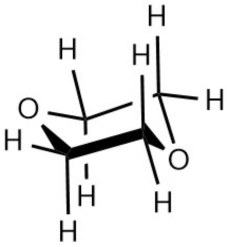
1. C_1 – contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation E) *e.g.* CHDFCl.



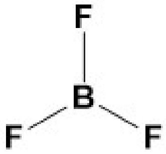
2. C_i - contains the identity E and a centre of inversion i.
3. C_s - contains the identity E and a plane of reflection σ.
4. C_n – contains the identity and an n-fold axis of rotation.
5. C_{nv} – contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.

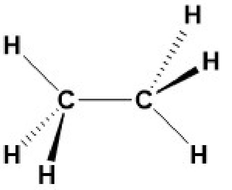


6. C_{nh} - contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a centre of inversion).



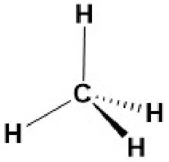
7. D_n - contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.
8. D_{nh} - contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.
9. D_{nd} - contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.
10. S_n - contains the identity and one S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).



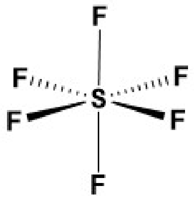


The following groups are the cubic groups, which contain more than one principal axis. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h). The icosahedral group also exists but is not included below.

11. T_d – contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes *e.g.* CH_4.



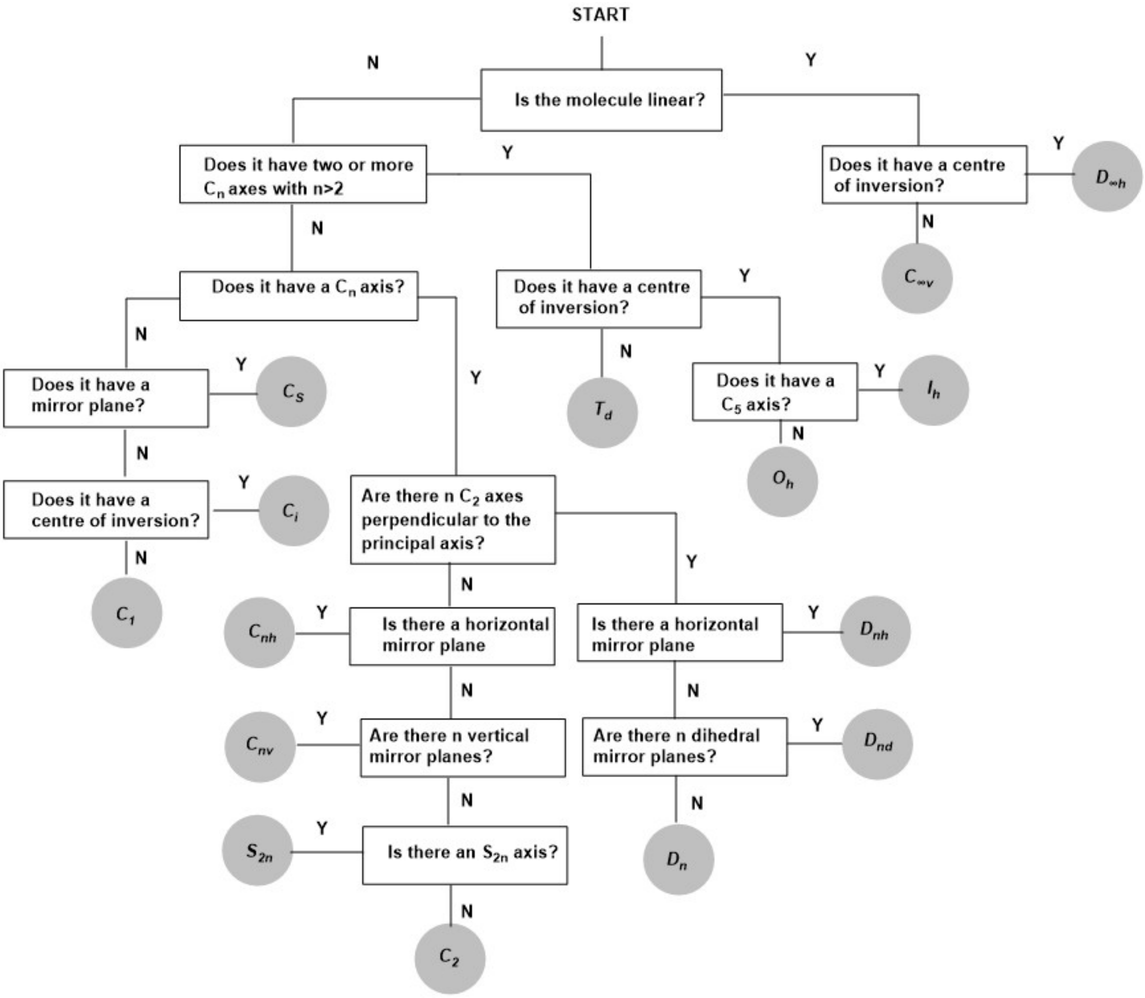
12. O_h – the group of the regular octahedron *e.g.* SF_6.



13. O – as for O_h but with no planes of reflection.

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics.

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.



2.2 Symmetry and physical properties

Carrying out a symmetry operation on a molecule must not change any of its physical properties. It turns out that this has some interesting consequences, allowing us to predict whether or not a molecule may be chiral or polar on the basis of its point group.

2.2.1 Polarity

For a molecule to have a permanent dipole moment, it must have an asymmetric charge distribution. The point group of the molecule not only determines whether the molecule may have a dipole moment, but also in which direction(s) it may point.

If a molecule has a C_n axis with $n > 1$, it cannot have a dipole moment perpendicular to the axis of rotation (for example, a C_2 rotation would interchange the ends of such a dipole moment and reverse the polarity, which is not allowed – rotations with higher values of n would also change the direction in which the dipole points). Any dipole must lie parallel to a C_n axis.

Also, if the point group of the molecule contains any symmetry operation that would interchange the two ends of the molecule, such as a σ_h mirror plane or a C_2 rotation perpendicular to the principal axis, then there cannot be a dipole moment along the axis.

The only groups compatible with a dipole moment are C_n, C_{nv} and C_s. In molecules belonging to C_n or C_{nv} the dipole must lie along the axis of rotation.

2.2.2 Chirality

Enantiomers are non-superimposable mirror images of each other, and one consequence of this symmetrical relationship is that they rotate the plane of polarised light passing through them in opposite directions. Such molecules are said to be chiral,[†] meaning that they cannot be superimposed on their mirror image. Formally, the symmetry element that precludes a molecule from being chiral is a rotation-reflection axis S_n. Such an axis is often implied by other symmetry elements present in a group. For example, a point group that has C_n and σ_h as elements will also have S_n. A centre of inversion is equivalent to S_2. As a rule of thumb, a molecule definitely cannot be chiral if it has a centre of inversion or a mirror plane of any type (σ_h, σ_v or σ_d), but if these symmetry elements are absent the molecule should be checked carefully for an S_n axis before it is assumed to be chiral.

3 Mathematical definition of a group: Combining symmetry operations

Now we will investigate what happens when we apply two symmetry operations in sequence. As an example, consider the NH_3 molecule, which belongs to the C_{3v} point group. Consider what happens if we apply a C_3^+ rotation followed by a σ_v reflection (Figure 2 and red shaded cell in Table 3.1). We write this combined operation $\sigma_v C_3^+$ (when written, symmetry operations operate on the thing directly to their right, just as operators do in quantum mechanics – we therefore have to work backwards from right to left from the notation to get the correct order in which the operators are applied). The combined operation $\sigma_v C_3^+$ is equivalent to $\sigma_v^{''}$, which is also a symmetry operation of the C_{3v} point group. Now let's see what happens if we apply the operators in the reverse order *i.e.* $C_3^+\sigma_v$ (σ_v followed by C_3^+) (yellow shaded cell). Again, the combined operation $C_3^+\sigma_v$ is equivalent to another operation of the point group, this time $\sigma_v^{'}$.

There are two important points that are illustrated by this example:

1. The order in which two operations are applied matters. For two symmetry operations A and B, AB is not necessarily the same as BA, *i.e.* symmetry operations do not in general *commute.* In some groups the symmetry elements do commute; such groups are said to be *Abelian.*
2. If two operations from the same point group are applied in sequence, the result will be equivalent to another operation from the point group. Symmetry operations that are related to each

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[†] The word chiral has its origins in the Greek word for hand ($\chi\epsilon\rho\iota$, pronounced 'cheri' with a soft ch as in 'loch') A pair of hands is also a pair of non-superimposable mirror images, and you will often hear chirality referred to as 'handedness' for this reason.

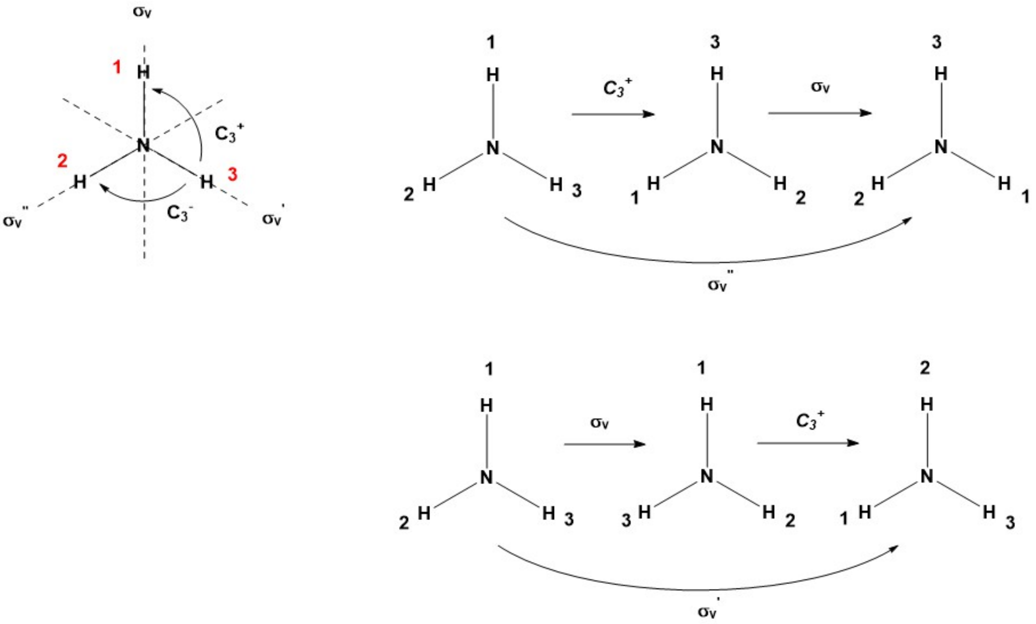

Figure 2: Effect of consecutive symmetry operations

other by other symmetry operations of the group are said to belong to the same class.[‡] In NH_3, the three mirror planes σ_v, σ_v' and σ_v'' belong to the same class (related to each other through a C_3 rotation), as do the rotations C_3^+ and C_3^- (anticlockwise and clockwise rotations about the principal axis, related to each other by a vertical mirror plane).

The effects of applying two symmetry operations in sequence within a given point group are summarised in *group multiplication tables*. As an example, the complete group multiplication table for C_{3v} using the symmetry operations as defined in the figures above is shown in Table 3.1. The operations written along the first row of the table are carried out first, followed by those written in the first column (note that the table would change if we chose to name σ_v, σ_v' and σ_v'' in some different order).

Now that we have explored some of the properties of symmetry operations and elements and their behaviour within point groups, we are ready to introduce the formal mathematical definition of a group.

A mathematical group is defined by a set of elements (g_1,g_2,g_3,...) together with a rule for forming combinations g_ig_j. The number of elements h is called the order of the group. For our purposes, the elements are the symmetry operations of a molecule and the rule for combining them is the sequential application of symmetry operations investigated in section 3. The elements of the group and the rule for combining them must satisfy the following criteria:

1. The group must include the *identity* E, for which $Eg_i = g_iE = g_i$ for all the elements of the

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[‡] We will refine what 'related to' means in section 5.5

		1st operation					
	C_{3v}	E	C_3^+	C_3^-	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$
2nd operation	E	E	C_3^+	C_3^-	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$
	C_3^+	C_3^+	C_3^-	E	$\sigma_v^{'}$	$\sigma_v^{''}$	σ_v
	C_3^-	C_3^-	E	C_3^+	$\sigma_v^{''}$	σ_v	$\sigma_v^{'}$
	σ_v	σ_v	$\sigma_v^{''}$	$\sigma_v^{'}$	E	C_3^-	C_3^+
	$\sigma_v^{'}$	$\sigma_v^{'}$	σ_v	$\sigma_v^{''}$	C_3^+	E	C_3^-
	$\sigma_v^{''}$	$\sigma_v^{''}$	$\sigma_v^{'}$	σ_v	C_3^-	C_3^+	E

Table 3.1: Group multiplication table for C_{3v}

group.

2. The elements must satisfy the group property that the combination of any pair of elements is also an element of the group ('*closure*').
3. Each element g_i must have an *inverse* g_i^{-1}, which is also an element of the group, such that $g_i g_i^{-1} = g_i^{-1} g_i = E$ (*e.g.* in C_{3v} the inverse of C_3^+ is C_3^-, the inverse of σ_v is σ_v; the inverse g_i^{-1} 'undoes' the effect of the symmetry operation g_i).
4. The rule of combination must be *associative i.e.* $g_i(g_j g_k) = (g_i g_j) g_k$

The above definition does not require the elements to *commute* (which would require $g_i g_k = g_k g_i$). As we showed in the C_{3v} example above, in many groups the outcome of consecutive application of two symmetry operations depends on the order in which the operations are applied. Groups for which the elements do not commute are called *non-Abelian* groups; those for which the elements do commute are *Abelian*. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems and learn about its consequences.

Many problems involving operators or operations (such as those found in quantum mechanics or group theory) may be reformulated in terms of matrices. For example, symmetry operations such as rotations and reflections may be represented by matrices. It turns out that the set of matrices representing the symmetry operations in a group obey all the conditions laid out above in the mathematical definition of a group, and using matrix representations of symmetry operations simplifies calculations in group theory. Before we learn how to use matrices in group theory, it will be helpful to review some basic definitions and properties of matrices.

4 Review of matrix algebra

This section should be a review of the material presented in the 1st year maths course, (HT, Vectors and Determinants, Lectures 5 and 6, TT, Matrix Algebra).

An $n \times m$ matrix is a two dimensional array of numbers with n rows and m columns. The integers n and m are called the dimensions of the matrix. If $n = m$ then the matrix is square. The numbers in the matrix are known as matrix elements (or just elements) and are usually given subscripts to signify their position in the matrix *e.g.* an element a_{ij} would occupy the i^{th} row and j^{th} column of the matrix. For example:

$$M = \begin{pmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{pmatrix} \text{ is a } 3 \times 3 \text{ matrix with } a_{11} = 1,\ a_{12} = 2,\ a_{13} = 3,\ a_{21} = 4 \textit{ etc.}$$

In a square matrix, diagonal elements are those for which $i = j$ (the numbers 1, 5 and 9 in the above example). *Off-diagonal* elements are those for which $i \neq j$ (2, 3, 4, 6, 7, and 8 in the above example). If all the off-diagonal elements are equal to zero then we have a diagonal matrix. We will see later that diagonal matrices are of considerable importance in group theory.

A unit matrix or identity matrix (usually given the symbol I) is a diagonal matrix in which all the diagonal elements are equal to 1. A unit matrix acting on another matrix has no effect – it is the same as the identity operation in group theory and is analogous to multiplying a number by 1 in everyday arithmetic.

The transpose A^T of a matrix A is the matrix that results from interchanging all the rows and columns. A symmetric matrix is the same as its transpose ($A^T = A$ *i.e.* $a_{ij} = a_{ji}$ for all values of i and j). The transpose of matrix M above (which is not symmetric) is

$$M^T = \begin{pmatrix} 1 & 4 & 7 \\ 2 & 5 & 8 \\ 3 & 6 & 9 \end{pmatrix}$$

The sum of the diagonal elements in a square matrix is called the *trace* (or *character*) of the matrix (for the above matrix, the trace is $\chi = 1+5+9 = 15$). The traces of matrices representing symmetry operations will turn out to be of great importance in group theory.

A *vector* is just a special case of a matrix in which one of the dimensions is equal to 1. An $n \times 1$ matrix is a *column vector*; a $1 \times m$ matrix is a *row vector*. The components of a vector are usually only labelled with one index. A *unit vector* has one element equal to 1 and the others equal to zero (it is the same as one row or column of an identity matrix). We can extend the idea further to say that a single number is a matrix (or vector) of dimension 1×1.

4.1 Matrix algebra

1. Two matrices with the same dimensions may be added or subtracted by adding or subtracting the elements occupying the same position in each matrix:

$$A = \begin{pmatrix} 1 & 0 & 2 \\ 2 & 2 & 1 \\ 3 & 2 & 0 \end{pmatrix} \quad B = \begin{pmatrix} 2 & 0 & -2 \\ 1 & 0 & 1 \\ 1 & -1 & 0 \end{pmatrix} \quad A+B = \begin{pmatrix} 3 & 0 & 0 \\ 3 & 2 & 2 \\ 4 & 1 & 0 \end{pmatrix} \quad A-B = \begin{pmatrix} -1 & 0 & 4 \\ 1 & 2 & 0 \\ 2 & 3 & 0 \end{pmatrix}$$

2. A matrix may be multiplied by a constant by multiplying each element by the constant:

$$4B = \begin{pmatrix} 8 & 0 & -8 \\ 4 & 0 & 4 \\ 4 & -4 & 0 \end{pmatrix} \quad 3A = \begin{pmatrix} 3 & 0 & 6 \\ 6 & 6 & 3 \\ 9 & 6 & 0 \end{pmatrix}$$

3. Two matrices may be multiplied together provided that the number of columns of the first matrix is the same as the number of rows of the second matrix *i.e.* an $n \times m$ matrix may be multiplied by an $m \times l$ matrix. The resulting matrix will have dimensions $n \times l$. To find the element a_{ij} in the product matrix, we take the dot product of row i of the first matrix and column j of the second matrix (*i.e.* we multiply consecutive elements together from row i of the first matrix and column j of the second matrix and add them together *i.e.* $c_{ij} = \sum_k a_{ik}b_{kj}$

   e.g.. in the 3×3 matrices A and B used in the above examples, the first element in the product matrix $C = AB$ is $c_{11} = a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31}$

$$AB = \begin{pmatrix} 1 & 0 & 2 \\ 2 & 2 & 1 \\ 3 & 2 & 0 \end{pmatrix} \begin{pmatrix} 2 & 0 & -2 \\ 1 & 0 & 1 \\ 1 & -1 & 0 \end{pmatrix} = \begin{pmatrix} 4 & -2 & -2 \\ 7 & -1 & -2 \\ 8 & 0 & -4 \end{pmatrix}$$

Matrix multiplication is not generally commutative, a property that mirrors the behaviour found earlier for symmetry operations within a point group.

4.2 Inverse matrices and determinants

If two square matrices A and B multiply together to give the identity matrix I (*i.e.* $AB = I$) then B is said to be the inverse of A (written A^{-1}). If B is the inverse of A then A is also the inverse of B. Recall that one of the conditions imposed upon the symmetry operations in a group is that each operation must have an inverse. It follows by analogy that any matrices we use to represent symmetry elements (Section 4.4) must also have inverses. A square matrix only has an inverse if its *determinant*, usually written $det(A)$ or |A|, is non-zero.

For a 2×2 matrix

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \qquad det(A) = \left|A\right| = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

For a 3×3 matrix

$$B = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix} \qquad det(B) = \Big|B\Big| = a\begin{vmatrix} e & f \\ h & i \end{vmatrix} - b\begin{vmatrix} d & f \\ g & i \end{vmatrix} + c\begin{vmatrix} d & e \\ g & h \end{vmatrix}$$

and so on in higher dimensions. Note that the sub-matrices in the 3×3 example above are just the matrices formed from the original matrix B that don't include any elements from the same row or column as the pre-multiplying factors from the first row.

The inverse of a 2×2 matrix is formed as the transpose of the matrix of co-factors:

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

$$A^{-1} = \frac{1}{det(A)} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$$

$$AA^{-1} = \frac{1}{ab - cd} \begin{pmatrix} ad - bc & -ab + ab \\ cd - cd & -bc + ad \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

4.3 Direct sums and products

The *direct sum* of two matrices (given the symbol $\oplus$) is a special type of matrix sum that generates a matrix of higher dimensionality. If we take two 2×2 matrices, A and B

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \qquad B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}$$

The *direct sum* of the two matrices,

$$A \oplus B = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \oplus \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & 0 & 0 \\ a_{21} & a_{22} & 0 & 0 \\ 0 & 0 & b_{11} & b_{12} \\ 0 & 0 & b_{21} & b_{22} \end{pmatrix}$$

The *direct product* of two matrices (given the symbol $\otimes$) also generates a matrix of higher dimensionality if both matrices have dimension greater than one.

$$A \otimes B = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \otimes \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{11}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{pmatrix}$$

Though this may seem like a somewhat strange operation to carry out, direct products crop up a great deal in group theory. For example, there are many times when we would like to know whether a particular integral is necessarily zero, or whether there is a chance that it may be non-zero. If the former, then we do not need to calculate it explicitly. We can often use group theory to differentiate these two cases.

The use of symmetry properties of functions to determine whether or not a one-dimensional integral is zero is already familiar. For example, $sin(x)$ is an 'odd' function (anti-symmetric with respect to reflection through the origin), and it follows from this that $\int_{-a}^{+a} sin(x)dx = 0$. In the general case, we have integrals of the form:

$$I = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(x, y, z)dxdydz$$

which is often abbreviated as:

$$I = \int f(x, y, z)d\tau$$

where the symbol $d\tau$ indicates integration over all space. If the function is 'odd', the integral is zero:

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

by contrast for even functions the integral is not necessarily zero:

$$f(x) = f(-x) \qquad \int_{-\infty}^{+\infty} f(x)dx \neq 0$$

By extending these ideas to three dimensions, a general rule emerges which is that in a particular point group an integral over all space can only non zero if the function being integrated belongs to the totally symmetric irreducible representation (*i.e.* it is invariant to any symmetry operation).[§] If this condition is not satisfied the "odd" nature of the function under one or more symmetry operations always give rise to negative volume elements which cancel positive volume elements.

We will return to these ideas when we consider selection rules in Section 9.5.

[§] It should be noted that even when the irreps spanned by the integrand do include the totally symmetric irrep, it is still possible for the integral to be zero. All group theory allows us to do is identify integrals that are necessarily zero based on the symmetry (or lack thereof) of the integrand.

