

SYMMETRY II
LECTURE 1

**THE REDUCTION FORMULA AND
PROJECTION OPERATORS**

<http://course.chem.ox.ac.uk/symmetry-ii-year-2-2012-.aspx>

<http://goicoechea.chem.ox.ac.uk/teaching.html>

Revision of character tables for C_{2v} , C_{3v} and T_d

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	$(x,y) (R_x,R_y)$	$(x^2-y^2,xy) (xz,yz)$

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)

Degeneracy

Wavefunctions are degenerate with each other if a symmetry operation interconverts the functions or converts the functions into linear combinations of each other.

Symmetry operations cannot change the energy of a molecule so if wavefunctions are interconverted they must have the same energy.

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 looks abstract and somewhat impenetrable when first encountered, but is actually quite simple to use in practice.

$$n(i) = \frac{1}{h} \sum_R \chi_r(R) \chi_i(R)$$

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

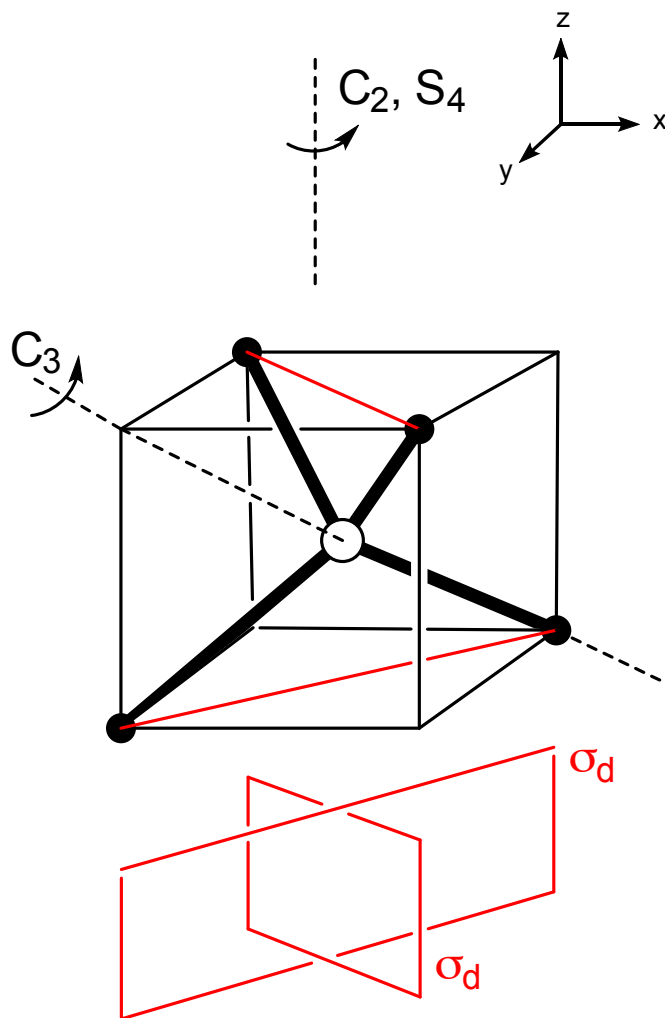
h = Order of group *i.e.* the number of operations in the group (this is not always the same as the number of classes of operations).

\sum_R = This denotes a summation over all the operations R in the group. If there is more than one operation in a given class we must remember to include each operation in the summation.

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

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

Consider for example 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.



Remembering that it is only when an atom is unshifted that it can contribute to this sum. It is easily seen that the characters $\chi_r(R)$ are given simply by the number of H atoms that are unshifted under each symmetry operation. Moreover, 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.