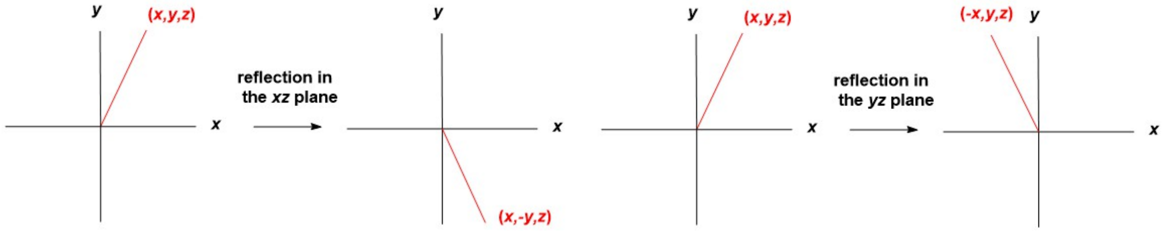
4.4 Transformation matrices

Matrices can be used to map one set of coordinates or functions onto another set. Matrices used for this purpose are called transformation matrices. In group theory, we can use transformation matrices to carry out the various symmetry operations considered at the beginning of the course. As a simple example, we will investigate the matrices we would use to carry out some of these symmetry operations on a 3-dimensional vector (x, y, z).

1. *The identity operation*
   The identity operation leaves the vector unchanged, and as you may already suspect, the appropriate matrix is the identity matrix.

$$\begin{pmatrix} x & y & z \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} x & y & z \end{pmatrix}$$

2. *Reflection in a plane*
   The simplest example of a reflection matrix corresponds to reflecting the vector (x, y, z) in either the xz or yz planes. Reflection in the xz plane maps y to $-y$ and leaves the other two components unchanged, while reflection in the yz plane maps x to $-x$. The appropriate matrices are very like the identity matrix but with a change in sign for the appropriate element. Reflection in the xz plane transforms the vector (x, y, z) to $(x, -y, z)$, reflection in the yz plane transforms the vector (x, y, z) to $(-x, y, z)$. The corresponding 3×3 transformation matrices are shown in the Figure below.



$$\begin{pmatrix} x & y & z \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} x & -y & z \end{pmatrix} \qquad \begin{pmatrix} x & y & z \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -x & y & z \end{pmatrix}$$

3. *Rotation about an axis.* Counter-clockwise rotations about the z axis acting on a vector (x, y, z) are represented by the following matrix.

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

4. *Inversion.* Inversion of the vector (x, y, z) through the origin is represented by the following matrix.

$$\begin{pmatrix} x & y & z \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

5. *Improper rotation.* A rotation about the z axis, followed by reflection in the xy plane is represented by the following matrix.

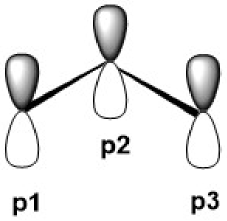
$$\begin{pmatrix} x & y & z \end{pmatrix} \begin{pmatrix} cos\theta & -sin\theta & 0 \\ sin\theta & cos\theta & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

5 Matrix representations of groups

We are now ready to integrate what we have just learned about matrices with group theory. The symmetry operations in a group may be represented by a set of transformation matrices $\Gamma(g)$, one for each symmetry element g. Each individual matrix is called a *matrix representative* of the corresponding symmetry operation, and the complete set of matrices is called a *matrix representation* of the group. The matrix representatives act on some chosen basis set of functions, and the actual matrices making up a given representation will depend on the basis that has been chosen. The representation is then said to *span* the chosen basis. In the examples above we were looking at the effect of some simple transformation matrices on an arbitrary vector (x, y, z). The basis was therefore a set of unit vectors pointing in the x, y and z directions. In most of the examples we will be considering in this course, we will use sets of atomic orbitals as basis functions for matrix representations, but sometimes we will use the (vibrating) bonds of a molecule.

5.1 Matrix representation of the C_{2v} point group using the p(π) orbitals of the allyl radical

In this example, we take as our basis the set of p orbitals on each carbon atom that lie perpendicular to the molecular plane, (p_1, p_2, p_3) *i.e* the orbitals that will form the π bonds.



The symmetry operations in the C_{2v} point group, and their effect on the three p orbitals, are as follows:

$E \quad (p_1, p_2, p_3) \rightarrow (p_1, p_2, p_3)$

$C_2 \quad (p_1, p_2, p_3) \rightarrow (-p_3, -p_2, -p_1)$

$\sigma_v \quad (p_1, p_2, p_3) \rightarrow (-p_1, -p_2, -p_3)$

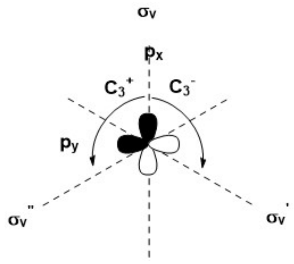
$\sigma_v^{'} \quad (p_1, p_2, p_3) \rightarrow (p_3, p_2, p_1)$

The matrices that carry out the transformation are:

- $E(p_1, p_2, p_3) = (p_1, p_2, p_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (p_1, p_2, p_3)$
- $C_2(p_1, p_2, p_3) = (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} = (-p_3, -p_2, -p_1)$
- $\sigma_v(p_1, p_2, p_3) = (p_1, p_2, p_3) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = (-p_1, -p_2, -p_3)$
- $\sigma_v^{'}(p_1, p_2, p_3) = (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} = (p_3, p_2, p_1)$

5.2 Matrix representation of the C_{3v} point group using the set of p orbitals at the origin

We have seen that the C_{3v} point group has 6 symmetry operations, E, C_3^+, C_3^-, σ_v, $\sigma_v^{'}$ and $\sigma_v^{''}$.



The p_z orbital is perpendicular to the plane, and remains unchanged by all of the symmetry operations. p_x and p_y, in contrast, are changed, and the resultant can be a linear combination of the original set. The precise effects of the symmetry operations on the p_x, p_y, p_z basis are as follows:

$$\begin{array}{ll}
E & (p_x, p_y, p_z) \to (p_x, p_y, p_z) \\
C_3^+ & (p_x, p_y, p_z) \to (-\frac{1}{2}p_x + \frac{\sqrt{3}}{2}p_y, -\frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y, p_z) \\
C_3^- & (p_x, p_y, p_z) \to (-\frac{1}{2}p_x - \frac{\sqrt{3}}{2}p_y, \frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y, p_z) \\
\sigma_v & (p_x, p_y, p_z) \to (p_x, -p_y, p_z) \\
\sigma_v^{'} & (p_x, p_y, p_z) \to (-\frac{1}{2}p_x + \frac{\sqrt{3}}{2}p_y, \frac{\sqrt{3}}{2}p_x + \frac{1}{2}p_y, p_z) \\
\sigma_v^{''} & (p_x, p_y, p_z) \to (-\frac{1}{2}p_x - \frac{\sqrt{3}}{2}p_y, -\frac{\sqrt{3}}{2}p_x + \frac{1}{2}p_y, p_z)
\end{array}$$

By inspection, the matrices that carry out the same transformations are:

- $E(p_x, p_y, p_z) = (p_x, p_y, p_z)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (p_x, p_y, p_z)$
- $C_3^+(p_x, p_y, p_z) = (p_x, p_y, p_z)\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = (-\frac{1}{2}p_x + \frac{\sqrt{3}}{2}p_y, -\frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y, p_z)$
- $C_3^-(p_x, p_y, p_z) = (p_x, p_y, p_z)\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = (-\frac{1}{2}p_x - \frac{\sqrt{3}}{2}p_y, \frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y, p_z)$
- $\sigma_v(p_x, p_y, p_z) = (p_x, p_y, p_z)\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} p_x & -p_y & p_z \end{pmatrix}$
- $\sigma_v^{'}(p_x, p_y, p_z) = (p_x, p_y, p_z)\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = (-\frac{1}{2}p_x + \frac{\sqrt{3}}{2}p_y, \frac{\sqrt{3}}{2}p_x + \frac{1}{2}p_y, p_z)$
- $\sigma_v^{''}(p_x, p_y, p_z) = (p_x, p_y, p_z)\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = (-\frac{1}{2}p_x - \frac{\sqrt{3}}{2}p_y, -\frac{\sqrt{3}}{2}p_x + \frac{1}{2}p_y, p_z)$

Collecting together the six matrix representatives, we see that they share a common *block diagonal* form (a square matrix is said to be block diagonal if all the elements are zero except for a set of submatrices lying along the diagonal):

Table 5.2: Fully reduced representations of the C_{3v} point group.

g	E	C_3^+	C_3^-	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$
$\Gamma^{(1)}(g)$	(1)	(1)	(1)	(1)	(1)	(1)
$\Gamma^{(2)}(g)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$

$$\begin{array}{ccc} \Gamma(E) & \Gamma(C_3^+) & \Gamma(C_3^-) \\ \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

$$\begin{array}{ccc} \Gamma(\sigma_v) & \Gamma(\sigma_v^{'}) & \Gamma(\sigma_v^{''}) \\ \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

A block diagonal matrix can be written as the *direct sum* of the matrices that lie along the diagonal. In the case of the C_{3v} matrix representation, each of the matrix representatives may be written as the direct sum of a 1×1 matrix and a 2×2 matrix.

$$\Gamma^{(3)}(g) = \Gamma^{(1)}(g) \oplus \Gamma^{(2)}(g)$$

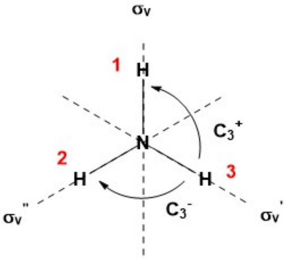
in which the bracketed superscripts denote the dimensionality of the matrices. Separation of the original representation into representations of lower dimensionality is called *reduction* of the representation. The block-diagonal form reflects the fact that none of the symmetry operations interconvert z with x or y. z is effectively isolated, and forms its own 1-dimensional representation. The reduced representations are shown in Table 5.2.

The reason why this result is useful in group theory is that the two sets of matrices $\Gamma^{(1)}(g)$ and $\Gamma^{(2)}(g)$ also satisfy all of the requirements for a matrix representation. Each set contains the identity and an inverse for each member, and the members multiply together associatively according to the group multiplication table.[¶]

[¶] The 1×1 representation in which all of the elements are equal to 1 is sometimes called the unfaithful representation,

5.3 Matrix representation of the C_{3v} point group using the s orbitals on N and H in the ammonia molecule

In this example we stick with the C_{3v} point group, but we choose a different basis, the set of s orbitals on the four atoms, (s_N,s_1,s_2,s_3). We would, of course, include the p orbitals on N as well in any meaningful calculation, but our purpose here is just to illustrate the machinery. Just as we did with the basis of cartesian vectors in the previous example, we need to consider what happens to this basis when it is acted on by each of the symmetry operations in the C_{3v} point group, and determine the matrices that would be required to produce the same effect. The basis set and the symmetry operations in the C_{3v} point group are summarised in the figure below:



The effects of the symmetry operations on our chosen basis are as follows:

$$\begin{array}{ll}
E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\
C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\
C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\
\sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\
\sigma_v^{'} & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\
\sigma_v^{''} & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1)
\end{array}$$

By inspection, the matrices that carry out the same transformations are:

- $E(s_N, s_1, s_2, s_3) = (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_1, s_2, s_3)$

---

since it satisfies the group properties in a fairly trivial way without telling us much about the symmetry properties of the group.

- $C_3^+(s_N, s_1, s_2, s_3) = (s_N, s_1, s_2, s_3)\begin{pmatrix}1&0&0&0\\0&0&0&1\\0&1&0&0\\0&0&1&0\end{pmatrix} = (s_N, s_2, s_3, s_1)$
- $C_3^-(s_N, s_1, s_2, s_3) = (s_N, s_1, s_2, s_3)\begin{pmatrix}1&0&0&0\\0&0&1&0\\0&0&0&1\\0&1&0&0\end{pmatrix} = (s_N, s_3, s_1, s_2)$
- $\sigma_v(s_N, s_1, s_2, s_3) = (s_N, s_1, s_2, s_3)\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix} = (s_N, s_1, s_3, s_2)$
- $\sigma_v^{'}(s_N, s_1, s_2, s_3) = (s_N, s_1, s_2, s_3)\begin{pmatrix}1&0&0&0\\0&0&1&0\\0&1&0&0\\0&0&0&1\end{pmatrix} = (s_N, s_2, s_1, s_3)$
- $\sigma_v^{''}(s_N, s_1, s_2, s_3) = (s_N, s_1, s_2, s_3)\begin{pmatrix}1&0&0&0\\0&0&0&1\\0&0&1&0\\0&1&0&0\end{pmatrix} = (s_N, s_3, s_2, s_1)$

These six matrices therefore form a *representation* for the C_{3v} point group in the (s_N, s_1, s_2, s_3) basis. We can build a group multiplication table, precisely analogous to Table 3.1, based on the representative matrices rather than the operations. To illustrate this, consider the matrix products below, which corresponds to the red and yellow shaded squares in Table 3.1:

$$\Gamma(\sigma_v C_3^+) = \Gamma(\sigma_v)\Gamma(C_3^+) = \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}\begin{pmatrix}1&0&0&0\\0&0&0&1\\0&1&0&0\\0&0&1&0\end{pmatrix} = \begin{pmatrix}1&0&0&0\\0&0&0&1\\0&0&1&0\\0&1&0&0\end{pmatrix} = \Gamma(\sigma_v^{''})$$

$$\Gamma(C_3^+\sigma_v) = \Gamma(C_3^+)\Gamma(\sigma_v) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \Gamma(\sigma_v^{'})$$

With a little work, you can show that, just like the operations themselves, the set of transformation matrices forms a group under the operation of matrix multiplication. Specifically:

1. The set includes the identity operation E (the ‘do nothing’ operation).
2. The combination of any pair of elements is also an element of the group (the *group property*, or *closure*). In fact, matrix representatives multiply together to give new representatives in exactly the same way as the corresponding symmetry operations combine. In the example above, the product of the matrix representatives of C_3^+ and σ_v gives the representative of $\sigma_v^{''}$.
3. Every operation has an inverse, which is also a member of the group. For example, the inverse of a reflection is another reflection, identical to the first, and it turns out that the representative matrices for the reflections are all self-inverses. The inverse of a rotation matrix is another rotation matrix corresponding to a rotation of the opposite sense to the first (*i.e.* $\Gamma(C_3^+)$ is the inverse of $\Gamma(C_3^-)$ and *vice versa.*
4. The multiplication is associative: this is automatically satisfied by the rules of matrix multiplication: $A(BC) = (AB)C$.

If we look closely at the representative matrices generated in section 5.3, we note again that they all take the same *block diagonal* form (see shading).

$$\begin{array}{ccc} \Gamma(E) & \Gamma(C_3^+) & \Gamma(C_3^-) \\ \\ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} \end{array}$$

$$\begin{array}{ccc} \Gamma(\sigma_v) & \Gamma(\sigma_v^{'}) & \Gamma(\sigma_v^{''}) \\ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \end{array}$$

$$\Gamma^{(4)}(g) = \Gamma^{(1)}(g) \oplus \Gamma^{(3)}(g)$$

Recall that the original four-dimensional representation had the s orbitals (s_N, s_1, s_2, s_3) of ammonia as its basis. The first set of reduced matrices, $\Gamma^{(1)}(g)$, forms a one-dimensional representation with (s_N) as its basis. Again, the block-diagonal form reflects the physical fact that none of the symmetry operations interconvert s_N with any of s_1, s_2, s_3. The second set, $\Gamma^{(3)}(g)$ forms a three-dimensional representation with the basis (s_1, s_2, s_3). Separation of the original representation into representations of lower dimensionality is called *reduction* of the representation. The two reduced representations are shown below: The 1-dimensional representation is *spanned by* s_N, the 3-dimensional representation is *spanned by* by (s_1, s_2, s_3)

Table 5.3: Representations of the C_{3v} point group using the (s_1, s_2, s_3) basis.

g	E	C_3^+	C_3^-	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$
$\Gamma^{(1)}(g)$	(1)	(1)	(1)	(1)	(1)	(1)
$\Gamma^{(3)}(g)$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$

The logical next step is to investigate whether or not the three dimensional representation $\Gamma^{(3)}(g)$ can be reduced any further. As it stands, the matrices making up this representation are not in block diagonal form so the representation is not reducible (the matrices representing E and σ_v are in the same block diagonal form, but in order for a representation to be reducible all of the matrix representatives must be in the same block diagonal form). However, we may be able to carry out a *similarity transformation* to a new representation spanned by a new set of basis functions (made up of linear combinations of (s_1, s_2, s_3)), which transforms the matrices of $\Gamma^{(3)}(g)$ in Table 5.3 to a block diagonal form, which then is reducible.

5.4 Similarity transforms

Suppose we have a basis set $(x_1, x_2, x_3, \ldots, x_n)$, and we have determined the matrix representatives for the basis in a given point group. There is nothing particularly special about the basis set we have chosen, and we could equally well have used any set of linear combinations of the original functions (provided the combinations were linearly independent). The matrix representatives for the two basis sets will certainly be different, but they are related by a *similarity transform.* Consider a basis set $(x_1^{'}, x_2^{'}, x_3^{'}, \ldots, x_n^{'})$, in which each basis function $x_i^{'}$ is a linear combination of our original basis $(x_1, x_2, x_3, \ldots, x_n)$.

$$x_j^{'} = \sum_i x_i c_{ij} = x_1 c_{1j} + x_2 c_{2j} + \ldots$$

The c_{ji} appearing in the sum are coefficients; c_{ij} is the coefficient multiplying the original basis function x_i in the new linear combination basis function $x_j^{'}$. We could also represent this transformation in terms of a matrix equation $\mathbf{x}^{'} = \mathbf{x}C$:

$$(x_1^{'}, x_2^{'}, x_3^{'}, \ldots, x_n^{'}) = (x_1, x_2, x_3, \ldots, x_n) \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1n} & & & & \\ c_{21} & c_{22} & \cdots & c_{2n} \cdots & \cdots & \cdots & \cdots & \\ & & & & & & & \\ c_{n1} & c_{n2} & \cdots & c_{nn} & & & & \end{pmatrix}$$

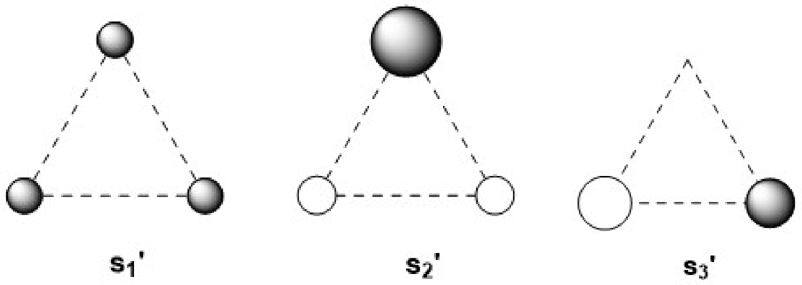
Now we look at what happens when we apply a symmetry operation g to our two basis sets. If $\Gamma(g)$ and $\Gamma^{'}(g)$ are matrix representatives of the symmetry operation in the x and $x^{'}$ bases, then we have:

$$\begin{aligned} &g\mathbf{x} = \mathbf{x}\Gamma(g) \\ &g\mathbf{x}^{'} = \mathbf{x}^{'}\Gamma^{'}(g) \\ &g\mathbf{x}C = \mathbf{x}C\Gamma^{'}(g) \qquad (using \qquad \mathbf{x}^{'} = \mathbf{x}C) \\ &g\mathbf{x}CC^{-1} = g\mathbf{x} = \mathbf{x}\Gamma(g) = \mathbf{x}C\Gamma^{'}(g)C^{-1} \end{aligned}$$

We can therefore identify the similarity transform relating $\Gamma(g)$, the matrix representative in our original basis, to $\Gamma^{'}(g)$, the representative in the transformed basis. The transform depends only on the matrix of coefficients used to transform the basis functions.

$$\begin{aligned} \Gamma(g) &= C\Gamma^{'}(g)C^{-1} \\ \Gamma^{'}(g) &= C^{-1}\Gamma(g)C \end{aligned}$$

We will learn how to generate the required linear combinations later in Section 6.4, but for now they are given below:



$$s_1^{'} = \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3) \quad s_2^{'} = \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3) \quad s_3^{'} = \frac{1}{\sqrt{2}}(s_2 - s_3)$$

The linear combinations of basis functions that convert a matrix representation into block diagonal form, allowing reduction of the representation, are called *symmetry-adapted linear combinations* or *SALCs*. In matrix form:

$$(s_1^{'}, s_2^{'}, s_3^{'}) = (s_1, s_2, s_3)C = (s_1, s_2, s_3)\begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

The matrices in this new representation can be generated using the expression $\Gamma^{'}(g) = C^{-1}\Gamma(g)C$, and are collected in Table 5.4.

Table 5.4: Representative matrices in the transformed basis.

$$\begin{array}{ccc} E & C_3^{+} & C_3^{-} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \end{array}$$

$$\begin{array}{ccc} \sigma_v & \sigma_v^{'} & \sigma_v^{''} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \end{array}$$

Each matrix is now in block diagonal form, and so the 3 × 3 representation can now be further reduced into the direct sum of a 1 × 1 representation spanned by $(s_1^{'})$ and a 2 × 2 representation spanned by $(s_2^{'}, s_3^{'})$ (Table 5.5). The complete set of reduced representations obtained from the original 4-dimensional representation is:

Table 5.5: Irreducible representations of C_{3v} spanned by the $(s_N, s_1^{'}, s_2^{'}, s_3^{'})$ basis.

basis		E	C_3^+	C_3^-	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$
s_N	$\Gamma^{(1)}(g)$	(1)	(1)	(1)	(1)	(1)	(1)
$s_1^{'}$	$\Gamma^{(1)}(g)$	(1)	(1)	(1)	(1)	(1)	(1)
$(s_2^{'}, s_3^{'})$	$\Gamma^{(2)}(g)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$

Note that the 2-dimensional representation is **precisely** the same as the one we derived for the set of p orbitals on the central atom in Table 5.2. This is not a coincidence - the set of matrices in $\Gamma^2(g)$ is somehow a fundamental property of the group, and none of the three representations above can be reduced any further; they are therefore called *irreducible representations*, or '*irreps*', of the point group. The definition of an irrep is one that cannot be converted to a block-diagonal form by a similarity transformation.

5.5 Characters of representations and classes

Comparing the representative 3×3 matrices in Tables 5.3 and 5.4, we reiterate the obvious point that the similarity transform has changed the representation. However, one feature of each matrix that is not affected by the similarity transformation is their trace (the sum of the diagonal elements). So for example, the trace of $\Gamma(E)$ is 3 in both tables, the trace of $\Gamma(C_3^+)$ is 0 and the trace of $\Gamma(\sigma_v)$ is 1. The trace of $\Gamma(g)$ is usually referred to as the *character* of the representation, χ_g, under the symmetry operation g. The characters of a matrix representation are often just as useful than the matrix representatives themselves, and they are certainly easier to deal with.

The characters of the representations under the symmetry operations C_3^+ and C_3^- are the same (0), as are the characters for σ_v, $\sigma_v^{'}$ and $\sigma_v^{''}$ (1). This reflects the fact that they are similar kinds of operation: we say that the two C_3 operations belong to the same *class*, and the three σ_v operations belong to a different *class*. Formally, two operations, R and $R^{'}$, are members of the same class if there is a symmetry operation in the group, S, such that:

$$R^{'} = S^{-1} R S \tag{5.5.1}$$

The two operations, R and $R^{'}$, are then said to be conjugate. For example, from the group multiplication table, Table 3.1, we see that

$$\sigma_v^{-1}C_3^+\sigma_v = \sigma_v(C_3^+\sigma_v) = \sigma_v\sigma_v^{'} = C_3^- \tag{5.5.2}$$

The two one-dimensional irreps spanned by s_N and $s_1^{'}$ in Table 5.5 are identical. This means that s_N and $s_1^{'}$ have the 'same symmetry', transforming in the same way under all of the symmetry operations of the point group and forming bases for the same matrix representation. More formally, they are said to belong to the *same symmetry species*.

There are several different ways of expressing the symmetry of a function: the following statements about a function f all mean the same thing.

"f has E symmetry"

"f transforms as E"

"f has the same symmetry as E"

"f forms a basis for the E irrep"

5.6 Character tables

There is only a limited number of ways in which an arbitrary function can transform under the symmetry operations of a group, giving rise to a limited number of symmetry species, which are identified by the collection of characters for the different classes of symmetry operation. A *character table* summarises the behaviour of all of the possible irreps of a group under each of the symmetry operations of the group. The character table for C_{3v} is shown below.

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)

The various sections of the table are as follows:

1. The first element in the table gives the name of the point group, sometimes in both Schoenflies (C_{3v}) and Hermann-Mauguin ($3m$) notation.
2. Along the first row are the symmetry operations of the group, E, $2C_3$ and $3\sigma_v$, followed by the order h of the group. Because operations in the same class have the same character, symmetry operations are grouped into classes in the character table and not listed separately.
3. In the first column are the irreps of the group. In C_{3v} there are only three possible irreps, A_1, A_2 and E (the representation we considered above spans $2A_1 + E$). The number of irreps is always equal to the number of classes of symmetry operation.
4. The characters of the irreps under each symmetry operation are given in the bulk of the table.

5. The final column of the table lists a number of functions that transform as the various irreps of the group. These are the Cartesian axes (x, y, z) the Cartesian products $(z^2, x^2+y^2, xy, xz, yz)$ and the rotations (R_x, R_y, R_z).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y, T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. As we shall see later, the transformation properties of x, y, and z can also be used to determine whether or not a molecule can absorb a photon of x-, y- or z-polarised light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

The labelling of irreps of a point group is based on the following conventions:

1. 1-dimensional representations are labelled A or B, depending on whether they are symmetric (character +1) or antisymmetric (character –1) under rotation about the principal axis.
2. 2-dimensional representations are labelled E, 3-dimensional representations are labelled T.
3. In groups containing a centre of inversion, g and u labels (from the German *gerade* and *ungerade*, meaning symmetric and antisymmetric) denote the character of the irrep under inversion (+1 for g, -1 for u)
4. In groups with a horizontal mirror plane but no centre of inversion, the irreps are given prime and double prime labels to denote whether they are symmetric (character +1) or antisymmetric (character –1) under reflection in the plane.
5. If further distinction between irreps is required, subscripts 1 and 2 are used to denote the character with respect to a C_2 rotation perpendicular to the principal axis, or with respect to a vertical reflection if there are no C_2 rotations.

For example, the 1-dimensional irrep in the C_{3v} point group is symmetric (has character +1) under all the symmetry operations of the group. It therefore belongs to the irrep A_1. The 2-dimensional irrep has character 2 under the identity operation, -1 under rotation, and 0 under reflection, and belongs to the irrep E.

Character tables for common point groups are given in Appendix B.

5.7 Shortcut to generating a representation

In many applications of group theory, we only need to know the characters of the representative matrices, rather than the matrices themselves. We could generate the characters by generating the representative matrices and then taking the trace, but there is a much simpler shortcut. All we have to do is to look at the way the individual basis functions transform under each symmetry operation: a non-zero element on the diagonal of the representative matrix (and hence in the trace) will only appear if the basis function is mapped onto itself (or partially onto itself) by the operation in question. So, for a given operation, step through each of the basis functions as follows:

1. Add 1 to the character if the basis function is unchanged by the symmetry operation (*i.e.* the basis function is mapped onto itself);
2. Add −1 to the character if the basis function changes sign under the symmetry operation (*i.e* the basis function is mapped onto minus itself);
3. Add 0 to the character if the basis function moves when the symmetry operation is applied (*i.e* the basis function is mapped onto something different from itself).
4. In some cases, a basis function is transformed into a linear combination of itself and another basis function. A case in point is the p_x orbital in Section 5.2, which is transformed into $(-\frac{1}{2}p_x + \frac{\sqrt{3}}{2}p_y$ by the C_3^+ operation *i.e.* $-\frac{1}{2}$ of itself plus $\frac{\sqrt{3}}{2}$ of p_y. In this case, we add the fraction of itself $(-\frac{1}{2})$ to the character.

Try this for the s orbital basis we have been using for the C_{3v} group. You should find you get the same characters as we obtained from the traces of the matrix representatives.

6 Great and Little Orthogonality Theorems

In order to make full use of group theory, we need to develop a little more 'machinery'. Specifically, given a basis set (of atomic orbitals, for example) we need to establish:

1. How to determine the irreps spanned by the basis functions
2. How to construct the linear combinations of the original basis functions that transform as a given irrep/symmetry species.

It turns out that both of these problems can be solved using the 'Great Orthogonality Theorem' (GOT for short). The GOT summarises a number of orthogonality relationships implicit in matrix representations of symmetry groups, and may be derived in a somewhat qualitative fashion by considering these relationships in turn. The detailed derivation of the GOT is not critical for us, but it underpins everything you will do with group theory.

6.1 Orthogonality relationships in group theory

Two vectors are said to be *orthogonal* if their dot product (*i.e.* the projection of one vector onto the other) is zero. An example of a pair of orthogonal vectors is provided by the x and y cartesian unit vectors: $x.y = 0$. A consequence of the orthogonality of x and y is that *any* general vector in the xy plane may be written as a linear combination of these two basis vectors: $r = ax + by$

Mathematical functions may also be orthogonal. Two functions, $f_1(x)$ and $f_2(x)$, are defined to be orthogonal if the integral over their product is equal to zero *i.e.* $\int f_1(x)f_2(x)dx = \delta_{12}$. This simply means that there must be 'no net overlap' between orthogonal functions, which is the same as the orthogonality requirement for vectors, above. In the same way as for vectors, any general function may be written as a linear combination of a suitably chosen set of orthogonal basis functions.

The irreps of a point group satisfy a number of orthogonality relationships:

1. If corresponding matrix elements in all of the matrix representatives of an irrep are squared and added together, the result is equal to the order of the group divided by the dimensionality of the irrep. *i.e.*

$$\sum_g \Gamma_k(g)_{ij}\Gamma_k(g)_{ij} = \frac{h}{d_k} \tag{6.1.1}$$

   where k labels the irrep, i and j label the row and column position within the irrep, h is the order of the group, and d_k is the order of the irrep.

   For example, the order of the group C_{3v} is 6. If we apply the above operation to the first element in the matrices for the 2×2 (E) irrep derived in Table 5.5, the result should be equal to $\frac{h}{d_k} = \frac{6}{2} = 3$. Carrying out this operation gives:

$$(1)^2 + (-\frac{1}{2})^2 + (-\frac{1}{2})^2 + (1)^2 + (-\frac{1}{2})^2 + (-\frac{1}{2})^2 = 1 + \frac{1}{4} + \frac{1}{4} + 1 + \frac{1}{4} + \frac{1}{4} = 3$$

2. If instead of summing the squares of matrix elements in an irrep, we sum the product of two *different* elements from within each matrix, the result is equal to zero. *i.e.*

$$\sum_g \Gamma_k(g)_{ij}\Gamma_k(g)_{i'j'} = 0 \tag{6.1.2}$$

   where $i \neq i^{'}$ and/or $j \neq j^{'}$

   If we perform this operation using the two elements in the first row of the 2-dimensional irrep used in step 1, we get:

$$\begin{aligned}&(1)(0) + (-\frac{1}{2})(-\frac{\sqrt{3}}{2}) + (-\frac{1}{2})(\frac{\sqrt{3}}{2}) + (1)(0) + (-\frac{1}{2})(\frac{\sqrt{3}}{2}) + (-\frac{1}{2})(-\frac{\sqrt{3}}{2})\\ =&0 + \frac{\sqrt{3}}{4} - \frac{\sqrt{3}}{4} + 0 - \frac{\sqrt{3}}{4} + \frac{\sqrt{3}}{4} = 0\end{aligned}$$

3. If we sum the product of two elements from the matrices of two *different* irreps k and m, the result is equal to zero:

$$\sum_g \Gamma_k(g)_{ij}\Gamma_m(g)_{i'j'} = 0 \tag{6.1.3}$$

   where there is now no restriction on the values of the indices $i, j, i^{'}, j^{'}$ (apart from the rather obvious restriction that they must be less than or equal to the dimensions of the irrep). Performing this operation on the first elements of the A_1 and E irreps we derived for C_{3v} gives:

$$(1)(1) + (1)(-\frac{1}{2}) + (1)(-\frac{1}{2}) + (1)(1) + (1)(-\frac{1}{2}) + (1)(-\frac{1}{2}) = 1 - \frac{1}{2} - \frac{1}{2} + 1 - \frac{1}{2} - \frac{1}{2} = 0$$

We can combine Equations 6.1.1, 6.1.2 and 6.1.3 into one general equation, the *Great Orthogonality Theorem*, or *GOT*[‖].

$$\sum_g \Gamma_k(g)_{ij}\Gamma_m(g)_{i'j'} = \frac{h}{\sqrt{d_k d_m}}\delta_{km}\delta_{ii'}\delta_{jj'} \tag{6.1.4}$$

For most applications we don't actually need the full power of the Great Orthogonality Theorem. A little mathematical trickery transforms Equation 6.1.4 into the *Little Orthogonality Theorem* (or *LOT*), which is expressed in terms of the characters of the irreps rather than the matrix elements of the irreps themselves.

$$\sum_g \chi_k(g)\chi_m(g) = h\delta_{km} \tag{6.1.5}$$

Recall that the characters for two symmetry operations in the same class are the same; we can therefore rewrite the sum over symmetry operations as a sum over classes.

$$\sum_C n_C\chi_k(C)\chi_m(C) = h\delta_{km} \tag{6.1.6}$$

where n_C is the number of symmetry operations in class C.

if we set $k = m$ in either of the last equations, we find that the sum of the squares of the characters for any irrep is equal to the order of the group, h:

$$\sum_g \chi_k^2(g) = \sum_C n_C\chi_k^2(C) = h \tag{6.1.7}$$

Further useful results that emerge from the LOT are:

1. The number of irreducible representations of the group is equal to the number of classes of operation. This means that all character tables are square (same number of rows as columns)
2. The sum of the squares of the characters of the i different irreps under the identity operation ($\chi(E)$) equals the order of the group:

$$\sum_i \chi_i^2(E) = h \tag{6.1.8}$$

6.2 Generating character tables from the LOT

You might have wondered where the character tables shown in Section 5.6 and in the appendix actually come from. And how do we know whether there are complete - are they more irreps to find? The process for generating a character table, in this case C_{4v}, is shown below.

[‖] The δ_{ij} appearing in Equation 6.1.4 are called Dirac delta functions. They are equal to 1 if $i = j$ and 0 otherwise.

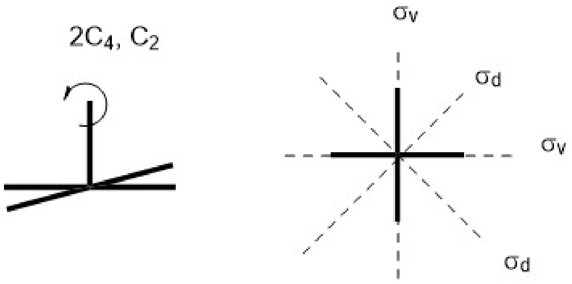


Figure 3: Classes of symmetry operation in C_{4v}.

1. There are five classes of symmetry operation for C_{4v}: E, $2C_4$, C_2, $2\sigma_v$ and $2\sigma_d$, giving a total order of 8. If there are five classes, there must be precisely five irreps to find.
2. The sum of the squares of the character under E must equal the order of the group, in this case 8. $\chi(E)$ must be positive so the only way we can achieve this with five irreps is for $\chi(E)$ to be 1, 1, 1, 1 and 2.
3. For each irrep, we have:
$$\sum_C n_C \chi_k^2(C) = h \qquad (6.2.1)$$
This means that $\chi_k^2(E) + 2\chi_k^2(C_4) + \chi_k^2(C_2) + 2\chi_k^2(\sigma_v) + 2\chi_k^2(\sigma_d) = 8$.
4. For 1-dimensional irreps (*i.e.* those with $\chi_k(E) = 1$), the only way we can achieve this is if each of the other classes has $\chi = \pm 1$.
5. One of these must be the totally symmetric representation with all $\chi = +1$
6. The three remaining 1-dimensional irreps must be orthogonal to the totally symmetric one and to each other (Equation 6.1.5), and the only way we can do this if the characters of precisely two of the three classes with two operations (C_4, σ_v, σ_d) are -1 and the remaining one is +1. These constraints give us the four 1-dimensional irreps shown in the character table, Table 6.6.
7. The fifth irrep is 2-dimensional, with $\chi(E) = 2$. The only possible combinations consistent with $\sum_C n_C \chi_k^2(C) = 8$ are (a) $\chi(C_2) = \pm 2$, all others are zero and (b) two of C_4, σ_v and σ_d have $\chi = -1$, the others are zero. Option (b) is not orthogonal to the totally-symmetric irrep (or indeed to any of the other 1-dimensional irreps) so we are left only with possibility (a). $\chi(C_2)$ must then be -2, not +2, to satisfy orthogonality with the 1-dimensional irreps (all of which have $\chi(C_2) = 1$).

So, finally, we arrive at the complete character table for C_{4v}. The labels are added afterwards (following the conventions set out in Section 5.5), but the irreps themselves emerge logically from the LOT.

6.3 The LOT and the *reduction formula*

In Section 5.4 we discovered that we can often carry out a similarity transform on a general matrix representation so that all the representatives end up in the same block diagonal form. When this is possible, each set of sub-matrices also forms a valid matrix representation of the group. If none

Table 6.6: Character Table for C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	–1
B_1	1	–1	1	1	-1
B_2	1	–1	1	–1	1
E	2	0	–2	0	0

of the sub-matrices can be reduced further by carrying out another similarity transform, they are said to form an irreducible representation of the point group. An important property of matrix representatives (see Section 5.5) is that their character is invariant under a similarity transform. This means that the character of the original representatives must be equal to the sum of the characters of the irreps into which the representation is reduced. *e.g.* if we consider the representative for the C_3^+ symmetry operation in our NH_3 example, we have:

$$\underset{\chi=1}{\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}} \quad \xrightarrow{similarity\ transform} \quad \underset{\chi=1}{\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}} \quad \underset{\chi = 1+1+(-1) = 1}{= (1) \oplus (1) \oplus \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}}$$

It follows that we can write the characters for a general representation $\Gamma(g)$, which may be the sum of several irreps, in terms of the characters of the irreps $\Gamma_k(g)$ into which it can be reduced.

$$\chi(g) = \sum_k n_k \chi_k(g) \tag{6.3.1}$$

where the coefficients n_k in the sum are the number of times each irrep appears in the representation.

Expressed in terms of classes rather than individual operations:

$$\chi(C) = \sum_k n_k \chi_k(C) \tag{6.3.2}$$

This means that in order to determine the irreps spanned by a given basis, all we have to do is determine the coefficients n_k in the above equation. This is where the Little Orthogonality Theorem comes in handy. If we take the LOT in the form of Equation **??**, and multiply each side through by n_k, we get

$$\sum_C n_C n_k \chi_k(C) \chi_m(C) = h n_k \delta_{km} \tag{6.3.3}$$

Summing both sides of the above equation over k gives

$$\sum_C n_C \left(\sum_k n_k \chi_k(C) \right) \chi_m(C) = h \sum_k n_k \delta_{km} \tag{6.3.4}$$

noting that δ_{km} is only non-zero (and equal to 1) when $k = m$.

$$\sum_C n_C \left(\sum_k n_k \chi_k(C) \right) \chi_m(C) = h n_m \tag{6.3.5}$$

Substituting Equation 6.3.2 into the brackets on the left hand side gives:

$$\sum_C n_C \chi(C) \chi_m(C) = h n_m \tag{6.3.6}$$

where note now that $\chi(C)$ is the general representation, which may be a sum of several irreps.

Dividing both sides through by h (the order of the group), gives us an expression for the coefficient n_m in terms of the characters $\chi(C)$ of the original representation and the characters $\chi_m(C)$ of the m^{th} irrep.

$$n_m = \frac{1}{h} \sum_C n_C \chi(C) \chi_m(C) \tag{6.3.7}$$

As an example, in Section 5.4 we showed, with some effort, that the matrix representations for the C_{3v} point group using the (s_N, s_1, s_2, s_3) could be reduced to two identical 1-dimensional irreps ($\Gamma(1)(g)$) and a 2-dimensional irrep, $\Gamma(2)(g)$, Table 5.5. If we take the traces of the representative matrices, we see that the characters of $\Gamma(1)(g)$ are all 1, so it corresponds to the A_1 representation, while the characters of $\Gamma(2)(g)$ correspond to those of the E irrep: the representation can be reduced to the sum $2A_1 + E$.

We could have obtained the same result using Equation 6.3.7, starting from the original 4 × 4 representatives in Section 5.3. The characters, χ, are collected in the top row of the table below, and the irreps of the C_{3v} point group (A_1, A_2 and E) are given in the rows below. The top row is clearly not one of the irreducible representations (irreps), so it must be reducible to a linear combination of the irreps.

C_{3v}	E	$2C_3$	$3\sigma_v$
χ	4	1	2
$\Gamma(A_1)$	1	1	1
$\Gamma(A_2)$	1	1	-1
$\Gamma(E)$	2	-1	0

From 6.3.7, the number of times each irrep occurs in the reducible representation is therefore

$$n(A_1) = \frac{1}{6}(1 \times 4 \times 1 + 2 \times 1 \times 1 + 3 \times 2 \times 1) = 2$$
$$n(A_2) = \frac{1}{6}(1 \times 4 \times 1 + 2 \times 1 \times 1 + 3 \times 2 \times -1) = 0$$
$$n(E) = \frac{1}{6}(1 \times 4 \times 2 + 2 \times 1 \times -1 + 3 \times 2 \times 0) = 1$$

i.e. Our basis is spanned by $2A_1 + E$, as we found before.

6.4 Symmetry-adapted linear combinations

Once we know the irreps spanned by an arbitrary basis set, we can work out the appropriate linear combinations of basis functions that transform the matrix representatives of our original representation into block diagonal form (*i.e.* the *symmetry-adapted linear combinations*, or SALCs). Each of the SALCs transforms as one of the irreps of the reduced representation. We have already seen this in our NH_3 example. The two linear combinations of A_1 symmetry were s_N and $s_1^{'} = \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3)$, both of which are symmetric under all the symmetry operations of the point group. We also chose another pair of functions, $\frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3)$ and $\frac{1}{\sqrt{2}}(s_2 - s_3)$, which together transform as the symmetry species E. We wil now see how to generate these SALCs using *projection operators*.

To generate a SALC from a given basis function that transforms as irrep k, we use the following formula:

$$f_i^{'} = \sum_g \chi_k(g)(gf_i) \tag{6.4.1}$$

Here, f_i is a basis function (s_1 of the (s_1, s_2, s_3) basis, for example), and gf_i is the result of applying the operation g to it. For example, the C_3^+ operation converts s_1 into s_2. $\chi_k(g)$ is the character of the operation g for irrep k.

The way in which this operation is carried out will become much more clear if we work through an example. We can break down the above equation into a fairly straightforward 'recipe' for generating SALCs:

1. Make a table with rows labelled by the basis functions and columns labelled by the symmetry operations of the molecular point group. In each row, show the effect of the symmetry operations on a particular basis function (this is the (gf_i) part of Equation 6.4.1).

2. For each irrep in turn, multiply each member of the table by the character of the appropriate symmetry operation (we now have $\chi_k(g)gf_i$ for each operation). Summing over the columns (symmetry operations) generates all the SALCs that transform as the chosen irrep.
3. Normalise the SALCs.