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	$(x, y, z) \quad (xy, xz, yz)$
$\Gamma(H1s)$	4	1	0	0	2	

$$n(i) = \frac{1}{h} \sum_R \chi_r(R) \chi_i(R)$$

$$n(A_1) = 1/24\{(4 \times 1 \times 1) + (1 \times 1 \times 8) + (0 \times 1 \times 3) + (0 \times 1 \times 6) + (2 \times 1 \times 6)\} = 1$$

$$n(A_2) = 1/24\{(4 \times 1 \times 1) + (1 \times 1 \times 8) + (0 \times 1 \times 3) + (0 \times 1 \times 6) + (2 \times -1 \times 6)\} = 0$$

$$n(E) = 1/24\{(4 \times 2 \times 1) + (1 \times -1 \times 8) + (0 \times 2 \times 3) + (0 \times 0 \times 6) + (2 \times 0 \times 6)\} = 0$$

$$n(T_1) = 1/24\{(4 \times 3 \times 1) + (1 \times 0 \times 8) + (0 \times -1 \times 3) + (0 \times 1 \times 6) + (2 \times -1 \times 6)\} = 0$$

$$n(T_2) = 1/24\{(4 \times 3 \times 1) + (1 \times 0 \times 8) + (0 \times -1 \times 3) + (0 \times 1 \times 6) + (2 \times 1 \times 6)\} = 1$$

$$\Gamma(H1s) = A_1 + T_2$$

Some notes about application of the reduction formula

In evaluating the summation given in the reduction formula we deal with each class of symmetry operation in turn. We multiply the character for $\Gamma(\text{H}1\text{s})$ (appearing underneath the character table) 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.

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.

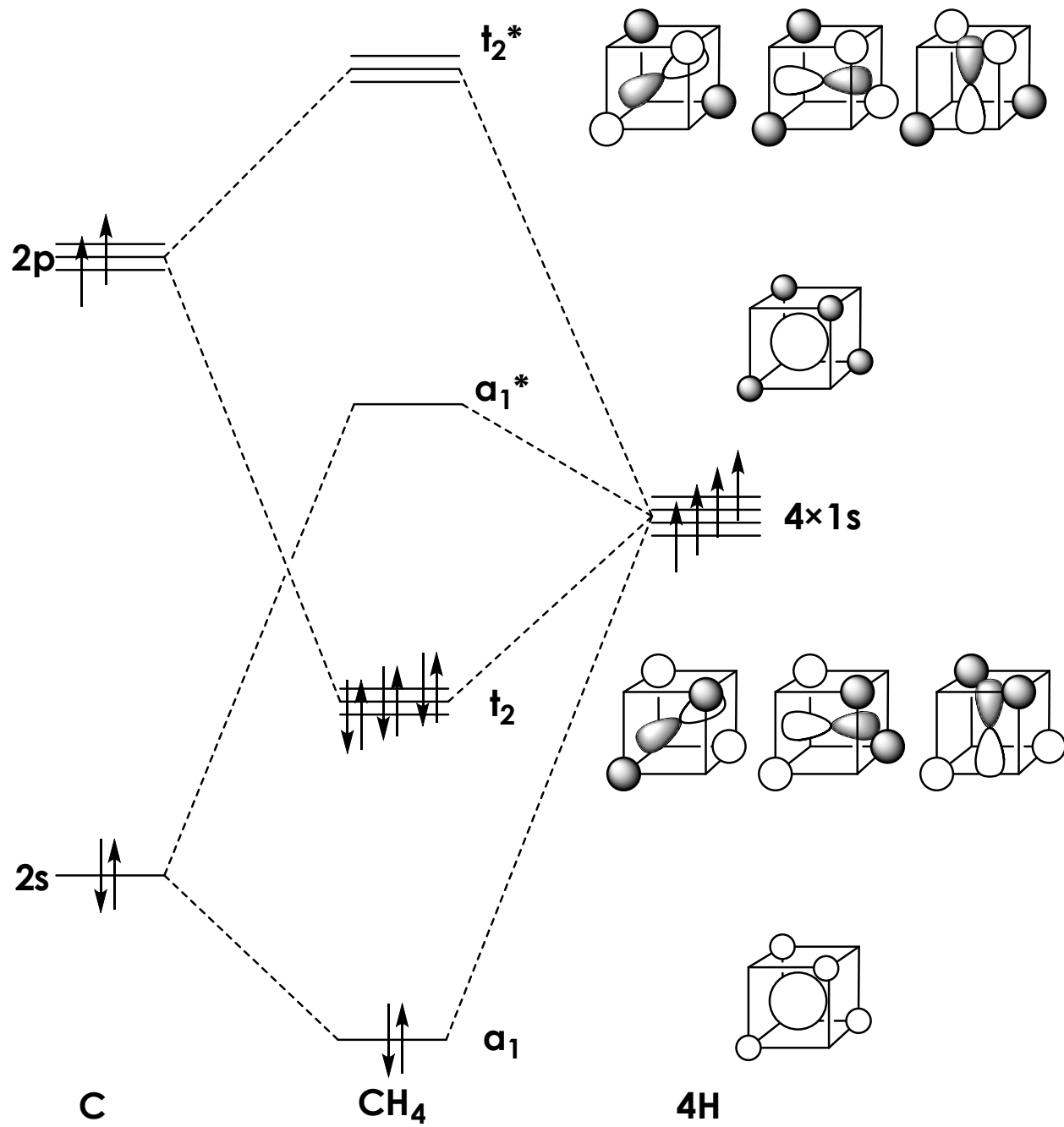
The $n(i)$ must always be zero or integral. If they are not something has gone wrong somewhere!