Earlier (see Section 5), we worked out the effect of all the symmetry operations in the C_{3v} point group on the (s_N, s_1, s_2, s_3) basis.

$$\begin{array}{ll}
E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\
C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\
C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\
\sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\
\sigma_v^{'} & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\
\sigma_v^{''} & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1)
\end{array}$$

This is all we need to construct the table described in step 1 above.

f_i	Ef_i	$C_3^+f_i$	$C_3^-f_i$	σ_vf_i	$\sigma_v^{'}f_i$	$\sigma_v^{''}f_i$
s_N	s_N	s_N	s_N	s_N	s_N	s_N
s_1	s_1	s_2	s_3	s_1	s_2	s_3
s_2	s_2	s_3	s_1	s_3	s_1	s_2
s_3	s_3	s_1	s_2	s_2	s_3	s_1

The character table C_{3v}, listed by operation rather than by class, is:

C_{3v}	E	C_3^+	C_3^+	σ_v	$\sigma_v^{'}$	$\sigma_v^{''}$
$\Gamma(A_1)$	1	1	1	1	1	1
$\Gamma(A_2)$	1	1	1	-1	-1	-1
$\Gamma(E)$	2	-1	-1	0	0	0

To determine the SALCs of A_1 symmetry, we multiply the rows of gf_i through by the characters of the A_1 irrep (all of which take the value 1). Summing over the rows gives

$$\begin{aligned}
&s_N + s_N + s_N + s_N + s_N + s_N = 6s_N \\
&s_1 + s_2 + s_3 + s_1 + s_2 + s_3 = 2(s_1 + s_2 + s_3) \\
&s_2 + s_3 + s_1 + s_3 + s_1 + s_2 = 2(s_1 + s_2 + s_3) \\
&s_3 + s_1 + s_2 + s_2 + s_3 + s_1 = 2(s_1 + s_2 + s_3)
\end{aligned}$$

We appear to have four linear combinations, but the last three results are the same, irrespective of whether we choose s_1, s_2 or s_3, and they are (aside from the normalising factor which we can always account for later) identical to the $s_1^{'}$ linear combination identified earlier.

$$\begin{aligned}\phi(1) &= s_N\\ \phi(2) &= \frac{1}{\sqrt{3}}(s_1+s_2+s_3) = s_1^{'}\end{aligned}$$

We now move on to determine the SALCs of E symmetry. Multiplying the rows of gf_i by the appropriate characters for the E irrep gives:

$$\begin{aligned}
&2s_N - s_N - s_N + 0 + 0 + 0 = 0\\
\text{a}\ &2s_1 - s_2 - s_3 + 0 + 0 + 0 = 2s_1 - s_2 - s_3\\
\text{b}\ &2s_2 - s_3 - s_1 + 0 + 0 + 0 = 2s_2 - s_3 - s_1\\
\text{c}\ &2s_3 - s_1 - s_2 + 0 + 0 + 0 = 2s_3 - s_1 - s_2
\end{aligned}$$

We therefore appear to get three SALCs from s_1, s_2 and s_3 (a, b, and c), from this procedure but this can't be correct because the number of SALCs must match the dimensionality of the irrep, in this case two. The problem arises because the three SALCs above are not *linearly independent*: any one of them can be written as a linear combination of the other two. To solve the problem, we can combine the three SALCs to make two that are orthogonal to each other, a process known as *Schmidt orthogonalisation*:

Let us choose one of the linear combinations, $\Phi(3) = a$ and seek a linear combination of b and c, $\Phi(4) = b + \lambda c$, that is orthogonal to it (*i.e.* we set $\Phi(3) \cdot \Phi(4) = 0$):

$$a \cdot (b + \lambda c) = (2s_1 - s_2 - s_3) \cdot (2s_2 - s_3 - s_1 + \lambda\,(2s_3 - s_1 - s_2)) = 0$$

$$(2s_1 - s_2 - s_3) \cdot ((-1-\lambda)\,s_1 + (2-\lambda)\,s_2 - (1+2\lambda)\,s_3) = 0$$

$$2\,(-1-\lambda) - 1\,(2-\lambda) - 1\,(1+2\lambda) = -3 - 3\lambda = 0 \implies \lambda = -1$$

After normalisation, we have:

$$\begin{aligned}\phi(3) &= \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3) = s_2^{'}\\ \phi(4) &= \frac{1}{\sqrt{2}}(s_2 - s_3) = s_3^{'}\end{aligned}$$

These are precisely the linear combinations $s_2^{'}$ and $s_3^{'}$ that we used in Section 5.4

We now have all the machinery we need to apply group theory to a range of chemical problems. In our first application, we will learn how to use molecular symmetry and group theory to help us understand chemical bonding.

7 Advanced applications: reduction formula and projection operators.

7.1 The reduction formula

The reduction formula gives us a “handle turning” procedure for reducing the representation spanned by a set of basis functions. The formula shown below looks abstract and somewhat impenetrable when first encountered, but is actually quite simple to use in practice. It is expressed either in terms of the individual symmetry operations, g (Equation **??**), or in terms of the classes of symmetry operation, C (Equation 6.3.7). In practice, we will always use the latter.

$$n(i) = \frac{1}{h}\sum_{g} \chi_i(g)\chi_r(g) = \frac{1}{h}\sum_{C} n_C \chi_i(C)\chi_r(C) \tag{7.1.1}$$

where:

$n(i)$ = Number of times that the i^{th} reducible representation
occurs in the representation χ_r that we are aiming to reduce.

h = Order of the group *i.e.* the number of operations in the group (this is not necessarily equal to the number of classes of operation)

$\sum\limits_{g}$ = A summation over all the operations g in the group.

If there is more than one operation in a given class we must remember to
include each operation in the summation.

$\chi_r(g)$ = Character of the reducible representation r under the symmetry operation g.

$\chi_i(g)$ = Character of the irreducible representation i under the symmetry operation g.

$\chi_r(C)$ = Character of the reducible representation r under the class of symmetry operation C.

n_C = Number of operations in a given class.

7.2 Use of projection operators to deduce the form of SALCS

It is not always possible to deduce the form of a SALC by “matching” to a central atom orbital of appropriate symmetry. There exists however a handle turning group theoretical procedure to deduce the form of the SALCS. This uses so-called projection operators.

$$\Psi_i^{SALC} = P_i\phi_a = \sum_g \chi_i(g)(g\phi_a)$$

where:

Ψ_i^{SALC} = The wavefunction for the SALC belonging to the irreducible representation.

P_i = the projection operator for the i^{th} irreducible representation

ϕ_a = one of the basis functions.

$\sum_g$ = A summation over all the operations g in the group.

$g\phi_a$ = The basis function generated by applying the operation g to basis function ϕ_a.

$\chi_i(g)$ = Character of the irreducible representation i under the symmetry operation g.

We saw (relatively) simple examples of how to use both of these in the context of NH_3 in sections 6.3 and 6.4: here we explore some more advanced applications.

7.3 Example 1: the π-type MOs of C_6H_6

The point group of C_6H_6 is D_{6h}, and the character table below looks very daunting, with 24 operations. However, the specific problem that we are dealing with suggests a simplification. We are interested here only in the linear combinations of p_z orbitals that form the π system of benzene, and all of these p orbitals (and therefore all linear combinations of them) are antisymmetric with respect to reflection in the plane of the molecule (σ_h). From the character table, we can see that only half of the irreps, B_{1g}, B_{2g}, E_{1g}, A_{1u}, A_{2u} and E_{2u} have negative characters for this operation, so we can focus our attention on these.

We also know that the number of irreps is equal to the number of classes of operation, so if we have halved the number of irreps, we might reasonably look for a simpler point group that has half the number of classes. This brings us to the concept of *Direct Product Groups.*

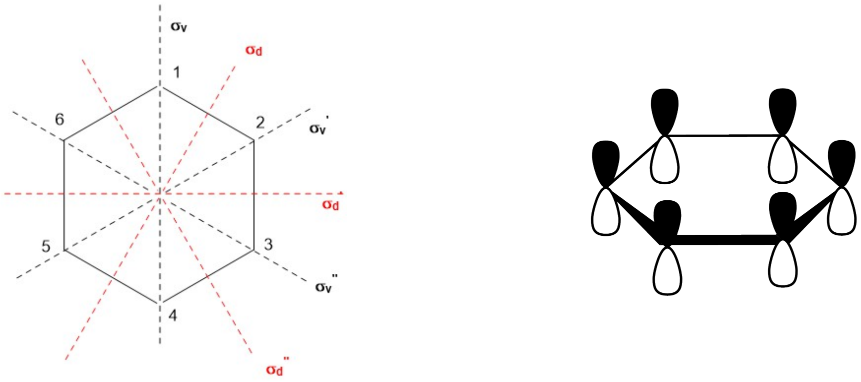


Figure 4: Symmetry elements for D_{6h} and the $p(\pi)$ basis for benzene

Table 7.7: Character Table for D_{6h}

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	–1	–1	1	1	1	1	–1	–1
B_{1g}	1	–1	1	–1	1	–1	1	–1	1	–1	1	–1
B_{2g}	1	–1	1	–1	–1	1	1	–1	1	–1	–1	1
E_{1g}	2	1	–1	–2	0	0	2	1	–1	–2	0	0
E_{2g}	2	–1	–1	2	0	0	2	–1	–1	2	0	0
A_{1u}	1	1	1	1	1	1	–1	–1	–1	–1	–1	–1
A_{2u}	1	1	1	1	–1	–1	–1	–1	–1	–1	1	1
B_{1u}	1	–1	1	–1	1	–1	–1	1	–1	1	–1	1
B_{2u}	1	–1	1	–1	–1	1	–1	1	–1	1	1	–1
E_{1u}	2	1	–1	–2	0	0	–2	–1	1	2	0	0
E_{2u}	2	–1	–1	2	0	0	–2	1	1	–2	0	0

7.3.1 Direct Product Groups

If we have two groups, G and $G^{'}$ which have only the identity operation in common, and the elements of G commute with those of $G^{'}$, we can construct a larger group, $G^{''}$, based on the consecutive application of an operation from one group and one from the other. To illustrate this, take the direct product group of C_{3v} (3 classes, E, C_3 and σ_v) and C_s (2 classes, E and σ_h), which is D_{3h}, which has 6 classes (3×2). The S_3 operation of D_{3h} is, by definition, a combination of the C_3 rotation of C_{3v} and the σ_h of C_s. Likewise, the C_2 operation of D_{3h} is a combination of σ_v of C_{3v} and σ_h of C_s. We can get the characters in the D_{3h} character table by multiplying the characters in the corresponding positions in the two sub-groups.

Table 7.8: Character Tables for C_{3v} and C_s

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	
A_2	1	1	–1	
E	2	–1	0	

C_s	E	σ_h	$h = 2$
$A^{'}$	1	1	
$A^{''}$	1	–1	

Table 7.9: Character Table for D_{3h}, constructed as the direct product of the C_{3v} and C_s groups.

D_{3h}	$E(=EE)$	$2C_3=(C_3E)$	$3\sigma_v(=\sigma_vE)$	$\sigma_h(=E\sigma_h)$	$2S_3=(C_3\sigma_h)$	$3C_2(=\sigma_v\sigma_h)$
$A_1^{'}=A_1A^{'}$	1	1	1	1	1	1
$A_2^{'}=A_2A^{'}$	1	1	-1	1	1	-1
$E^{'}=EA^{'}$	2	-1	0	2	-1	0
$A_1^{''}=A_2A^{''}$	1	1	-1	-1	-1	1
$A_2^{''}=A_1A^{''}$	1	1	1	-1	-1	-1
$E^{''}=EA^{''}$	2	-1	0	-2	1	0

With somewhat more effort, we could build the character table of D_{6h} from the direct product of C_{6v} and C_s. We can use this process in reverse: if we can identify a sub-group of the full point group that contains all the information that is relevant to the problem in hand, we can save time by using the sub-group. In the present case, the symmetry element in the C_s sub-group, σ_h, is not relevant to the problem because we know from the outset that all the p orbitals must be antisymmetric with respect to it.

The character table for C_{6v} is shown below, and the bottom row shows the reducible representation generated by the basis of six p_z orbitals on the six carbons (using the shortcut defined in section 5.7 or, if you wish(!), by generating the full matrix representation and taking the traces).

Table 7.10: Character Table for C_{6v}

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_d$	$3\sigma_v$	$h=12$
A_1	1	1	1	1	1	1	z,z^2,x^2+y^2
A_2	1	1	1	1	–1	–1	
B_1	1	–1	1	–1	1	–1	
B_2	1	–1	1	–1	–1	1	
E_1	2	1	–1	–2	0	0	(x,y),(xz,yz)
E_2	2	–1	–1	2	0	0	(xy,x^2-y^2)
$\Gamma(\pi)$	6	0	0	0	0	2	

7.3.2 Applying the reduction formula

- In evaluating the summation given in Equation 7.1.1 we deal with each class of symmetry operation in turn. We multiply the character for $\Gamma(\pi)$ by the character for the relevant irreducible representation and then multiply by the number of operations in a given class. Thus each term is a product of three numbers, and will be zero if any of the three is zero. In this case we only need to worry about the E and σ_v operations because the other characters in $\Gamma(\pi)=0$:

- We can check that we have obtained the correct answer by verifying that the characters for the irreducible representations we have derived add up to the set of characters for the representation we are trying to reduce.
- The $n(i)$ must always be zero or integral. If they are not something has gone wrong somewhere!

$$
\begin{aligned}
n(A_1) &= \frac{1}{12}[(6 \times 1 \times 1) + (2 \times 1 \times 3)] = 1 \\
n(A_2) &= \frac{1}{12}[(6 \times 1 \times 1) + (2 \times (-1) \times 3)] = 0 \\
n(B_1) &= \frac{1}{12}[(6 \times 1 \times 1) + (2 \times -1 \times 3)] = 0 \\
n(B_2) &= \frac{1}{12}[(6 \times 1 \times 1) + (2 \times (1) \times 3)] = 1 \\
n(E_1) &= \frac{1}{12}[(6 \times 2 \times 1) + (2 \times 0 \times 3)] = 1 \\
n(E_2) &= \frac{1}{12}[(6 \times 2 \times 1) + (2 \times 0 \times 3)] = 1
\end{aligned}
$$

Thus in C_{6v} symmetry, the $p(\pi)$ SALCS for C_6H_6 transform as $A_1 + B_2 + E_1 + E_2$. Note that this analysis tells us nothing at this stage about the form of the SALCs or about their relative energy ordering. For that, we need to apply the projection operator.

7.3.3 Using the projection operator

Following the recipe set out in Section 6.4,

1. Make a table with rows labelled by the basis functions and columns labelled by the symmetry operations of the molecular point group. In the rows, show the effect of the symmetry operations on the basis functions (again, C_{6v} is used for simplicity - the results are identical to D_{6h}). We could do this for all six basis functions, but in this case we only need to do three.

Table 7.11: Results of different symmetry operations, gf_i, on the (p_1, p_2, p_3) basis of benzene

f_i	Ef_i	$C_6^+ f_i$	$C_6^- f_i$	$C_3^+ f_i$	$C_3^- f_i$	$C_2 f_i$	$\sigma_d f_i$	$\sigma_d' f_i$	$\sigma_d'' f_i$	$\sigma_v f_i$	$\sigma_v' f_i$	$\sigma_v'' f_i$
p_1	p_1	p_6	p_2	p_5	p_3	p_4	p_2	p_4	p_6	p_1	p_3	p_5
p_2	p_2	p_1	p_3	p_6	p_4	p_5	p_1	p_3	p_5	p_6	p_2	p_4
p_3	p_3	p_2	p_4	p_1	p_5	p_6	p_6	p_2	p_4	p_5	p_1	p_3

2. For each irrep in turn, multiply each member of a row by the character of the corresponding symmetry operation to generate $\chi_k(g)(gf_i)$ for each operation and sum them.

   Using the values of gf_i generated by p_1 (*i.e.* the first row of the table) and the characters of the A_1 representation, which are all +1 (see section 5.6).

$$\begin{aligned}\Phi(A_1) &= p_1 + p_6 + p_2 + p_5 + p_3 + p_5 + p_2 + p_4 + p_6 + p_4 + p_1 + p_3 \\ &= 2(p_1 + p_2 + p_3 + p_4 + p_5 + p_6)\end{aligned}$$

Following the same process for the B_2 representation, we have $\chi(E) = 1, \chi(C_6) = -1, \chi(C_3) = 1, \chi(C_2) = -1, \chi(\sigma_d) = -1, \chi(\sigma_v) = 1)$.

$$\begin{aligned}\Phi(B_2) &= p_1 - p_6 - p_2 + p_5 + p_3 - p_4 - p_2 - p_4 - p_6 + p_1 + p_3 + p_5 \\ &= 2(p_1 - p_2 + p_3 - p_4 + p_5 - p_6)\end{aligned}$$

Following the same process for the E_1 representation ($\chi(E) = 2, \chi(C_6) = 1, \chi(C_3) = -1, \chi(C_2) = -2, \chi(\sigma_d) = 0, \chi(\sigma_v) = 0$), we will need to find two orthogonal linear combinations. Taking the first row (p_1) first:

$$\begin{aligned}\Phi(E_1a) &= 2p_1 + p_6 + p_2 - p_5 - p_3 - 2p_4 \\ &= (2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6)\end{aligned}$$

the orthogonal combination then comes from summing the results using the second and third rows (Schmidt orthogonalisation):

$$\Phi(E_1b) = (3p_2 + 3p_3 - 3p_5 - 3p_6)$$

and for E_2 ($\chi(E) = 2, \chi(C_6) = -1, \chi(C_3) = -1, \chi(C_2) = 2, \chi(\sigma_d) = 0, \chi(\sigma_v) = 0$), the first row gives:

$$\begin{aligned}\Phi(E_2a) &= 2p_1 - p_6 - p_2 - p_5 - p_3 + 2p_4 \\ &= (2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6)\end{aligned}$$

and the orthogonal combination (in this case from the difference of the second and third rows):

$$\Phi(E_2b) = (3p_2 - 3p_3 + 3p_5 - 3p_6)$$

3. Finally, normalise the SALCs.

$$
\begin{aligned}
\Phi(A_1) &= \frac{1}{\sqrt{6}}(p_1 + p_2 + p_3 + p_4 + p_5 + p_6) \\
\Phi(B_2) &= \frac{1}{\sqrt{6}}(p_1 - p_2 + p_3 - p_4 + p_5 - p_6) \\
\Phi(E_1 a) &= \frac{1}{2\sqrt{3}}(2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6) \\
\Phi(E_1 b) &= \frac{1}{2}(p_2 + p_3 - p_5 - p_6) \\
\Phi(E_2 a) &= \frac{1}{2\sqrt{3}}(2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6) \\
\Phi(E_2 b) &= \frac{1}{2}(p_2 - p_3 + p_5 - p_6)
\end{aligned}
$$

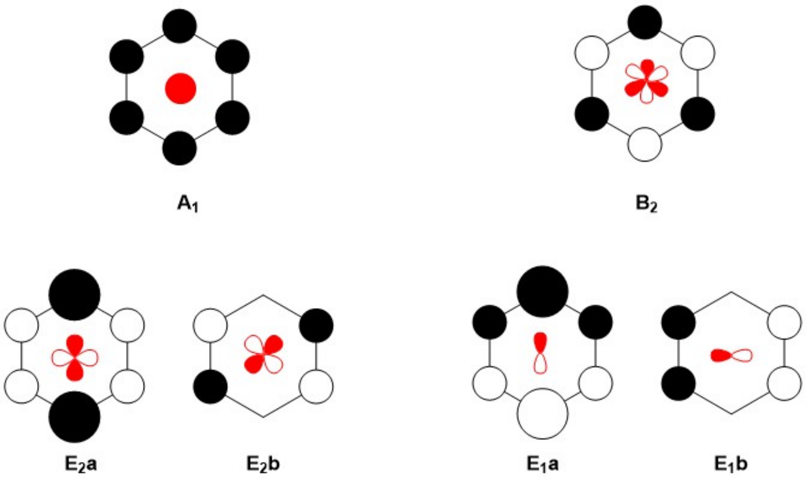


Figure 5: SALCs for the π orbitals of benzene, with the orbital of the same symmetry at an invariant point shown in red. Note that the p orbitals are viewed from above, so only the upper lobe is visible. A black circle therefore indicates a p orbital with the lobe with positive phase above the molecular plane, a white circle a p orbital with positive phase below the molecular plane.

Even after we have identified that we can save time by using the simpler C_{6v} character table, the application of the projection operator is still somewhat laborious. Fortunately, there is a shortcut that works (most of the time!). If we look at the right-hand column of the character table, we are given the symmetry properties of a set of orbitals *on an invariant point*: in C_{6v}, any point along the principal axis is invariant because it unchanged by any of the symmetry operations. So we can immediately identify the fact that the A_1 linear combination must 'match' the symmetry properties of an s orbital placed anywhere on the principal axis (an s orbital on an invariant point is always totally symmetric). Likewise, the two components of the E_1 linear combination 'match' the p_x and p_y orbitals, and the two components of E_2 'match' d_{xy} and $d_{x^2-y^2}$.

The atomic orbitals at the invariant point are shown in red in Figure 5. With this knowledge,

	p_1	p_2	p_3	p_4	p_5	p_6
θ	0	$\pi/3$	$2\pi/3$	π	$4\pi/3$	$5\pi/3$
$\cos\theta$	1	$\frac{1}{2}$	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	$\frac{1}{2}$
$\sin\theta$	0	$-\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$
$\cos 2\theta$	1	$-\frac{1}{2}$	$-\frac{1}{2}$	1	$-\frac{1}{2}$	$-\frac{1}{2}$
$\sin 2\theta$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$

we can predict the phases of the atomic components on the carbon atoms by matching the positive (black) phases on the carbon atoms with the red phases of the orbital on the invariant point. For E_1a, for example, the phases in the upper half are positive while the phases on the lower half are negative.

We can push this technique even further, and predict the relative size of the coefficients. Note that in E_1a, the coefficient of p_1 (the top-most atom) is twice as large as those on the neighbouring atoms (p_2 and p_6). Qualitatively, this maps on to the observation that the red p orbital on the invariant point in E_1a points directly at p_1, but less directly at p_2 and p_6. We can quantify this by noting that the p orbital on the invariant point (in red) varies as $cos\theta$, and evaluating this function at the angular coordinates of p_1 to p_6 (taking the former as 0°) delivers the (un-normalised) coefficients in E_1a. Likewise, the d orbital at the invariant point in E_2a varies as $\cos 2\theta$, and evaluating this function at the positions of the atoms delivers the required coefficients.

The limitations of this approach become apparent when we consider the final orbital, B_2, for which there is nothing in the right-hand column of the character table. In fact, this orbital matches the $f_{x(x^2-3y^2)}$ orbital, but f orbitals are not always included in character tables (and even if they were, few people remember what the $f_{x(x^2-3y^2)}$ orbital looks like!). So it is good to have the projection operator as a back-up for tricky cases.

Finally, we need to convert these C_{6v} irreducible representations back to those of the full D_{6h} character table. The missing information is simply whether we add a g or u to the labels of the irreps. The relevant information is captured in the descent in symmetry table, Table 7.12.

Table 7.12: Descent in symmetry from D_{6h} to C_{6v}.

D_{6h}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}
C_{6v}	A_1	A_2	B_1	B_2	E_1	E_2	A_2	A_1	B_2	B_1	E_1	E_2

We see that A_1 in C_{6v} correlates with A_{1g} and A_{2u} in D_{6h}. However, the A_1 SALC, like all the others from the $p(\pi)$ basis) is antisymmetric with respect to reflection in σ_h ($\chi(\sigma_u) = -1$ (Table 7.7), confirming that it is A_{2u} and not A_{1g}. Likewise, B_2 correlates with B_{2g} and B_{1u}, but the antisymmetry under σ_h identifies it as the former. Similar logic dictates that E_1 and E_2 correlate with E_{1g} and E_{2u}, respectively, and not E_{1u} and E_{2g}.

We could have reached the same conclusion by noting, as we did at the beginning, that all the orbitals must be antisymmetric with respect to reflection in σ_h, which restricts us to B_{1g}, B_{2g}, E_{1g},

A_{1u}, A_{2u} and E_{2u} This type of information is usually collected in the *descent in symmetry* table, Table 7.12, that is available in many books.

This is as far as we can go using symmetry alone. We can anticipate based on the number of nodes in the SALCs that the energetic order will be $A_{2u} < E_{1g} < E_{2u} < B_{2g}$ (0, 1, 2 and 3 nodes perpendicular to the σ_h plane, respectively), but if we want to evaluate the energies of the orbitals we need to resort to quantum mechanics in some form (Hückel theory, for example), and this a topic for other courses (*Bonding in Molecules*, *Valence*, *Quantum supp*)

7.4 Example 2: the molecular orbitals of CH$_4$

Consider next the problem of finding the irreducible representations spanned by the set of 4 H 1s basis functions in the methane molecule. Each operation is represented by a (4×4) matrix, but we are only interested in the diagonal sum of the transformation matrix, the character.