The number of symmetry adapted function must always be the same as the number of basis functions. In the present case we start with 4 basis functions and end up with $A_1 + T_2$ irreducible representations. The latter is 3-fold degenerate so there are 4 symmetry adapted combinations.

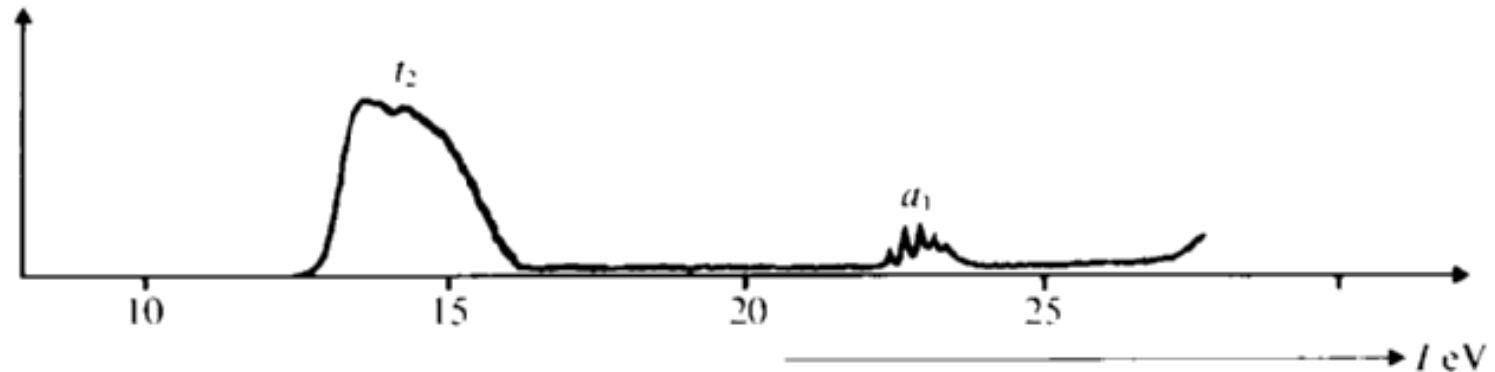
The form of the SALCS for a tetrahedral system and the MO diagram for CH₄

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 CH₄ transform like t_2 . It is therefore possible to deduce the form of the t_2 SALCS simply by matching the phases of the H1s 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 CH₄ 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 thus arrive at the familiar MO diagram for methane, with two occupied MOs of different energy. This description of the molecule is confirmed by the observation of two bands in the photoelectron spectrum.



PES - bombardment of a sample with radiation from a high-energy monochromatic source and the subsequent determination of the kinetic energies of the ejected electrons.



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.

$$\psi_i^{SALC} = P_i \phi_a = \sum_R R \phi_a \chi_i(R)$$

ψ_i^{SALC} = the wavefunction for the SALC belonging to the i^{th} irreducible representation.

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

ϕ_a = one of the basis functions.

\sum_R = a summation over all operations in the group.

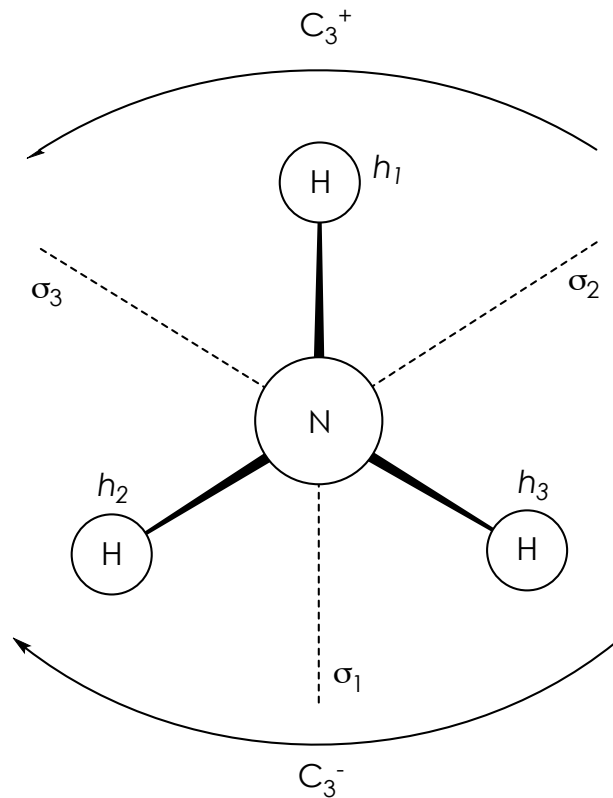
$R\phi_a$ = the atomic basis function generated by the operation of R on ϕ_a

$\chi_i(R)$ = the character of the i^{th} irreducible representation under R .

The projection operator technique is often 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!

A simple application of the technique is to derivation of the SALCs formed by the H 1s orbitals in NH_3 . It is simple to show by application of the reduction formula that the SALCs in this case span irreducible representations $\mathbf{a}_1 + \mathbf{e}$.

The effects of the symmetry operations on the basis functions h_1 , h_2 and h_3 which can be seen in the figure on the next slide are summarised in the table below, which also gives the characters $\chi_i(R)$.



C_{3v}	E	C_3^+	C_3^-	σ_1	σ_2	σ_3
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0
Rh_1	h_1	h_2	h_3	h_1	h_3	h_2
Rh_2	h_2	h_3	h_1	h_3	h_2	h_1
Rh_3	h_3	h_1	h_2	h_2	h_1	h_3

Thus we have the following SALCS:

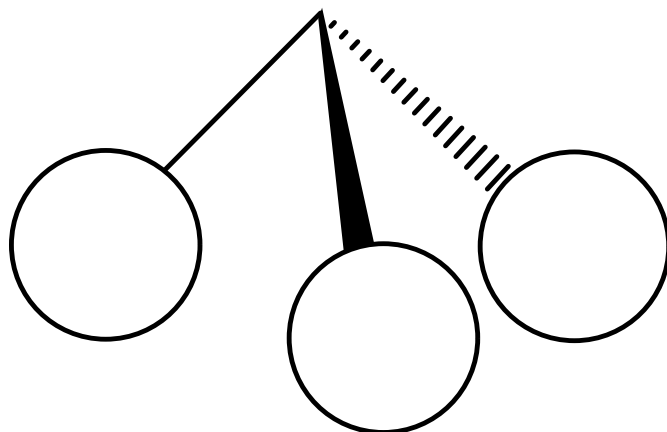
$$\psi_{A_1} = h_1 + h_2 + h_3 + h_1 + h_2 + h_3 \quad (\text{from } h_1 \text{ basis function})$$

$$\psi_{A_1} = h_2 + h_3 + h_1 + h_3 + h_2 + h_1 \quad (\text{from } h_2 \text{ basis function})$$