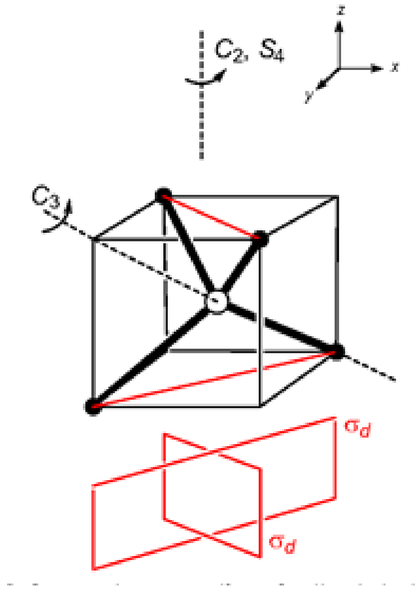


Figure 6: Symmetry elements for a tetrahedron

Remembering that it is only when an atom is unshifted that it can contribute to this sum, the characters $\chi_r(R)$ are given simply by the number of H atoms that are unshifted under each class of symmetry operation. It is always the case that the character is the same for each symmetry operation of a given class so we need inspect the effects of only one operation within each class. The basis of the four $1s$ orbitals on the hydrogen atoms generates $\Gamma(H_{1s})$.

7.4.1 Applying the reduction formula

Applying the formula (Equation 7.1.1) in the standard way, we get the following values of n_m:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	–1	–1		
E	2	–1	2	0	0		$(2z^2x^2y^2,\ x^2y^2)$
T_1	3	0	–1	1	–1	(R_x, R_y, R_z)	
T_2	3	0	–1	–1	1	(x, y, z)	$(xy,\ xz,\ yz)$
$\Gamma(H_{1s})$	4	1	0	0	2		

$$
\begin{aligned}
n(A_1) &= \frac{1}{24}[(4\times 1\times 1)+(1\times 1\times 8)+(0\times 1\times 3)+(0\times 1\times 6)+(2\times 1\times 6)] &&=1\\
n(A_2) &= \frac{1}{24}[(4\times 1\times 1)+(1\times 1\times 8)+(0\times 1\times 3)+(0\times(-1)\times 6)+(2\times(-1)\times 6)] &&=0\\
n(E) &= \frac{1}{24}[(4\times 2\times 1)+(1\times(-1)\times 8)+(0\times 2\times 3)+(0\times 0\times 6)+(2\times 0\times 6)] &&=0\\
n(T_1) &= \frac{1}{24}[(4\times 3\times 1)+(1\times 0\times 8)+(0\times(1)\times 3)+(0\times 1\times 6)+(2\times(-1)\times 6)] &&=0\\
n(T_2) &= \frac{1}{24}[(4\times 3\times 1)+(1\times 0\times 8)+(0\times(-1)\times 3)+(0\times(-1)\times 6)+(2\times 1\times 6)] &&=1
\end{aligned}
$$

$$\Gamma(H_{1s}) = A_1 + T_2$$

7.4.2 The form of the SALCS for a tetrahedral system and the MO diagram for CH_4

The projection operator technique is tedious to apply because the summation extends over each operation and it is necessary to inspect the effects of each operation in turn. Thus for the T_d point group we would have to inspect the effects of all 24 operations in turn! We can again use the idea of matching to orbitals on an invariant point to make life easier.

Inspection of the character table for the T_d point group reveals that the p orbitals on the central atom of a molecule such as CH_4 (an invariant point) transform like T_2. As always, an s orbital on the invariant point transforms as A_1. It is therefore possible to deduce the form of the T_2 SALCS simply by matching the phases of the H 1s orbitals to the phases (signs) of the three orthogonal p orbitals. Likewise it is trivially obvious that the A_1 SALC must be simply a completely in-phase combination of H 1s orbitals.

In constructing the MO diagram for CH_4 we then allow the C 2s orbital to interact with the A_1 H 1s SALC and each C 2p orbital to interact with its matching T_2 SALC. We have used group theory to establish which linear combinations do not interact with each other: the overlap between the A_1 SALC on the H atoms and the T_2 orbitals on C do not overlap, and so do not interact. What group theory can not tell us is the extent of overlap between the a_1 SALC on H_4 and the T_1 orbital

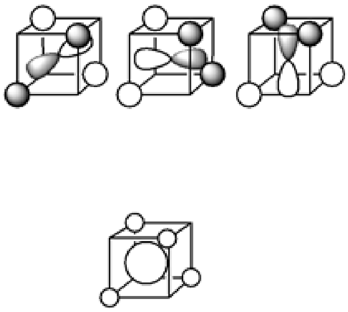


Figure 7: SALCs of CH_4

on C (2*s*) (beyond the fact that it is not necessarily zero). To get this information we need to go a step further and use quantum mechanics (again, see *Bonding in Molecules*, *Valence*, *Quantum supp*). However, using the simple concept that when two orbitals interact we get a bonding and an antibonding combination, we can generate the qualitative MO diagram in Figure 8. There are two occupied MOs of different energy, a picture that is confirmed by the observation of two bands in the photo-electron spectrum.

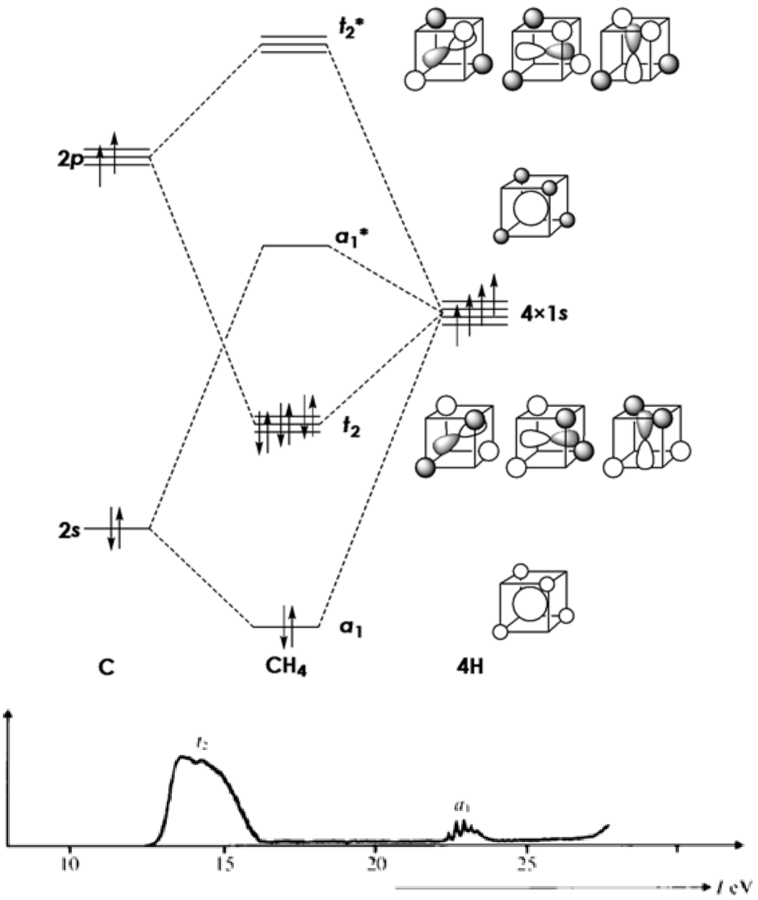


Figure 8: Molecular orbital diagram and photo-electron spectrum of CH_4

8 Degeneracy and descent in symmetry.

Degeneracy, where two or more orbitals/states/vibrations have the same energy, is intimately connected with symmetry: specifically, degeneracy occurs when a rotation axis of order 3 or more (C_3, C_4 *etc.*) is present. The connection between symmetry and degeneracy can be understood with the following qualitative argument: a symmetry operation, by definition, leaves all observable properties of the molecule, including its energy, unchanged. Therefore, if a symmetry operation converts one orbital into another, either fully or partially, then the implication is that the two orbitals involved necessarily have the same energy.

We have already seen this in action when we looked at the transformation properties of the three p orbitals, p_x, p_y and p_z in C_{3v} symmetry in Section 5.2. There, the C_3^+ operation converts p_x into $-\frac{1}{2}p_x + \frac{\sqrt{3}}{2}p_y$, and so p_x and p_y must be degenerate. Indeed, we find that they form a basis for the E representation of the group.

A logical place to start the discussion of degeneracy is therefore with the most symmetric of all groups, the full rotation group, given the symbol R_3. This is the point group for spherical objects, including atoms, and so is useful for discussing atomic orbitals. The dimension of R_3 is infinite: it includes all possible rotations about the origin.

8.1 The full rotation group, R_3, and atomic orbital wavefunctions

The wavefunction for any atomic orbital may be written in terms of polar co-ordinates r, θ, ϕ, and is then separable into radial (R) and angular (Y) parts: the latter are known as the spherical harmonics:

$$\psi(r,\theta,\phi) = R(r)Y_l^{m_l}(\theta,\phi)$$

The spherical harmonics have the general form:

$$Y_l^{m_l}(\theta,\phi) = P_{lm_l}(\theta)e^{im_l\phi}$$

All rotations belong to the same class, and therefore have the same characters - we can therefore select the most convenient rotation axis (z) to explore the effects of rotations. Consider the effect of rotating a set of degenerate atomic orbitals with $m_l = l, (l-1)\cdots-(l-1), -l$ by an angle α about the z axis: the function described by $P_{lm_l}(\theta)e^{im_l\phi}$ will rotate into another described by $P_{lm_l}(\theta)e^{im_l(\phi-\alpha)} = P_{lm_l}(\theta)e^{im_l\phi}e^{-im_l\alpha}$. We can describe this by the transformation matrix:

$$\begin{pmatrix} Y_l^l & Y_l^{l-1} & \dots & \dots & Y_l^{-l} \end{pmatrix} \begin{pmatrix} e^{-il\alpha} & 0 & 0 & \dots & 0 \\ 0 & e^{-i(l-1)\alpha} & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & \dots & e^{il\alpha} \end{pmatrix}$$

The character under the rotation, the trace of the matrix, is given by:

$$\chi(\alpha) = e^{-il\alpha} + e^{-i(l-1)\alpha} + \cdots + e^{il\alpha}$$

This is a finite geometric series,[**] the sum of which is given by:

$$\chi(\alpha) = \sum_{m_l=-l}^{l} e^{-im\alpha} = \frac{e^{-il\alpha}\left(e^{i(2l+1)\alpha} - 1\right)}{e^{i\alpha} - 1} = \frac{e^{i(l+1)\alpha} - e^{-il\alpha}}{e^{i\alpha} - 1} = \frac{e^{i(l+\frac{1}{2})\alpha} - e^{-i(l+\frac{1}{2})\alpha}}{e^{\frac{i\alpha}{2}} - e^{-\frac{i\alpha}{2}}} = \frac{sin(l+\frac{1}{2})\alpha}{sin(\frac{\alpha}{2})}$$

Alternatively, we can formulate the trace as:

$$\chi(\alpha) = e^0 + \left(e^{-i\alpha} + e^{i\alpha}\right) + \cdots + \left(e^{-il\alpha} + e^{+il\alpha}\right) = 1 + 2cos\alpha + \cdots + 2cos(l\alpha)$$

This second expression proves useful for C_5 rotations, where characters are non-integer for odd l.

Either of these expressions can be used to find the characters of p, d and f orbitals under E ($\alpha = 0$) and the C_2, C_3, C_4, C_5, C_5^2 and C_6 rotations.

e.g. for a basis of f orbitals ($l = 3$) under a C_3 rotation ($\alpha = \frac{2\pi}{3}$):

$$\chi(\frac{2\pi}{3}) = \frac{sin((3+\frac{1}{2}) \times \frac{2\pi}{3})}{sin(\frac{2\pi}{2\times 3})} = \frac{sin(\frac{7}{2} \times \frac{2\pi}{3})}{sin(\frac{\pi}{3})} = \frac{sin(\frac{7}{3}\pi)}{sin(\frac{\pi}{3})} = +1$$

Table 8.13: Characters, $\chi(\alpha)$, for rotations of the p, d and f orbitals

		$p \quad (l = 1)$	$d \quad (l = 2)$	$f \quad (l = 3)$
E	$\alpha = 0$	3	5	7
C_2	$\alpha = \pi$	–1	1	–1
C_3	$\alpha = \frac{2\pi}{3}$	0	–1	1
C_4	$\alpha = \frac{\pi}{2}$	1	–1	–1
C_5	$\alpha = \frac{2\pi}{5}$	$1 + 2cos(\frac{2\pi}{5})$	0	$1 + 2cos(\frac{2\pi}{5}) + 4cos(\frac{4\pi}{5})$[††]
C_5^2	$\alpha = \frac{4\pi}{5}$	$1 + 2cos(\frac{4\pi}{5})$	0	$1 + 2cos(\frac{4\pi}{5}) + 4cos(\frac{8\pi}{5})$
C_6	$\alpha = \frac{\pi}{3}$	0	-1	–1

[**] A geometric series takes the form ar^n. In the present case, $a = e^{-il\alpha}$, $r = e^{i\alpha}$ and $n = 0, 1, \ldots, 2l$. The sum of the first $2l + 1$ terms is $S_{2l+1} = \frac{a\left(r^{(2l+1)}-1\right)}{r-1}$

[††] $cos(n\pi + a) = cos(n\pi - a)$

Let us now consider the representations of these atomic orbitals in a finite point group, O (note the O point group contains only C_4, C_3 and C_2 rotations - it is a sub-group of the more familiar O_h):

O	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
A_1	1	1	1	1	1
A_2	1	1	1	–1	–1
E	2	–1	2	0	0
T_1	3	0	–1	1	–1
T_2	3	0	–1	–1	1
p	3	0	–1	1	–1
d	5	–1	1	–1	1
f	7	1	–1	–1	–1

Applying the reduction formula to a set of d orbitals, for example:

$$n(E) = \frac{1}{24}\left[1 \times 5 \times 2 + 8 \times (-1) \times (-1) + 3 \times 2 \times 1\right] = 1$$

$$n(T_2) = \frac{1}{24}\left[1 \times 5 \times 3 + 3 \times (-1) \times 1 + 6 \times (-1) \times (-1) + 6 \times 1 \times 1\right] = 1$$

So we see that the d orbitals split into a two-fold (E) and a three-fold (T_2) set in O symmetry. The same process for p and f orbitals generates the following *descent in symmetry* table.

$$p \rightarrow T_1$$
$$d \rightarrow E + T_2$$
$$f \rightarrow A_2 + T_1 + T_2$$

In full octahedral symmetry we simply need to add u subscripts for p and f orbitals and a g subscript for d orbitals.

8.2 *d* orbital splitting in axial fields - sandwich complexes and related species

Sandwich complexes such as ferrocene, $Fe(C_5H_5)_2$ and *bis*-benzene chromium, $Cr(C_6H_6)_2$ have played an important part in the development of inorganic chemistry (both earned Nobel Prizes!).

You will encounter them in the *Organometallics* course in TT. These have high symmetry: D_{5h} and D_{6h}, respectively, in their eclipsed conformers, D_{5d} and D_{6d} if they are staggered. It is useful, therefore, to consider the properties of the d orbitals from a group-theoretical perspective. As was the case for the octahedron, it is easiest to work with D_5 and D_6, which are sub-groups of both D_{nh} and D_{nd} that contain only the rotations.

For D_5, we have the following character table:

D_5	E	$2C_5$	$2C_5^2$	$5C_2$
A_1	1	1	1	1
A_2	1	1	1	–1
E_1	2	$2cos(\frac{2\pi}{5})$	$2cos(\frac{4\pi}{5})$	0
E_2	2	$2cos(\frac{4\pi}{5})$	$2cos(\frac{2\pi}{5})$	0
$\Gamma(p)$	3	$1+2cos(\frac{2\pi}{5})$	$1+2cos(\frac{4\pi}{5})$	-1
$\Gamma(d)$	5	0	0	1

and, through the reduction formula or by inspection, we have $\Gamma(d) = A_1{+}E_1{+}E_2$ and $\Gamma(p) = A_2{+}E_1$.

For D_6, we have the following character table:

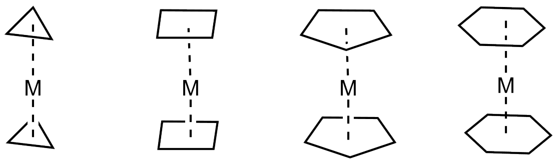
D_6	E	$2C_6$	$2C_3$	C_2	$3C_2^{'}$	$3C_2^{''}$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0
$\Gamma(p)$	3	0	0	-1	-1	-1
$\Gamma(d)$	5	-1	-1	1	1	1

and, through the reduction formula or by inspection, we again have $\Gamma(d) = A_1 + E_1 + E_2$ and $\Gamma(p) = A_2 + E_1$.

Repeat the same procedure with D_3 and D_4 for practice.

The splitting of the d orbitals in various axial symmetries is collected in Table 8.14. An important qualitative result is that in, D_5 and D_6, there is a 2:2:1 splitting pattern. d_{z^2} is unique but (d_{xz}, d_{yz}) and (d_{xy}, $d_{x^2-y^2}$) convert into linear combinations of each other under rotational operations and therefore form two degenerate pairs. D_4 is an exception to this pattern: (d_{xz}, d_{yz}) inter-convert under the C_4 operation, but d_{xy}, $d_{x^2-y^2}$ simply convert into minus themselves under the C_4 operation. They are therefore no longer degenerate and we find a 2:1:1:1 splitting pattern that is unique

Table 8.14: d-orbital splittings in axial groups, D_n, $n = 3 - 6$



	D_3	D_4	D_5	D_6
d_{z^2}	A_1	A_1	A_1	A_1
d_{yz} d_{xz}	E	E	E_1	E_1
d_{xy} $d_{x^2-y^2}$	E	B_2 B_1	E_2	E_2

to the D_4 point group.

To avoid having to go through the same process every time, the essential information is usually summarised in ”descent in symmetry tables” such as Table 8.15 which can be found online and in your tables of group theory.

Table 8.15: Descent in symmetry table from R_3 to O, D_6, D_5, D_4 and D_3

R_3	O	D_6	D_5	D_4	D_3
S	A_1	A_1	A_1	A_1	A_1
P	T_1	$A_2 + E_1$	$A_2 + E_1$	A_2+E	$A_2 + E$
D	$E + T_2$	$A_1 + E_1 + E_2$	$A_1 + E_1 + E_2$	$A_1 + B_1 + B_2 + E$	$A_1 + 2E$

8.3 Jahn-Teller Theorem

The Jahn-Teller theorem states the following: ***A non-linear molecule in an orbitally degenerate state will distort to relieve the degeneracy***.

Note that the Jahn-Teller theorem is unambiguous: the molecule will distort. What the theorem does not tell us is what the nature of the distortion is (which bonds or angles will change), or how much it will distort (the distortion may be large but equally it may be so small that it lies within the error limits of any technique we might use to measure it).

8.3.1 A brief note on states

The state of an atom or molecule is a collective property of all the electrons present, and its symmetry therefore reflects all of the electrons. We will see in Section 9 how to deal with systems with more than one unpaired electron, but for now we will deal only with the rather simpler case where only one unpaired electron is present. The symmetry of the state is then determined by the symmetry of the orbital in which the unpaired electron is located. So, for example, if the unpaired electron is in an orbital of a_1 symmetry, the resulting state will have $^2A_1$ symmetry. If the unpaired electron is in an e_g orbital, we will have a ^2E_g state and so on. For the one-electron case, an 'orbitally-degenerate' state is therefore associated with the presence of an unpaired electron in a degenerate orbital. Note that we use lower case letters to describe the orbitals, upper case letters to describe the state. The ”^{2}” is read as 'doublet', and is equal to the multiplicity, $2S+1$.

Tables of descent in symmetry are useful in deciding which sort of distortion will lift the symmetry as required by this theorem. Consider for example an octahedral system. Compression or elongation along one of the C_4 axes takes us into the D_{4h} point group. Compression or elongation along one of the C_3 axes takes us into the D_{3d} point group. If we have a d^1 configuration with one electron in a t_{2g} orbital we have a T_{2g} state. The degeneracy of such a state is lifted by either distortion. By contrast in a d^9 state with a ${t_{2g}}^6{e_g}^3$ configuration and an E_g ground state only the distortion to D_{4h} will lift the degeneracy.

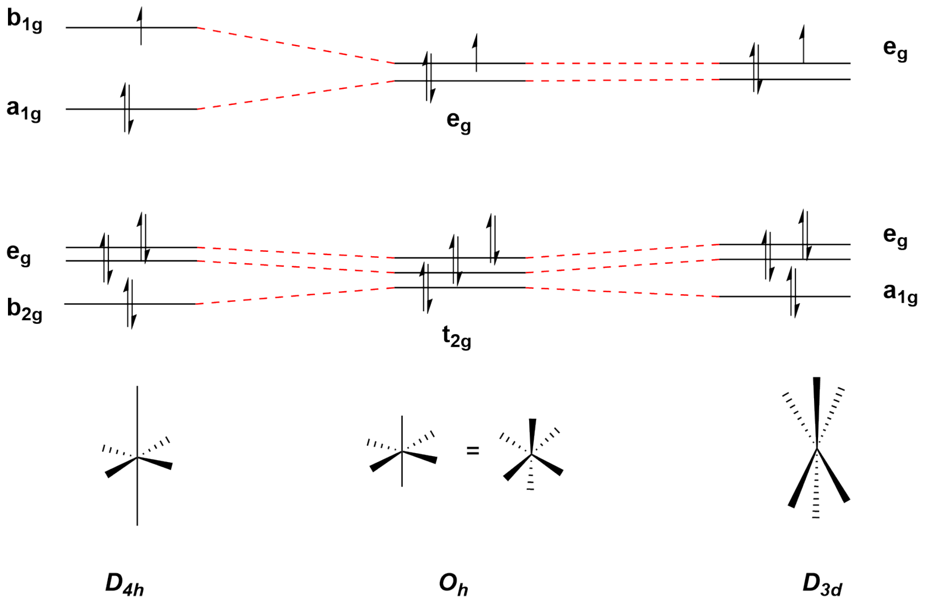


Figure 9: Jahn-Teller splittings for a d^9 configuration in D_{4h} and D_{3d} (Cu^{2+}, for example)

O_h	D_{4h}	D_{3d}
A_{1g}	A_{1g}	A_{1g}
A_{2g}	B_{1g}	A_{2g}
E_g	$A_{1g} + B_{1g}$	E_g
T_{1g}	$A_{2g} + E_g$	$A_{2g} + E_g$
T_{2g}	$B_{2g} + E_g$	$A_{1g} + E_g$
A_{1u}	A_{1u}	A_{1u}
A_{2u}	B_{1u}	B_{1u}
E_u	$A_{1u} + B_{1u}$	E_u
T_{1u}	$A_{2u} + E_u$	$A_{2u} + E_u$
T_{2u}	$B_{2u} + E_u$	$A_{1u} + E_u$

8.4 "2nd order" Jahn Teller effects

The starting point for the Jahn-Teller theorem discussed in section 8.3 is that the orbitals that are unequally occupied are strictly degenerate: if this is the case then a distortion will occur. The "2nd order" Jahn Teller effect occurs when the orbitals in question are nearly, but not quite, degenerate. These orbitals typically transform as different irreps in some high-symmetry point group, but as the same irrep in some sub-group. The distortion from high to low symmetry will then allow the two orbitals to interact, stabilising the lower (filled) one. The example of SF_4 serves to illustrate the principle.

Let us first consider the problem from the classic VSEPR perspective: what is the most stable geometry of SF_4? We would not anticipate a T_d geometry because we have 5 pairs of valence electrons, 1 more than in CF_4. VSEPR then predicts a structure based on a trigonal bipyramid, with a single vertex occupied by the lone pair. This gives us two possibilities, one with the lone pair axial (C_{3v}), the other with the lone pair equatorial (C_{2v}). The greater lone-pair-bond-pair repulsion if the lone pair is in the axial positions (3× repulsion at 90 °) then leads us to predict that the C_{2v} structure is the most stable, and this is indeed the case.

Now let us consider the same problem from a symmetry perspective. If we consider a hypothetical tetrahedral geometry, the MO diagram in Figure 10 is much like that for CH_4 (Figure 6) except that the antibonding a_1 level is occupied by the two additional electrons. The higher-lying t_2 antibonding level remains empty, but the energetic separation between a_1 and t_2 is now relatively small - they are 'nearly' degenerate. If we can find a distortion to a lower-symmetry structure that allows the filled a_1 to have the same symmetry with one of the components of the empty t_2, this will stabilise the former, and therefore stabilise the molecule.

We can imagine three possible distortions:

1. A flattening of the tetrahedron, giving D_{2d}
2. A motion of three of the F atoms to give C_{3v}

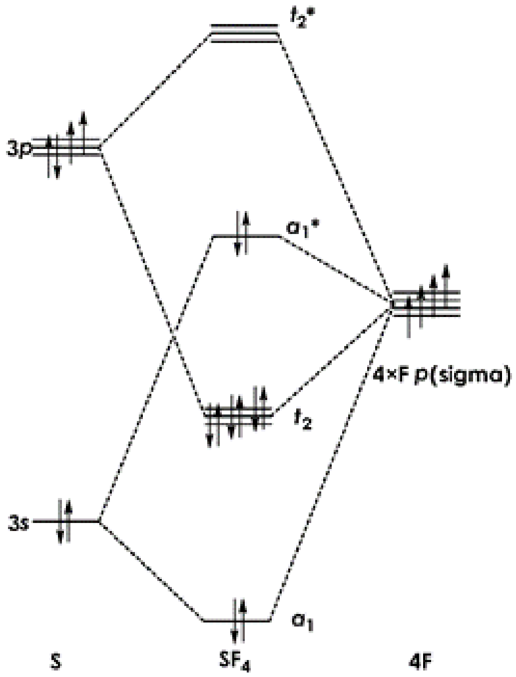


Figure 10: Molecular orbital diagram for (hypothetical) tetrahedral SF_4

3. A motion of two of the F atoms to give C_{2v}

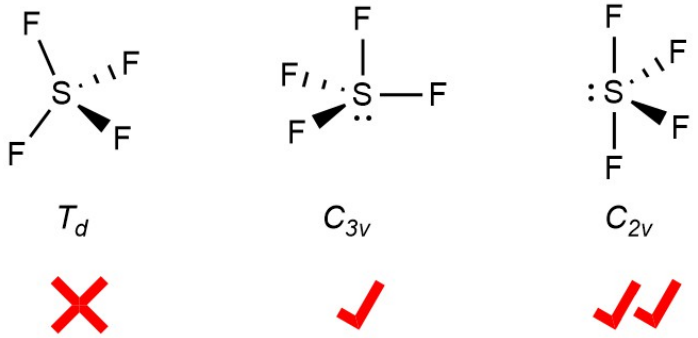


Figure 11: VSEPR predictions for the structure of SF_4

Which of these would achieve the desired stabilisation of the a_1 orbital? Descent in symmetry tables (Table 8.16) tell us that the a_1 orbital will remain totally symmetric, whichever distortion we choose. The threefold degeneracy of the t_2 level will also be lifted and, if one of its component also becomes totally symmetric, the occupied orbital will be stabilised. On this basis distortions to C_{2v} or C_{3v} symmetry *would* lower the electronic energy, but distortion to D_{2d} would not. The former two structures are exactly those introduced in simple VSEPR arguments.

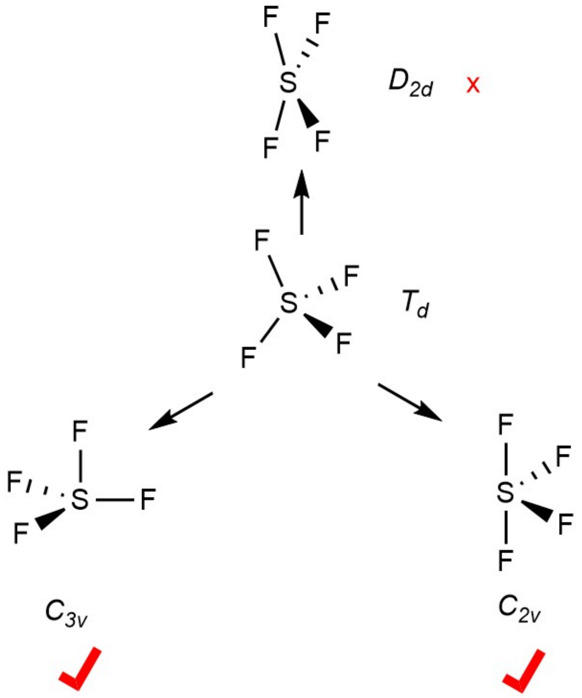


Figure 12: Possible distortions of SF_4

Table 8.16: Descent in symmetry from T_d to D_{2d}, C_{3v} and C_{2v}

T_d	D_{2d}	C_{3v}	C_{2v}
A_1	A_1	A_1	A_1
A_2	B_1	A_2	A_2
E	$A_1 + B_1$	E	$A_1 + A_2$
T_1	$A_2 + E$	$A_2 + E$	$A_2 + B_1 + B_2$
T_2	$B_2 + E$	$A_1 + E$	$A_1 + B_1 + B_2$

9 Direct products and selection rules

9.1 Direct products and many electron states

In the section on matrix algebra (Section 4.3) we met the concept of a 'direct product', often denoted $\otimes$. These prove to be very useful when we are dealing with the symmetry properties of collections of two or more objects rather than a single one. The most obvious chemical application comes in determining the symmetry of many electron states which arise from configurations where we know the symmetry of the occupied orbitals, but also in formulating spectroscopic selection rules between orbitals or electronic states of known symmetry or between vibrational states.

We introduced states briefly in the discussion of the Jahn-Teller theorem. To reiterate, by convention small letters such as a_1, t_2 *etc.* are used to specify configurations *e.g.* ${a_1}^2$, ${t_2}^4$, e^3; and upper case letters are used to label the many electron states *e.g.* ${}^3A_2$, ${}^2T_1$ *etc.* The notation for the many electron states also introduces the multiplicity $(2S + 1)$ as a superscript. These conventions are reminiscent of those used in atomic theory and indeed the derivation of Russell-Saunders term symbols for a specified configuration can be considered as a group theoretical problem analogous to that being treated here.

9.2 Non-degenerate representations

Suppose we take the direct product of a function belonging to the irreducible representation Γ_1 by another function belonging to Γ_2. The characters of the product function, Γ_{12}, is given by: $\chi_{12}(R) = \chi_1(R)\chi_2(R)$ (check this with matrices A and B in Section 4.3). We can therefore assign the product function to one of the irreducible representations of the relevant point group by simply multiplying out the characters and inspecting the character table.

Consider for example the point group C_{2v}.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(xz)$		
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_z	yz

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(xz)$	
$A_1 \otimes B_1$	1	-1	1	-1	$= B_1$
$A_2 \otimes A_2$	1	1	1	1	$= A_1$
$A_2 \otimes B_1$	1	–1	–1	1	$= B_2$
$A_2 \otimes B_2$	1	–1	1	–1	$= B_1$
$B_1 \otimes B_2$	1	1	–1	–1	$= A_2$

Trivially, multiplying a function of any symmetry by a totally symmetric function (A_1) does not alter the symmetry of the original function: for example $A_1 \otimes B_1 = B_1$. In addition, if we multiply together any two functions of the same symmetry we produce a function of A_1 symmetry: $A_2 \otimes A_2 = A_1$.

Following this process, we can set up a complete table of direct products. Note that the matrix is diagonal, and the elements below the diagonal are usually not listed.

Table 9.17: Direct product table for the C_{2v} point group

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

One simple use of this table is to demonstrate that closed shell configurations such as ${a_1}^2$, ${a_2}^2$, ${b_1}^2$ *etc.* must give rise to a totally symmetric A_1 state.

9.3 Degenerate representations

Consider the point group C_{3v}. The same ideas as developed for the point group C_{2v} apply to the non-degenerate A_1 and A_2 irreducible representations. In addition $A_1 \otimes E$ or $A_2 \otimes E$ is simply E. The interesting case is $E \otimes E$, which gives a set of characters that do not correspond to one of the irreducible representations of the group. However, inspection (or application of the reduction formula) allows us to deduce that this representation is reducible to $A_1 + A_2 + E$.

C_{3v}	E	$2C_3$	$3\sigma_v$				
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)
$E \otimes E$	4	1	0				

Thus the direct product table has the form shown below.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			$A_1 + [A_2] + E$

But what does the square bracket around A_2 mean? We can distinguish two possible situations where the $e \otimes e$ direct product occurs: (a) where the two electrons are in different orbitals of e symmetry (e^1e^1) and (b) where they are both in the same (degenerate) orbital of e symmetry. In the former case, there is no restriction on the spins of the two electrons, and we get both singlet and triplet versions of all spatial symmetries:

$$e^1e^1 \rightarrow\ ^3A_1 +^1 A_1 +^3 A_2 +^1 A_2 +^3 E +^1 E$$

If, however, the two electrons are in the same orbital (case (b)), the Pauli principle restricts the number of possible micro-states: we cannot have both electrons in the same orbital with the same spin. There are only six ways of arranging two electrons in a pair of degenerate orbitals so as not to violate the Pauli exclusion principle:

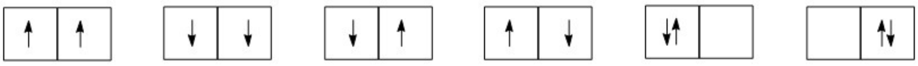


Figure 13: Microstates for a e^2 configuration

The only way we can arrive at a total of six from a combination of singlets and triplets, and singly and doubly-degenerate spatial components, is either $^3A_1 +^1 A_2 +^1 E$ or $^1A_1 +^3 A_2 +^1 E$.

The Pauli principle demands that the total wavefunction must be antisymmetric with respect to interchange of any two electrons. The wavefunction itself is the product of a spin part and a spatial part: if the product of the two is antisymmetric with respect to exchange, then one of the two components (spin and space) must be symmetric, the other antisymmetric.

If we look at the spin components, singlet and triplet, it is clear that the triplets are symmetric (they don't change if we swap the labels 1 and 2) but the singlet is antisymmetric. The triplet must therefore be associated with the antisymmetric spatial wavefunction, while the singlets are associated with symmetric spatial wavefunctions.

- **Singlet spin wavefunction**
- $\alpha(1)\beta(2) - \alpha(2)\beta(1)$
- **Triplet spin wavefunctions**
- $\alpha(1)\alpha(2)$
- $\beta(1)\beta(2)$
- $\alpha(1)\beta(2) + \alpha(2)\beta(1)$

Finally, the square bracket in the direct product tables identifies the spatial wavefunction that is antisymmetric, which we know must be combined with the symmetric (triplet) spin function. So the square bracket around $[A_2]$ in the table tells us that we have a $^3A_2$ state, and therefore also $^1A_1$ and ^1E.

We can use descent in symmetry to prove this point. The descent in symmetry table from C_{3v} to C_s (a sub-group of C_{3v}) shows that the two components of the e orbital transform differently, as $a' + a''$. The triplet state arising from the e^2 configuration therefore correlates with $a'^1 a''^1$ (we know that one electron must be in each orbital for a triplet), and so it must be $^3A''$ ($a' \otimes a'' = a''$). Correlating back to C_{3v}, the triplet must therefore be $^3A_2$ and not $^3A_1$.[‡‡]

[‡‡] Note here that the ground state ($^3A_2$) is not orbitally degenerate, despite the fact that we have unpaired electrons in degenerate orbitals (e^2). A degenerate state arises when we have an arbitrary choice of where to put an unpaired electron - for the $e_g{}^3$ configuration, we can put the 3rd electron in either of the two components of the e_g orbital without changing the energy. For the e^2 configuration we are dealing with here, the triplet multiplicity leaves us with no option other than to put one electron in each of the two components of e. We have no choice, so there is no degeneracy.

C_s	E	σ		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	–1	z, R_x, R_y	yz, xz

C_{3v}	C_s
A_1	A'
A_2	A''
E	$A' + A''$

Let us now extend these ideas to see which states arise in an tetrahedal transition metal complex with two *d* electrons. Hund's rule tells us that the triplet states will be most stable, so we will concern ourselves only with these.

For the ground state configuration, e^2, the direct product table, Table 9.18, tells us that $E \otimes E = A_1 + [A_2] + E$, so the triplet ground state is ${}^3A_2$.

For the first excited configuration, $e^1t_2^1$, the direct product table tells us that $E \otimes T_2 = T_1 + T_2$. In this case, the singly occupied orbitals must be different (one is e, the other t_2), so the Pauli principle is not relevant, there are no square brackets, and we get triplets (and singlets) for both T_1 and T_2.

For the second excited configuration, t_2^2, the direct product table tells us that $T_2 \otimes T_2 = A_1 + E + [T_1] + T_2$. So the only triplet state is ${}^3T_1$.

Table 9.18: Direct products for the T_d and O_h point groups.

	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2		A_1	E	T_2	T_1
E			$A_1 + [A_2] + E$	$T_1 + T_2$	$T_1 + T_2$
T_1				$A_1 + E + [T_1] + T_2$	$A_2 + E + T_1 + T_2$
T_2					$A_1 + E + [T_1] + T_2$

So we have a triplet ground state, ${}^3A_2$ and three triplet excited states, $2 \times {}^3T_1$ and ${}^3T_2$, arising from the distribution of two electrons over the five d orbitals in a tetrahedron. So we would predict a maximum of three transitions in the UV/vis spectrum, from the ground state to each of the three excited states (see *Spectroscopy and Magnetism*, year 3).

9.4 General features of tables of direct products

Tables of direct products are supplied in finals. They do not deal explicitly with all groups and the basic tables need to be supplemented with the additional rules:

$$\begin{array}{ll} g \times g = g & '\times' =' \\ u \times u = g & ''\times'' =' \\ g \times u = u & '\times'' ='' \end{array}$$

A general feature of all of the tables (illustrated by the specific examples above) is that the totally symmetrical irreducible representation only occurs on the diagonal in the tables, where we are multiplying together two functions belonging to the same irreducible representation.

9.5 Spectroscopic selection rules

In spectroscopy we are concerned with transitions between two states, each characterised by a wavefunction. Let ground and excited state wavefunctions be Ψ_1 and Ψ_2. In general a transition is mediated by an operator $\hat{O}$ and the intensity of the transition is such that:

$$I \propto |\int \Psi_1 \hat{O} \Psi_2 d\tau|^2$$

Hence for non-zero intensity the direct product $\Gamma(\Psi_1) \otimes \Gamma(\hat{O}) \otimes \Gamma(\Psi_2)$ must contain the totally symmetric irreducible representation. For both infrared and visible/UV spectroscopy the operator responsible for transitions driven by the oscillating electric fields associated with the incident electromagnetic radiation is the electric dipole moment operator, μ. This is a vector and has components which transform like the translations x, y and z. The irreducible representations corresponding to the three vectors always appear in character tables. Much weaker magnetic dipole transitions are mediated by oscillating magnetic fields. Here the operator transforms like the rotations R_x, R_y and R_z.

9.5.1 Transitions for d^2 in a tetrahedral environment

In the previous section we saw that the e^2 ground configuration gives a $^3A_2$ ground state, whilst the first excited configuration $e^1{t_2}^1$ gives triplet terms $^3T_1$ and $^3T_2$ and the second excited configuration, ${t_2}^2$ gives $^3T_1$. Are transitions from the ground state to all three excited states allowed?

The electric-dipole moment operator transforms as (x, y, z), which has T_2 symmetry in the T_d point group.

Is the $^3A_2 \rightarrow^3 T_1$ transition electric-dipole allowed?

$A_2 \otimes T_2 \otimes T_1 = (A_2 \otimes T_2) \otimes T_1 = T_1 \otimes T_1 = A_1 + E + T_1 + T_2$

This triple direct product contains A_1 and so the transition ${}^3A_2 \rightarrow {}^3T_1$ is electric-dipole allowed.

Is the ${}^3A_2 \rightarrow {}^3T_2$ transition electric-dipole allowed?

$A_2 \otimes T_2 \otimes T_2 = (A_2 \otimes T_2) \otimes T_2 = T_1 \otimes T_2 = A_2 + E + T_1 + T_2$

This triple product does <u>not</u> contain A_1 and so the transition ${}^3A_2 \rightarrow {}^3T_2$ is <u>not</u> electric-dipole allowed.

Is the ${}^3A_2 \rightarrow {}^3T_2$ transition magnetic-dipole allowed?

The magnetic-dipole moment operator transforms as (R_x, R_y, R_z), which has T_1 symmetry in the T_d point group.

$A_2 \otimes T_1 \otimes T_2 = A_1 + E + T_1 + T_2$

so the transition ${}^3A_2 \rightarrow {}^3T_2$ <u>is</u> magnetic-dipole allowed, but magnetic dipole transitions are typically several orders of magnitude weaker than electric-dipole transitions.

9.5.2 $d \rightarrow d$ Transitions in octahedral (O_h) complexes

All d-electron configurations necessarily give rise to gerade (g) terms because the d orbitals are g. The dipole moment operator is T_{1u}. Any direct product of the sort $g \otimes u \otimes g = u$ and so <u>cannot</u> contain A_{1g}. Hence $d \rightarrow d$ transitions are dipole forbidden in octahedral symmetry.

10 Molecular vibrations

10.1 Introduction

In general the vibration of a polyatomic molecule does not involve deformation of an individual bond or bond angle. Instead, molecular vibrations involve excitation of *normal modes.* A normal mode of vibration involves a synchronous deformation of the molecule in which the displacement vectors describing the motion of individual atoms combine so as to belong to one of the irreducible representations of the molecule. The atoms all undergo their displacements at the same frequency and all pass through the equilibrium configuration at the same time.

10.2 Types of vibrational spectroscopy

10.2.1 Infra-red spectroscopy

This is the most common form of vibrational spectroscopy, where the transition is induced by the electric-dipole moment of the electromagnetic field. Typically, transitions occur in the infra-red region of the spectrum (hence the name!), in contrast to the $d - d$ transitions discussed previously, which tend to fall at higher frequencies, in the visible or UV regions.

The principle behind determining whether a transition is allowed or not is exactly the same as we discussed for $d - d$ transitions: we require that the transition dipole moment integral:

$$\int \Psi_1 \hat{\mu} \Psi_2 d\tau$$

is non-zero, which in turn requires that the direct product $\Gamma(\Psi_1) \otimes \Gamma(x, y, z) \otimes \Gamma(\Psi_2)$ must contain the totally symmetric irreducible representation. $\Gamma(\Psi_1)$ and $\Gamma(\Psi_2)$ are the symmetries of the ground and excited state vibrational wavefunctions, respectively.

When dealing with closed shell molecules in their ground vibrational state (as we usually are), the ground state vibrational wavefunction is totally symmetric and does not therefore affect the direct product:

$$\Gamma(\Psi_1) \otimes \Gamma(x, y, z) \otimes \Gamma(\Psi_2) = \Gamma(x, y, z) \otimes \Gamma(\Psi_2)$$

It therefore follows that the only transitions that can be observed in IR involve vibrations of the same symmetry as the dipole moment operator (because only on the diagonal of the direct product table do we find totally symmetric irreducible representations), and we can deduce IR activity by simple inspection of the character table and matching symmetries to those of x, y and z.

10.2.2 Raman spectroscopy

In Raman spectroscopy, the incident electric field produces an oscillating polarisation of the molecule, which then emits radiation at the incident frequency minus a vibrational frequency (Stokes scattering). Raman activity is governed by the polarisability tensor, α, which relates the dipole induced in

x, y and z directions to electric fields E_x, E_y and E_z.

$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

The components of the polarisability tensor transform like x^2, y^2, xy, xz *etc.* or linear combinations of them. Since xy and yx, xz and zx and yz and zy have the same transformation properties, there are 6 components of the polarisability tensor to worry about. One component is always totally symmetrical, whilst the other 5 components behave like the d orbitals. Again for closed shell molecules one can deduce the pattern of Raman activity by comparing the symmetries of the vibrational modes to the components of the tensor in the character table.

10.3 Basis sets for molecular vibrations

For either infra-red or Raman spectroscopy, the critical piece of information that we require is the symmetry of the vibrations. We have two common choices of basis, depending on what level of information we wish to get from the calculation.

- If we want to know about all $3N-6$ vibrations of a molecule (stretches, bends, torsions), we choose a set of $3N$ displacement vectors, with 3 vectors attached to each of the N atoms in a polyatomic molecule. This will form the basis for construction of $3N$ symmetry adapted functions. However, 3 of these must correspond to translation of the molecule as whole in three orthogonal directions. In non-linear molecules a further 3 correspond to molecular rotation about three mutually perpendicular axes. For linear molecules there are only 2 rotational degrees of freedom. Thus we find $3N-6$ modes of normal modes of vibration for non-linear molecules and $3N-5$ for linear molecules. In high symmetry molecules some of these modes may be grouped together in degenerate sets.

- In many situations (especially on General Papers!) we may need to know only about the stretching vibrations. These typically dominate the spectrum at high frequencies: bends and torsions come lower down. A common example is where we want to know about stretching vibrations in AB_n polyatomics or about carbonyl stretches or cyanide stretches in $M(CO)_n$ or $M(CN)_n$ complexes. In these cases we can use a much simpler basis set which consists simply of a set of n vectors along the bond directions. This basis set will generate the n stretching vibrations, but will not give any information on bends or torsions.