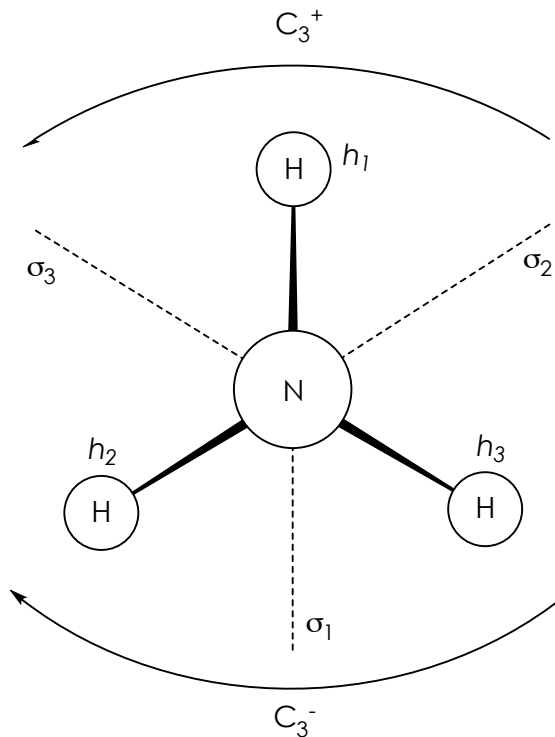
$$\psi_{A_1} = h_3 + h_1 + h_2 + h_2 + h_1 + h_3 \quad (\text{from } h_3 \text{ basis function})$$

These can all be expressed in the same normalised form:

$$\psi_{A_1} = (1/\sqrt{3}) (h_1 + h_2 + h_3)$$



Next consider the A_2
irreducible
representation:



C_{3v}	E	C_3^+	C_3^-	σ_1	σ_2	σ_3
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0
Rh_1	h_1	h_2	h_3	$-h_1$	$-h_3$	$-h_2$
Rh_2	h_2	h_3	h_1	$-h_3$	$-h_2$	$-h_1$
Rh_3	h_3	h_1	h_2	$-h_2$	$-h_1$	$-h_3$

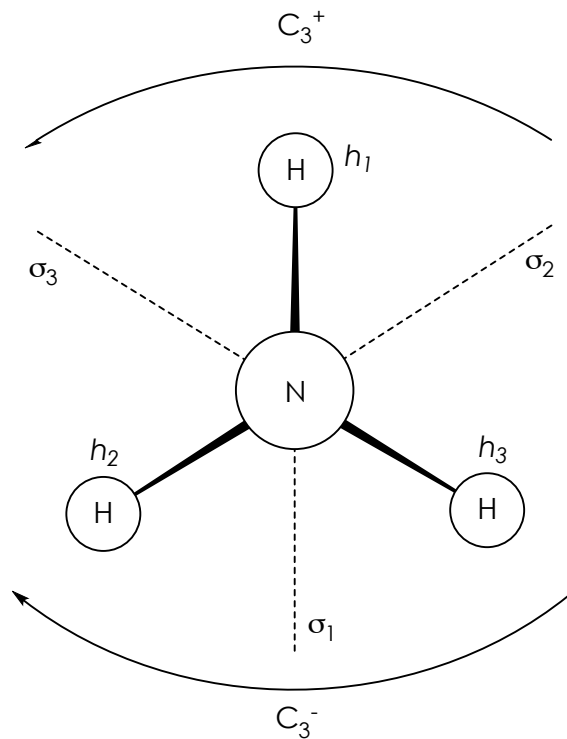
$$\psi_{A_2} = h_1 + h_2 + h_3 - h_1 - h_2 - h_3 = 0 \quad (\text{from } h_1 \text{ basis function})$$

$$\psi_{A_2} = h_2 + h_3 + h_1 - h_2 - h_3 - h_1 = 0 \quad (\text{from } h_2 \text{ basis function})$$

$$\psi_{A_2} = h_3 + h_1 + h_2 - h_2 - h_1 - h_3 = 0 \quad (\text{from } h_3 \text{ basis function})$$