10.4 Using bond stretching basis sets

Here, we place a vector along each bond. In principle we need to write down the transformation matrices which describe the effects of each symmetry operation on the chosen basis set and take their trace. However, we can use the same shortcut we adopted for atomic orbitals: vectors on a given bond only contribute to the diagonal sum if the bond is unshifted by the symmetry operation.

When we are dealing with the set of n bond stretching vectors in an AB_n molecule this gives us the simple rule: the character under operation R, $\chi(R)$ = the number of bonds (or, equivalently, the number of B atoms) that are unshifted under the operation.

We can now apply these ideas to deduce the irreducible representations spanned by bond stretching vectors in SF_4, CF_4 and XeF_4.

10.4.1 Stretching vibrations of SF_4: point group C_{2v}

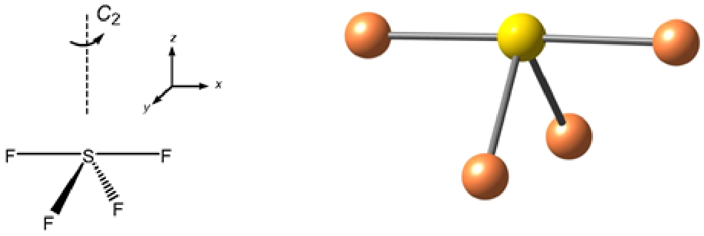


Figure 14: Axis definitions for SF_4

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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	$y,\ R_z$	yz
$\Gamma_{stretch}$	4	0	2	2		

Applying the reduction formula:

$$\begin{aligned}
n(A_1) &= \frac{1}{4}[4+0+2+2] = 2 \\
n(A_2) &= \frac{1}{4}[4+0-2-2] = 0 \\
n(B_1) &= \frac{1}{4}[4+0+2-2] = 1 \\
n(B_2) &= \frac{1}{4}[4+0-2+2] = 1
\end{aligned}$$

$$\Gamma_{stretch} = 2A_1 + B_1 + B_2$$

Comparing the symmetries to the character table, we see that all 4 modes are both IR and Raman active (there is at least one of (x, y, z) and one of $(x^2, y^2, z^2, xz, yz, xy)$ in the right-hand columns for each of A_1, B_1 and B_2). Note that a vibration of A_2 symmetry would be allowed in the Raman (xy) but not in the infra-red. However, there are no modes of A_2 symmetry in this case, so the point is moot.

We could derive the same result slightly more easily by recognising that there are two different sorts of F atom, equatorial and axial, and no symmetry element inter-converts them. This means that we can derive the symmetries of their stretches separately. For each pair an in phase combination of stretches gives an A_1 mode, whilst the out of phase combinations generate the B_1 and B_2 modes. This simple consideration allows us to sketch out the displacement vectors in the stretching modes.

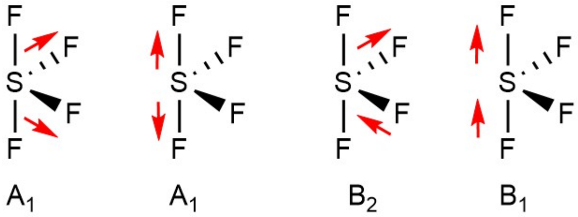


Figure 15: S-F stretching modes for SF_4

10.4.2 Stretching vibrations of CF_4: point group T_d

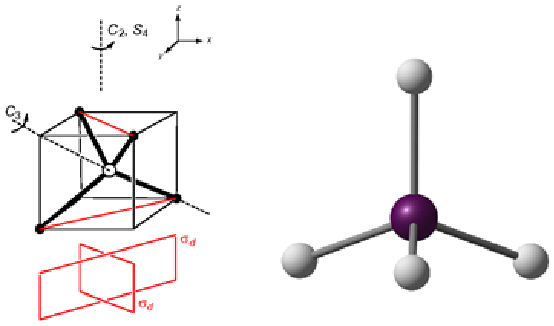


Figure 16: Axis definitions for CF_4

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	–1	–1		
E	2	–1	2	0	0		$(2z^2-x^2-y^2,\ x^2-y^2)$
T_1	3	0	–1	1	–1	(R_x, R_y, R_z)	
T_2	3	0	–1	–1	1	(x, y, z)	$(xy,\ xz,\ yz)$
$\Gamma_{stretch}$	4	1	0	0	2		

Applying the reduction formula:

$$
\begin{aligned}
n(A_1) &= \frac{1}{24}[(4 \times 1 \times 1) + (1 \times 1 \times 8) + 0 + 0 + (2 \times 1 \times 6)] = 1 \\
n(A_2) &= \frac{1}{24}[(4 \times 1 \times 1) + (1 \times 1 \times 8) + 0 + 0(2 \times 1 \times 6)] = 0 \\
n(E) &= \frac{1}{24}[(4 \times 2 \times 1) - (1 \times 1 \times 8) + 0 + 0 + 0] = 0 \\
n(T_1) &= \frac{1}{24}[(4 \times 3 \times 1) + 0 + 0 + 0(2 \times 1 \times 6)] = 0 \\
n(T_2) &= \frac{1}{24}[(4 \times 3 \times 1) + 0 + 0 + 0 + (2 \times 1 \times 6)] = 1
\end{aligned}
$$

$\Gamma_{stretch} = A_1 + T_2$

A_1 is only Raman active; T_2 is both IR and Raman active. The form of the A_1 mode is trivially obvious. We could work out the directions of the vectors in the T_2 modes using the projection operator, but this would entail a lot of work. A simpler way is to use the trick of 'matching' to the phases of an orbital of the same symmetry on an invariant point. In this case, the orbitals would be the three p orbitals on the central C atom, which also trasform as T_2. We use the convention that the displacement vector points towards the positive lobe of the orbital and away from the negative lobe.

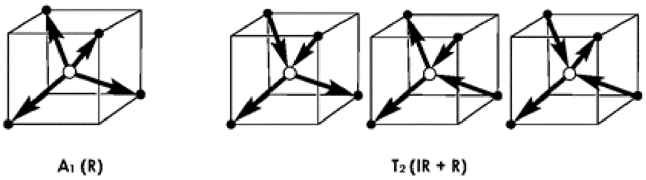


Figure 17: Vibrational modes of CF_4

10.4.3 Stretching vibrations of XeF_4: point group D_{4h}

Application of the reduction formula is somewhat tedious in this case but we arrive at:

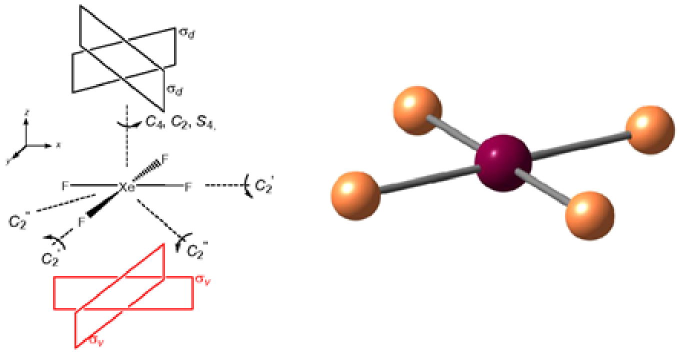


Figure 18: Axis definitions for XeF$_4$

Table 10.19: D_{4h} Character table

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	R_z	
B_{1g}	1	–1	1	1	–1	1	–1	1	1	–1		x^2y^2
B_{2g}	1	–1	1	–1	1	1	–1	1	–1	1	xy	
E_g	2	0	–2	0	0	2	0	–2	0	0	(R_x, R_y)	
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	z	
B_{1u}	1	–1	1	1	–1	–1	1	–1	–1	1		
B_{2u}	1	–1	1	–1	1	–1	1	–1	1	–1		
E_u	2	0	–2	0	0	–2	0	2	0	0	(x, y)	
$\Gamma_{stretch}$	4	0	0	2	0	0	0	4	2	0		

$$n(A_{1g}) = \frac{1}{16}[(4\times1\times1)+0+0+(2\times1\times2)+0+0+0+(4\times1\times1)+(2\times1\times2)+0] = 1$$

$$n(A_{2g}) = \frac{1}{16}[(4\times1\times1)+0+0(2\times1\times2)+0+0+0+(4\times1\times1)(2\times1\times2)+0)] = 0$$

$$n(B_{1g}) = \frac{1}{16}[(4\times1\times1)+0+0+(2\times1\times2)+0+0+0+(4\times1\times1)+(2\times1\times2)+0] = 1$$

$$n(B_{2g}) = \frac{1}{16}[(4\times1\times1)+0+0(2\times1\times2)+0+0+0+(4\times1\times1)(2\times1\times2)+0] = 0$$

$$n(E_u) = \frac{1}{16}[(4\times2\times1)+0+0+0+0+0+0+(4\times2\times1)+0+0] = 1$$

$\Gamma_{stretch} = A_{1g} + B_{1g} + E_u$

Of these modes A_{1g} and B_{1g} are Raman active and E_u is IR active. The mutual exclusion rule applies, as in all centrosymmetric systems. Because the dipole moment operator is u and the components of the polarisability tensor are g, no mode can be both Raman and IR active in a molecule with a centre of symmetry.

We have completed the job for XeF_4, but large character tables like D_{4h} are tedious and it is easy to make a mistake. We could have made our life easier by using the same trick we applied in dealing with the π orbitals of benzene. There, we used our knowledge of the basis functions involved (the $p\pi$ set) to reject all irreps that were symmetric under σ_h. That allowed us to work with the smaller C_{6v} sub-group. We apply the same thought process here - the basis functions, the vectors along the bonds, lie in the molecular plane, so any linear combination of them cannot possibly be antisymmetric under σ_h. Hence we can use the rather simpler character table of the C_{4v} sub-group, where the irrelevant information about σ_h has been taken out.

Table 10.20: Character Table for C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	z^2,x^2+y^2
A_2	1	1	1	-1	–1		
B_1	1	–1	1	1	-1		x^2-y^2
B_2	1	–1	1	–1	1		xy
E	2	0	–2	0	0	(x, y)	(xz, yz)
$\Gamma_{stretch}$	4	0	0	2	0		

Applying the reduction formula is now much easier: we get $A_1 + B_1 + E$.

All that is left to do is to restore the missing g and u labels. To do so, we need to look for the $A_{1g/u}$, $B_{1g/u}$ and $E_{g/u}$ irreps of D_{4h} in Table 10.19 that are symmetric with respect to σ_h: these are A_{1g}, B_{1g} and E_u, as we proved before.

Exercise: Sketch out the form of the modes.

10.5 All the vibrations of NH_3: stretches and bends

Thus far, we have used the bond vectors as a basis to explore the **stretching** modes of the molecules. This is typically the level required in general papers, but in more advanced applications (typically in the *Inorganic Spectroscopy* option paper) we might wish to know the symmetries of all $3N-6$ vibrations, including bends and torsions as well as stretches. If we want to separate the stretches from the bends, we can get the former from an analysis using the bond vectors (as we have just done for SF_4, CF_4 and XeF_4), and subtract them from the total to leave the bends.

We can tackle the problem of deriving the symmetry of its normal modes of vibration using a "complete" basis set with 3 vectors on each of the atoms: this captures all possible movements of atoms relative to each other. We take NH_3 as a simple example (point group C_{3v}).

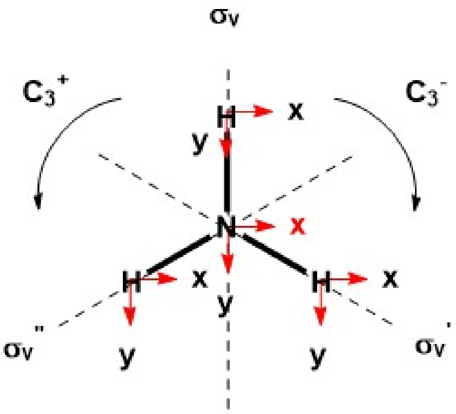


Figure 19: Plan view of the NH_3 molecule with a complete basis set of 3 displacement vectors. A "z" vector points upward from each atomic centre

C_{3v}	E	$2C_3$	$3\sigma_v$		
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 first need to work out the transformation properties of a set of (x,y,z) vectors on the central N atom. For the C_3 rotations, we could use the formula established in section 8, with $l=1$:

$$\chi(\alpha) = \frac{sin(l+\frac{1}{2})\alpha}{sin(\frac{\alpha}{2})}$$

$$\chi(\frac{2\pi}{3}) = 0$$

and for the reflections: σ_1, for example, converts $x \rightarrow -x$, $y \rightarrow y$ and $z \rightarrow z$, giving $\chi(\sigma_v) = 1$

$$\Gamma(N_{x,y,z}) = 3 \quad 0 \quad 1 \quad = \quad A_1 + E$$

Alternatively, we could just look to the right of the character table and note that an (x,y,z) basis on an invariant point (*i.e.* the N atom) gives $A_1 + E$!

The characters for the 9 remaining basis vectors on the hydrogens are somewhat easier to work out because if the atoms move, so too do the basis functions, and the contribution to χ will be zero. All three H atoms move under C_3, so $\chi(C_3) = 0$. For σ_v, only h_1 is unmoved (we choose σ_1, noting that the character is the same for all members of the σ class), and $x \rightarrow -x$, $y \rightarrow y$ and $z \rightarrow z$ on this atom, giving a total $\chi(\sigma_v) = 1$. The total representation is then:

$$\Gamma(x,y,z) = \; 3+9 \quad 0 \quad 1+1 \quad = \quad 12 \quad 0 \quad 2$$

C_{3v}	E	$2C_3$	$3\sigma_v$		
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)
Γ(atoms)	4	1	2		
$\Gamma(3N)$	12	0	2		

Application of the reduction formula gives:

$$\begin{aligned}
n(A_1) &= \frac{1}{6}[(12 \times 1 \times 1) + 0 + (2 \times 1 \times 3)] = 3 \\
n(A_2) &= \frac{1}{6}[(12 \times 1 \times 1) + 0 + (2 \times 1 \times 3)] = 1 \\
n(E) &= \frac{1}{6}[(12 \times 2 \times 1) + 0 + 0] = 4
\end{aligned}$$

$$\Gamma(3N) = 3A_1 + A_2 + 4E$$

We then need to subtract off the three translations (which transform as x, y, z) and the three rotations, which transform as (R_x, R_y, R_z), leaving the $3N - 6 = 6$ vibrational modes.

$$\begin{aligned}
\Gamma(trans) &= A_1 + E \\
\Gamma(rot) &= A_2 + E
\end{aligned}$$

$$\Gamma(vib) = \Gamma(stretch) + \Gamma(bend) = \Gamma(3N) - \Gamma(trans) - \Gamma(rot) = 2A_1 + 2E$$

Using a set of 3 stretching vectors it can be quickly shown that $\Gamma_{stretch} = A_1 + E$ and therefore the remainder is $\Gamma_{bend} = A_1 + E$. Where stretching and bending modes are of the same symmetry, mixing between them is allowed, so each A_1 mode will be a mixture of bending and stretching.

All of the above is rather cumbersome, and it is more difficult again when 3-fold rotation axes run through atoms other than the central one (as would have been the case in tetrahedral CH_4, for example). Identifying the characters for the $3N-3$ basis vectors on the outer atoms is then very time-consuming. Fortunately, there is a shortcut!

In the NH_3 example:

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma(atoms)$	4	1	2
$\Gamma(x,y,z)$	3	0	1
$\Gamma(atoms)\otimes\Gamma(x,y,z)$	12	0	2
$\Gamma(3N)$	12	0	2

$$\Gamma(3N)=\Gamma(atoms)\otimes\Gamma(x,y,z)$$

We can generate the representations spanned by the $3N$ basis vectors by taking the representation generated by the atoms and multiplying it by the representations spanned by (x,y,z), both of which are much easier to work out.

We can do this even more simply using the labels of the irreducible representations rather than representations themselves:

$$\Gamma(atoms)=2A_1+E$$

$$\Gamma(x,y,z)=A_1+E$$

$$\Gamma(atoms)\otimes(\Gamma(x,y,z))$$

$$=(2A_1+E)\otimes(A_1+E)=2A_1+E+2E+A_1+A_2+E=3A_1+A_2+4E=\Gamma(3N)$$

10.6 The vibrations of C_{60}

C_{60} is a remarkable molecule built up from 20 hexagonal rings and 12 pentagonal rings. Group theory played an important part in the discovery C_{60} by making the simple prediction that the molecule should have only 4 infrared active vibrations, a prediction which subsequently proved to be true.

C_{60} is a very rare example of a molecule belonging to the icosahedral point group I_h. The $3N$ - 6 rule tells us that there are no less than 174 modes of vibration and on the face of it the problem of deriving the symmetry of these modes is formidable. The character table (see appendix) looks particularly unfriendly and contains characters such as $\frac{1}{2}(1 \pm \sqrt{5})$. The group order is 120 and there are 10 irreducible representation including 4-fold degenerate G representations and five-fold degenerate H representations. These degeneracies are not encountered in other molecular point groups.

Nevertheless it turns out to be very easy to derive the normal modes of vibration. The simplicity arises because none of the rotational axes passes through any of the atoms, so we can immediately set the character of the basis set of 180 displacement vectors under all rotational operations to zero.

The character under inversion i is also zero.

The 15 mirror planes each contain 4 atoms so that the character under σ is $(4 \times 2 - 4 \times 1) = 4$. Two of the basis vectors on each atom will remain unchanged, one will change sign).

The only other operation where a non-zero character appears is under the identity operation, where $\chi(E) = 180$.

Note that we could also have generate $\Gamma(3N)$ by taking $\Gamma(atoms)$ and multiplying by $\Gamma(x, y, z)$ - in this case T_{1u}.

The large number of zeros in $\Gamma(3N)$ makes application of the reduction formula relatively straightforward: there are only 4 infrared active T_{1u} modes and 8 Raman active H_g modes.

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^2$	$20S_6$	15σ
Γ(at)	60	0	0	0	0	0	0	0	0	4
$\Gamma(3N)$	180	0	0	0	0	0	0	0	0	4

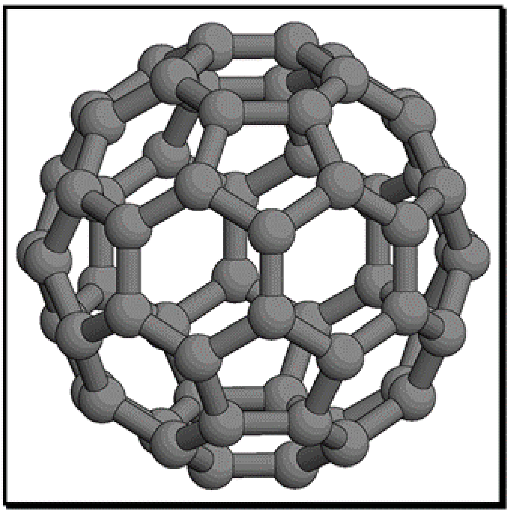


Figure 20: The C_{60} cluster, buckminsterfullerene

$$n(A_g) = \frac{1}{120}[(1 \times 180) + (4 \times 15)] = 2$$
$$n(A_u) = \frac{1}{120}[(1 \times 180)(4 \times 15)] = 1$$
$$n(T_{1g}) = \frac{1}{120}[(3 \times 180)(4 \times 15)] = 4$$
$$n(T_{1u}) = \frac{1}{120}[(3 \times 180) + (4 \times 15)] = 5$$
$$n(T_{2g}) = \frac{1}{120}[(3 \times 180) - (4 \times 15)] = 4$$
$$n(T_{2u}) = \frac{1}{120}[(3 \times 180) + (4 \times 15)] = 5$$
$$n(G_g) = \frac{1}{120}[(4 \times 180) + (0 \times 15)] = 6$$
$$n(G_u) = \frac{1}{120}[(4 \times 180) + (0 \times 15)] = 6$$
$$n(H_g) = \frac{1}{120}[(5 \times 180) + (4 \times 15)] = 8$$
$$n(H_u) = \frac{1}{120}[(5 \times 180)(4 \times 15)] = 7$$

$\Gamma(3N) = 2A_g + 4T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 5T_{1u} + 5T_{2u} + 6G_u + 7H_u$

$\Gamma(trans) = T_{1u} \qquad \Gamma(rot) = T_{1g}$

$\Gamma(vib) = 2A_g + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u$

10.7 Combination and overtone bands

For purely harmonic potential functions, only one vibrational quantum can be excited by absorption of one photon. However, anharmonicity allows simultaneous excitation of two or more quanta of one vibration in *overtone* bands or one quantum each of two or more different vibrations in *combination* bands.

Where two quanta are involved the selection rule is that the quadruple direct product $\Gamma_1 \otimes \Gamma(\hat{O}) \otimes (\Gamma_2 \otimes \Gamma_3)$ must contains the totally symmetric irreducible representation.

For closed shell molecules this effectively means that the direct product between the two vibrations involved, $\Gamma_2 \otimes \Gamma_3$, must contain $\Gamma(\hat{O})$. A special point is that because vibrations are bosons, only the symmetric part of the direct product (*i.e.* that part not appearing in brackets in multiplication tables) is relevant.

10.8 Vibronic transitions

In Section 9.5.2 we concluded that all $d - d$ transitions in octahedral complexes were forbidden because all the relevant states were symmetric with respect to inversion (g) while the dipole moment operator was antisymmetric (T_{1u}), meaning that the triple product could not possibly contain the totally symmetric representation, A_{1g}. However, one of the defining features of transition metal complexes is that they are coloured, so these transitions clearly are not completely forbidden. What have we missed?

A change in electronic state is usually accompanied by a simultaneous change in vibrational state. So rather than considering only the symmetry of the ground and excited electronic states, we need to consider their total symmetry, which is the product of electronic and vibronic components.

The vibrational wavefunction of the ground state is always totally symmetric, so we need to consider the quadruple direct product involving the symmetry of the electronic ground state (Γ_1), the symmetry of the electronic excited state (Γ_2), the symmetry of the vibrational wavefunction in the excited state (Γ_3) and the symmetry of the dipole moment operator ($\Gamma(x, y, z)$).

$$\Gamma(\Psi_1) \otimes \Gamma(x, y, z) \otimes (\Gamma(\Psi_2) \otimes \Gamma(\Psi_3))$$

An octahedron has stretching vibrations $A_{1g} + E_g + T_{1u}$ and bends $T_{1u} + T_{2u} + T_{2g}$.