The projected function is zero in each case, as expected because the A_2 irreducible representation is not covered by the basis of 3 H1s functions.

Finally consider the
E irreducible
representation:



C_{3v}	E	C_3^+	C_3^-	σ_1	σ_2	σ_3
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0
Rh_1	$2h_1$	$-h_2$	$-h_3$	0	0	0
Rh_2	$2h_2$	$-h_3$	$-h_1$	0	0	0
Rh_3	$2h_3$	$-h_1$	$-h_2$	0	0	0

$$\psi_{E(1)} = (2h_1 - h_2 - h_3) \quad (\text{from } h_1 \text{ basis function})$$

$$\psi_{E(2)} = (2h_2 - h_3 - h_1) \quad (\text{from } h_2 \text{ basis function})$$

$$\psi_{E(3)} = (2h_3 - h_1 - h_2) \quad (\text{from } h_3 \text{ basis function})$$

It will be seen that 3 different E SALCS have been generated but these are not orthogonal to each other. This is a problem with projection operators.

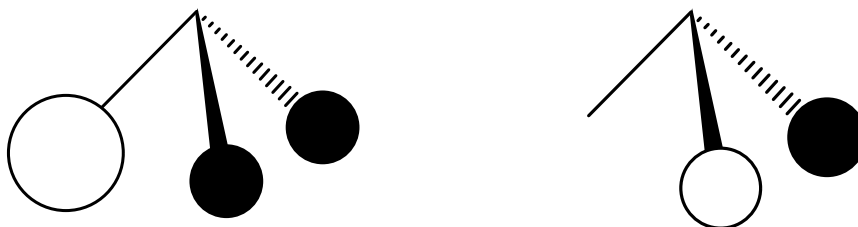
However if we subtract the 3rd SALC from the 2nd we obtain the function:

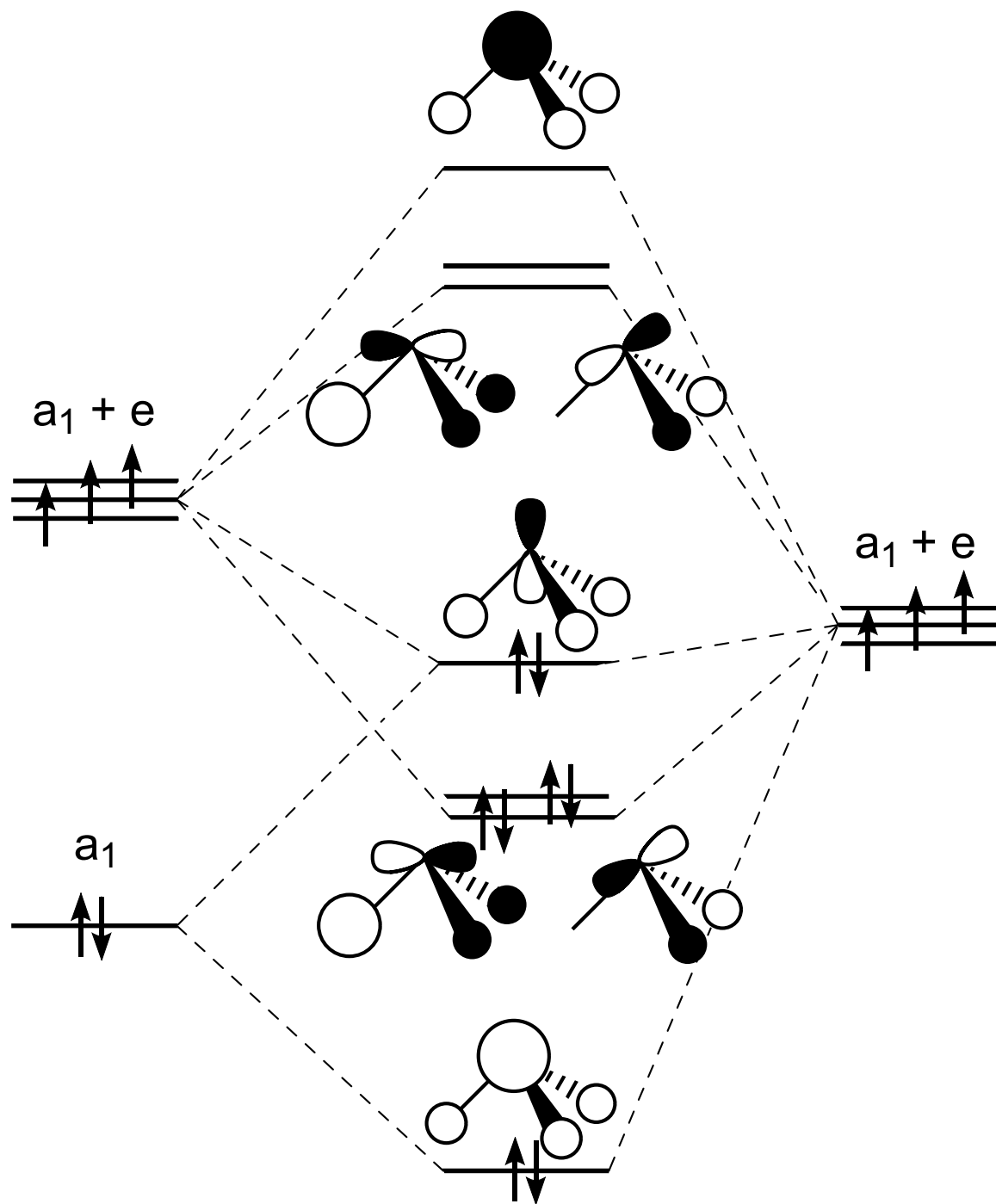
$$\psi_{E(4)} = \psi_{E(2)} - \psi_{E(3)} = (2h_2 - h_3 - h_1) - (2h_3 - h_1 - h_2) = 3h_2 - 3h_3$$

$\psi_{E(4)}$ is orthogonal to $\psi_{E(1)}$ and we can finally write out the wavefunctions for E SALCS in the normalised forms:

$$\psi_E = (1/\sqrt{6})(2h_1 - h_2 - h_3) = (1/\sqrt{2})(h_2 - h_3)$$

These function match up with two orthogonal p orbitals.





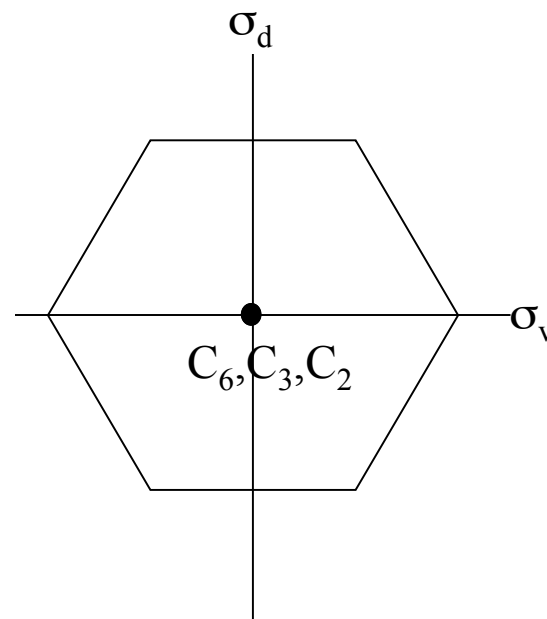
The π -type MOs of C_6H_6

The character table for the D_{6h} point group of C_6H_6 is very unfriendly and any problem involving its use would appear to be daunting! However we can derive the irreducible representations of the π type MOs of C_6H_6 using the character table for the much friendlier group C_{6v} , which is a sub-group of D_{6h} lacking the σ_h mirror plane.