Consider excitation of a d^1 complex from its ${}^2T_{2g}$ ground state to the ${}^2E_g$ excited state. This is electronically forbidden, but what if we couple the electronic excitation with excitation of a T_{1u}-symmetric vibrational mode?

$$T_{2g} \otimes T_{1u} \times (E_g \otimes T_{1u}) = (T_{2g} \otimes T_{1u}) \otimes (T_{1u} + T_{2u}) = (A_{2u} + E_u + T_{1u} + T_{2u}) \otimes (T_{1u} + T_{2u})$$

The final direct product step would generate 22 components so it has not been expanded in full, but in fact we don't need to do so: it is immediately obvious that it contains two diagonal products ($T_{1u} \otimes T_{1u}$ and $T_{2u} \otimes T_{2u}$), both of which will generate the required totally symmetric A_{1g} representation. So the transition is allowed if it is vibronically promoted by a T_{1u} mode. This would not have been the case if we had chosen a vibration of E_g or A_{1g} symmetry - the transition would still have been forbidden. The key difference is that the T_{1u} mode eliminates the centre of symmetry while the others do not (much more on this next year in *Spectroscopy and Magnetism*!).

11 Character tables

C_i	E	i		
A_g	1	1	R_x,R_y,R_z	x^2, y^2, z^2, xy, xz, yz
A_u	1	–1	x,y,z	

C_s	E	σ_h		
$A^{'}$	1	1	x,y	x^2, y^2, z^2, xy
$A^{''}$	1	–1	z	xz,yz

C_{nv} point groups

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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_z	yz

C_{3v}	E	$2C_3$	$3\sigma_v$				
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)

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_v'$			
A_1	1	1	1	1	1	z		x^2+y^2, z^2
A_2	1	1	1	–1	–1	R_z		
B_1	1	–1	1	1	–1			x^2-y^2
B_2	1	–1	1	–1	1			xy
E	2	0	–2	0	0	(x,y)	(R_x,R_y)	(xz,yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	$x^2+y^2,\ z^2$
A_2	1	1	1	–1	R_z	
E_1	2	$2cos(2\pi/5)$	$2cos(4\pi/5)$	0	$(x,y)\ \ (R_x,R_y)$	(xz,yz)
E_2	2	$2cos(4\pi/5)$	$2cos(2\pi/5)$	0		(x^2-y^2,xy)

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_d$	$3\sigma_v$		
A_1	1	1	1	1	1	1	z	z^2,x^2+y^2
A_2	1	1	1	1	–1	–1	R_z	
B_1	1	–1	1	–1	1	–1		
B_2	1	–1	1	–1	–1	1		
E_1	2	1	–1	–2	0	0	(x,y),(R_x,R_y)	(xz,yz)
E_2	2	–1	–1	2	0	0		(xy,x^2-y^2)

D_{nh} **point groups**

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		z^2,x^2,y^2
B_{1g}	1	1	–1	–1	1	1	–1	–1	R_z	xy
B_{2g}	1	–1	1	–1	1	–1	1	–1	R_y	xz
B_{3g}	1	–1	–1	1	1	–1	–1	1	R_x	yz
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	

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2$	$3\sigma_v$		
$A_1^{'}$	1	1	1	1	1	1		z^2,x^2+y^2
$A_2^{'}$	1	1	1	1	–1	–1	R_z	
$A_1^{''}$	1	–1	1	–1	1	–1		
$A_2^{''}$	1	–1	1	–1	–1	1	z	
$E^{'}$	2	2	–1	–1	0	0	(x, y)	(xy, x^2-y^2)
$E^{''}$	2	–2	–1	1	0	0	(xz, yz) (R_x, R_y)	

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	R_z	
B_{1g}	1	–1	1	1	–1	1	–1	1	1	–1		x^2-y^2
B_{2g}	1	–1	1	–1	1	1	–1	1	–1	1	xy	
E_g	2	0	–2	0	0	2	0	–2	0	0	(R_x, R_y)	
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	z	
B_{1u}	1	–1	1	1	–1	–1	1	–1	–1	1		
B_{2u}	1	–1	1	–1	1	–1	1	–1	1	–1		
E_u	2	0	–2	0	0	–2	0	2	0	0	(x, y)	

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^2$	$5\sigma_d$		
A_1'	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	1	–1	1	1	1	–1	R_z	
E_1'	2	$2cos(2\pi/5)$	$2cos(4\pi/5)$	0	2	$2cos(2\pi/5)$	$2cos(4\pi/5)$	0	(x, y)	
E_2'	2	$2cos(4\pi/5)$	$2cos(2\pi/5)$	0	2	$2cos(4\pi/5)$	$2cos(2\pi/5)$	0		(xy, x^2-y^2)
A_1''	1	1	1	1	–1	–1	–1	–1		
A_2''	1	1	1	–1	–1	–1	–1	1	z	
E_1''	2	$2cos(2\pi/5)$	$2cos(4\pi/5)$	0	–2	$-2cos(2\pi/5)$	$-2cos(4\pi/5)$	0		(xz, yz)
E_2''	2	$2cos(4\pi/5)$	$2cos(2\pi/5)$	0	–2	$-2cos(4\pi/5)$	$-2cos(2\pi/5)$	0		

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2,z^2
A_{2g}	1	1	1	1	–1	–1	1	1	1	1	–1	–1	R_z	
B_{1g}	1	–1	1	–1	1	–1	1	–1	1	–1	1	–1		
B_{2g}	1	–1	1	–1	–1	1	1	–1	1	–1	–1	1		
E_{1g}	2	1	–1	–2	0	0	2	1	–1	–2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	–1	–1	2	0	0	2	–1	–1	2	0	0		(xy, x^2-y^2)
A_{1u}	1	1	1	1	1	1	–1	–1	–1	–1	–1	–1		
A_{2u}	1	1	1	1	–1	–1	–1	–1	–1	–1	1	1	z	
B_{1u}	1	–1	1	–1	1	–1	–1	1	–1	1	–1	1		
B_{2u}	1	–1	1	–1	–1	1	–1	1	–1	1	1	–1		
E_{1u}	2	1	–1	–2	0	0	–2	–1	1	2	0	0	(x, y)	
E_{2u}	2	–1	–1	2	0	0	–2	1	1	–2	0	0		

D_{nd} point groups

D_{2d}	E	$2S_4$	C_2	$2C'_2$	$2\sigma_d$		
A_1	1	1	1	1	1		z^2,x^2+y^2
A_2	1	1	1	–1	–1	R_z	
B_1	1	–1	1	1	–1		x^2-y^2
B_2	1	–1	1	–1	1	z	xy
E	2	0	–2	0	0	(x,y),(R_x,R_y)	(xz,yz)

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		z^2,x^2+y^2
A_{2g}	1	1	–1	1	1	–1	R_z	
E_g	2	–1	0	2	–1	0	(R_x,R_y)	(xz,yz),(xy,x^2-y^2)
A_{1u}	1	1	1	–1	–1	–1		
A_{2u}	1	1	–1	–1	–1	1	z	
E_u	2	–1	0	–2	1	0	(x,y)	

D_{4d}	E	$2C_4$	C_2	$4C'_2$	$2S_8$	$2S_8^3$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_2	1	1	1	–1	1	1	–1	R_z	
B_1	1	1	1	1	–1	–1	–1		
B_2	1	1	1	–1	–1	–1	1	z	
E_1	2	0	–2	0	$\sqrt{2}$	$-\sqrt{2}$	0	(x,y)	
E_2	2	–2	2	0	0	0	0		(xy,x^2-y^2)
E_3	2	0	–2	0	$-\sqrt{2}$	$\sqrt{2}$	0	(R_x,R_y)	(xz,yz)

D_{5d}	E	$2C_5$	$2C_5^2$	$5C_2$	i	$2S_{10}^3$	$2S_{10}$	$5\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_{2g}	1	1	1	–1	1	1	1	–1	R_z	
E_{1g}	2	$2cos(2\pi/5)$	$2cos(4\pi/5)$	0	2	$2cos(2\pi/5)$	$2cos(4\pi/5)$	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	$2cos(4\pi/5)$	$2cos(2\pi/5)$	0	2	$2cos(4\pi/5)$	$2cos(2\pi/5)$	0		(xy, x^2-y^2)
A_{1u}	1	1	1	1	–1	–1	–1	–1		
A_{2u}	1	1	1	–1	–1	–1	–1	1	z	
E_{1u}	2	$2cos(2\pi/5)$	$2cos(4\pi/5)$	0	–2	$-2cos(2\pi/5)$	$-2cos(4\pi/5)$	0	(x, y)	
E_{2u}	2	$2cos(4\pi/5)$	$2cos(2\pi/5)$	0	–2	$-2cos(4\pi/5)$	$-2cos(2\pi/5)$	0		

D_{6d}	E	$2C_6$	$2C_3$	C_2	$6C_2'$	$2S_{12}$	$2S_{12}^5$	$2S_4$	$6\sigma_d$		
A_1	1	1	1	1	1	1	1	1	1		x^2+y^2,z^2
A_2	1	1	1	1	–1	1	1	1	–1	R_z	
B_1	1	1	1	1	1	–1	–1	–1	–1		
B_2	1	1	1	1	–1	–1	–1	–1	1	z	
E_1	2	1	–1	–2	0	$\sqrt{3}$	$\sqrt{3}$	0	0	(x, y)	
E_2	2	–1	–1	2	0	1	1	–2	0		(xy, x^2-y^2)
E_3	2	–2	2	–2	0	0	0	0	0		
E_4	2	–1	–1	2	0	–1	–1	2	0		
E_5	2	1	–1	–2	0	$\sqrt{3}$	$\sqrt{3}$	0	0	(R_x, R_y)	(xz, yz)

Rotation groups, D_n

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A_1	1	1	1	1		z^2,x^2+y^2
B_1	1	1	–1	–1	R_z,z	xy
B_2	1	–1	1	–1	R_y,y	xz
B_3	1	–1	–1	1	R_x,x	yz

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		z^2,x^2+y^2
A_2	1	1	–1	z,R_z	
E	2	–1	0	(x,y),(R_x,R_y)	(xz,yz),(xy,x^2-y^2)

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	–1	–1	R_z,z	
B_1	1	–1	1	1	–1		x^2-y^2
B_2	1	–1	1	–1	1	xy	
E	2	0	–2	0	0	(x,y),(R_x,R_y)	(xz,yz)

D_5	E	$2C_5$	$2C_5^2$	$5C_2$		
A_1	1	1	1	1		x^2+y^2,z^2
A_2	1	1	1	–1	z,R_z	
E_1	2	$2cos\,(2\pi/5)$	$2cos\,(4\pi/5)$	0	(x,y),(R_x,R_y)	(xz,yz)
E_2	2	$2cos\,(4\pi/5)$	$2cos\,(2\pi/5)$	0		(xy,x^2-y^2)

D_6	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$		
A_1	1	1	1	1	1	1		x^2+y^2,z^2
A_2	1	1	1	1	–1	–1	z,R_z	
B_1	1	–1	1	–1	1	–1		
B_2	1	–1	1	–1	–1	1		
E_1	2	1	–1	–2	0	0	(x,y),(R_x,R_y)	(xz,yz)
E_2	2	–1	–1	2	0	0		(xy,x^2-y^2)

Cubic point groups

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	–1	–1		
E	2	–1	2	0	0		$(z^2,\, x^2-y^2)$
T_1	3	0	–1	1	–1	(R_x, R_y, R_z)	
T_2	3	0	–1	–1	1	(x, y, z)	$(xy,\, xz,\, yz)$

T	E	$4C_3$	$4C_3^2$	$3C_2$		
A	1	1	1	1		$x^2+y^2+z^2$
E	1	ϵ	ϵ^2	1		z^2
	1	ϵ^2	ϵ	1		x^2-y^2
T	3	0	0	1	(x, y, z),(R_x, R_y, R_z)	$(xy,\, xz,\, yz)$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	–1	–1	1	1	–1	1	1	–1		
E_g	2	–1	0	0	2	2	0	–1	2	0		$(z^2,\, x^2-y^2)$
T_{1g}	3	0	–1	1	–1	3	1	0	–1	–1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	–1	–1	3	–1	0	–1	1		$(xy,\, xz,\, yz)$
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	–1	–1	1	–1	1	–1	–1	1		
E_u	2	–1	0	0	2	–2	0	1	–2	0		
T_{1u}	3	0	–1	1	–1	–3	–1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	–1	–1	–3	1	0	1	–1		

O	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	–1	1		
E	2	–1	2	0	0		$(z^2,\, x^2-y^2)$
T_1	3	0	–1	1	–1	(x, y, z),(R_x, R_y, R_z)	
T_2	3	0	–1	–1	1		$(xy,\, xz,\, yz)$

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^2$	$20S_6$	15σ		
A_g	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
T_{1g}	3	η^+	η	0	–1	3	η	η^+	0	–1	(R_x, R_y, R_z)	
T_{2g}	3	η	η^+	0	–1	3	η^+	η	0	–1		
G_g	4	–1	–1	1	0	4	–1	–1	1	0		
H_g	5	0	0	–1	1	5	0	0	–1	1		$(z^2, x^2-y^2, xy, yz, xz)$
A_u	1	1	1	1	1	–1	–1	–1	–1	–1		
T_{1u}	3	η^+	η	0	–1	–3	$-\eta$	$-\eta^+$	0	1	(x, y, z)	
T_{2u}	3	η	η^+	0	–1	–3	$-\eta^+$	$-\eta$	0	1		
G_u	4	–1	–1	1	0	–4	1	1	–1	0		
H_u	5	0	0	–1	1	–5	0	0	1	–1		

$\eta^+ = \frac{1}{2}(1+\sqrt{5}) = 2cos(4\pi/5)$ $\eta^- = \frac{1}{2}(1-\sqrt{5}) = 2cos(2\pi/5)$

Linear point groups, $D_{\infty h}$ and $C_{\infty v}$

$D_{\infty h}$	E	$2C_\infty^\phi$	...	$\infty\sigma_v$	i	$2S_\infty^\phi$	...	∞C_2	
$A_{1g} = \Sigma_g^+$	1	1	...	1	1	1	...	1	x^2+y^2,z^2
$A_{1g} = \Sigma_g$	1	1	...	–1	1	1	...	–1	
$E_{1g} = \Pi_g$	2	$2cos(\phi)$	...	0	2	$-2cos(\phi)$	...	0	(xz, yz)
$E_{2g} = \Delta_g$	2	$2cos(2\phi)$	...	0	2	$2cos(2\phi)$	...	0	(xy, x^2-y^2)
$E_{3g} = \Phi_g$	2	$2cos(3\phi)$	...	0	2	$-2cos(3\phi)$	...	0	
...	...		...				...		
$A_{1u} = \Sigma_u^+$	1	1	...	1	–1	–1	...	–1	z
$A_{1u} = \Sigma_u$	1	1	...	–1	–1	–1	...	1	
$E_{1u} = \Pi_u$	2	$2cos(\phi)$	...	0	–2	$2cos(\phi)$	...	0	(x, y)
$E_{2u} = \Delta_u$	2	$2cos(2\phi)$	...	0	–2	$-2cos(2\phi)$	...	0	
$E_{3u} = \Phi_u$	2	$2cos(3\phi)$	...	0	–2	$2cos(3\phi)$	...	0	

$C_{\infty v}$	E	$2C_{\infty}^{\phi}$	...	$\infty\sigma_v$		
$A_1 = \Sigma^+$	1	1	...	1	z	$x^2 + y^2$,z^2
$A_2 = \Sigma$	1	1	...	–1	R_z	
$E_1 = \Pi$	2	$2cos(\phi)$	...	0	(x, y),(R_x, R_y)	(xz, yz)
$E_2 = \Delta$	2	$2cos(2\phi)$	...	0		$(xy, x^2 - y^2)$
$E_3 = \Phi$	2	$2cos(3\phi)$	...	0		

12 Problems

12.1 Basic features of symmetry

1. Draw sketches to illustrate the following symmetry elements:
    (a) a vertical mirror plane and a C_2 axis in O_3 (ozone)
    (b) a horizontal mirror plane in CO_2
    (c) an S_4 axis in methane
    (d) all of the symmetry elements in CH_3F (point group C_{3v})
    (e) all of the symmetry elements in ethene (point group D_{2h})
2. Determine the symmetry elements possessed by an s orbital, a p orbital, a d_{z^2} orbital, and a d_{xy} orbital
3. Which of the following molecules has:
    (a) a centre of inversion
    (b) an S_4 axis?

$$CO_2 \quad C_2H_2 \quad BF_3 \quad {SO_4}^{2-}$$

4. Identify the symmetry elements in the following molecules, and assign each one to a point group (use the flow diagram in the lecture notes if you find this helpful).

$$NH_2Cl \quad SiF_4 \quad HCN \quad SiFClBrI \quad NO_2 \quad H_2O_2$$

5. What are the symmetry elements that prevent a molecule from being polar? Which of the molecules in Q 4 are polar?
6. What are the symmetry elements that exclude chirality? Which (if any) of the molecules in Q 4 may be chiral?
7. By examining the effect of sequential application of the various symmetry operations in the C_{2v} group on an appropriate molecule, construct the group multiplication table.
8. Consider the chlorobenzene molecule C_6H_5Cl.
    (a) What is the molecular point group?
    (b) Use a basis made up of a p orbital on each carbon atom (pointing perpendicular to the benzene ring) to construct the π molecular orbitals using the following steps:
        i. determine the character of each symmetry operation
        ii. determine the irreps spanned by the basis
        iii. construct a set of SALCs and take linear combinations to form the molecular orbitals of each symmetry species.

12.2 More advanced problems

1. Consider the hydronium ion H_3O^+. This ion has a pyramidal structure with one HOH bond angle smaller than the other two, and belongs to the point group C_s.
   (a) Using a basis set consisting of a 1s orbital on each H atom and $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals on the O atom (*i.e.* (s_O,p_x,p_y,p_z,s_1,s_2,s_3)), construct a matrix representation.
   (b) What are the characters of each of the matrix representatives?
   (c) What are the irreps spanned by the basis?
   (d) Use the basis to construct a set of SALCs.
   (e) Write down the general form of the molecular orbitals of H_3O^+.
2. The transformation matrix C in section 5.4 is given by:

$$C = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

   By showing that $CC^{-1} = C^{-1}C = I$ (or otherwise), verify that its inverse, C^{-1}, is given by:

$$C^{-1} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

   Show that $C^{-1}\Gamma(g)C$ gives the transformed matrices $\Gamma(g)'$ given in the text.
3. Apply the reduction formula to derive the irreducible representations of the SALCS formed by the nine F $2p$ orbitals in BF_3. There needs to be a set of three orthogonal p orbitals on each F atom, but you can orient the x, y, z axes on each atom in the way that most conveniently reflects the symmetry of the system. A physically intuitive choice is to align one p orbital along the B-F bond, another perpendicular to the B-F bond but in the molecular plane and a third perpendicular to the molecular plane.
4. Construct an MO diagram for the σ-like levels of XeF_6 in a hypothetical octahedral (O_h) geometry. Using tables of descent of symmetry, discuss possible distortions which would be expected to lower the energy of this molecule.
5. Use the reduction formula to derive the irreducible representations spanned by the π-type C $2p$ orbitals in square C_4H_4 (you could use D_{4h} but C_{4v} is easier). Repeat the process for rectangular C_4H_4, where two bonds are longer than the other two. Comment on your results in light of the descent in symmetry table shown below:
6. How can group theory be used to determine whether an integral can be non-zero?
7. Use group theory to determine whether the following integrals are non-zero (use the tables of direct products provided in the lecture handout).

D_{4h}	D_{2h}
A_{1g}	A_g
A_{2g}	B_{1g}
B_{1g}	B_{1g}
B_{2g}	A_g
E_g	$B_{2g}+B_{3g}$
A_{1u}	A_u
A_{2u}	B_{1u}
B_{1u}	B_{1u}
B_{2u}	A_u
E_u	$B_{2u}+B_{3u}$

   (a) the overlap integral between a p_x orbital and a p_z orbital in the point group C_{2v}
   (b) the overlap integral between a p_x orbital and a d_{xz} orbital in the point group C_{3v}
   (c) the overlap integral between a p_y orbital and a d_{z^2} orbital in the point group T_d
   (d) the overlap integral between a p_z orbital and a d_{z^2} orbital in the point group D_{2h}

8. Which of the following electronic transitions are symmetry allowed?
   (a) a transition from a state of A_1 symmetry to a state of E_1 symmetry excited by z-polarised light in a molecule belonging to the point group C_{5v}.
   (b) a transition from a state of A_{1g} symmetry to a state of A_{2u} symmetry excited by z-polarised light in a molecule belonging to the point group $D_{\infty h}$.
   (c) a transition from a state of B_2 symmetry to a state of B_1 symmetry excited by y-polarised light in a molecule belonging to the point group C_{2v}.
9. The sequence of electronic states for d^7 Co(II) ions in a tetrahedral environment is ${}^4A_2 >{}^4 T_2 >{}^4 T_1 >{}^4 T_1$. Show that in absorption from the ${}^4A_2$ ground state, only two of the possible three transitions are electronically allowed by an electric dipole mechanism, but that in emission from the highest ${}^4T_1$ state, all three transitions are allowed.
10. Show that the transition ${}^2T_{2g} \rightarrow{}^2 E_g$ in an octahedral d^1 compound is magnetic dipole allowed.
11. Use the reduction formula to show that the bond stretching vibrations in SF_6 belong to irreducible representations $A_{1g}+E_g+T_{1u}$. By matching the displacement vectors to atomic orbitals on S of the same symmetry (or otherwise), sketch out the atomic displacements in these normal modes. Which of these modes is IR active? Which are Raman active?
12. Derive the irreducible representations of the C–H stretching vibrations in benzene (C_6H_6) and sketch out the displacements in these normal modes of vibration. (Hint: the working relating to the π MOs in benzene should both be useful to you.)

13. A useful shortcut to deriving the stretching modes of vibration in an AB_n polyatomic is to recognise that the set of irreducible representations spanned by the n bond stretching vectors is the same as that spanned by the atomic wavefunctions on A which are used to construct hybrid orbitals along the bond directions. Verify that this approach gives the same answers as those derived from application of the reduction formula for bond stretching vibrations in SF_6 (sp^3d^2), CF_4 (sp^3) and XeF_4 (sp^2d). What is the symmetry of the stretching vibrations in BF_3 (sp^2) and PF_5 (sp^3d). (Hints. Remember that a central atom s orbital is always totally symmetric, and that transformation properties of p and d orbitals are always given in the character table. Be careful that the irreducible representations you choose correspond to the correct number of atomic orbitals.)

14. Use a full set of displacement vectors to derive the normal modes of vibration of *cis* and *trans* isomers of N_2F_2. Discuss the pattern of infrared and Raman activity for the two isomers and show how vibrational spectroscopy can be used to distinguish the two isomers.

15. Use a basis set with three vectors on each H atom but no vectors on N to derive the complete set of vibrations for NH_3. Compare your calculation with that given in the handout, where a "full" basis set was used.

16. Derive the normal modes of vibration of BF_3 (D_{3h}) and discuss the activity of these modes in IR and Raman spectroscopy. Compare these results with those for NH_3. Which overtone and combination bands would be active in IR spectroscopy of BF_3?