C_{6v} has half the numbers of classes of operation of D_{6h} and half the number of irreducible representations. Thus each irreducible representation of C_{6v} may be derived from two different irreducible representations of D_{6h} , as detailed in tables of descent in symmetry (whose use will be further explored next week). To decide on which of the two alternatives to adopt, we need merely inspect the character table for D_{6h} and choose the alternative which has a negative character under the σ_h mirror plane operation: since the $p(\pi)$ functions all change sign under this operation any SALCs derived from them must do also.

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

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$
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
$\Gamma(\pi)$	6	0	0	0	2	0



Application of the reduction formula only involves consideration of the E and σ_v operations:

$$n(A_1) = 1/12\{(6 \times 1 \times 1) + (2 \times 1 \times 3)\} = 1$$

$$n(A_2) = 1/12\{(6 \times 1 \times 1) + (2 \times -1 \times 3)\} = 0$$

$$n(B_1) = 1/12\{(6 \times 1 \times 1) + (2 \times 1 \times 3)\} = 1$$

$$n(B_2) = 1/12\{(6 \times 1 \times 1) + (2 \times -1 \times 3)\} = 0$$

$$n(E_1) = 1/12\{(6 \times 2 \times 1) + (2 \times 0 \times 3)\} = 1$$

$$n(E_2) = 1/12\{(6 \times 2 \times 1) + (2 \times 0 \times 3)\} = 1$$

We next consider the table of descent in symmetry:

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_2	B_1	E_1	E_2	A_2	A_1	B_1	B_2	E_1	E_2

Consideration of the requirement that the character under σ_h is negative (p_z orbitals change sign due to an xy mirror plane) leads to the following correlations for the $p(\pi)$ orbitals:

$$A_1 \rightarrow A_{2u}$$

$$B_1 \rightarrow B_{2g}$$

$$E_1 \rightarrow E_{1g}$$

$$E_2 \rightarrow E_{2u}$$

Thus the **$p(\pi)$ SALCS for C_6H_6 are $A_{2u} + B_{2g} + E_{1g} + E_{2u}$** . Note that this analysis tells nothing at this stage about the form of the SALCs or about their relative energy ordering. It is left as an exercise to derive the form of the SALCS and to deduce their relative energies.

SYMMETRY II
LECTURE 2

**DEGENERACY AND DESCENT IN
SYMMETRY: LIGAND FIELD SPLITTINGS
AND RELATED MATTERS**

Degeneracy

When dealing with non-degenerate symmetry adapted wavefunctions the effects of symmetry operations can be written simply as:

$$R\psi_i = \pm\psi_i$$

i.e. wavefunctions either remain unchanged or change sign under symmetry operations (see characters for singly degenerate irreducible representations).

When this is the case ψ_i^2 is unchanged under the operation and all physical observables such as energy or electron density are unchanged also.

NON-DEGENERATE WAVEFUNCTIONS EITHER REMAIN UNCHANGED OR CHANGE SIGN WHEN SUBJECT TO A SYMMETRY TRANSFORMATION.

However in point groups which possess a rotational axis of order 3 or higher we encounter degeneracy and one or more of the irreducible representations will be of dimension 2 or higher.

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	$(x,y) (R_x,R_y)$	$(x^2-y^2,xy) (xz,yz)$

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)

A k dimensional representation consists of $k \times k$ matrices and k basis functions taken together provide a basis for the representation. The effects of a symmetry operation may be written in the form:

$$R\psi_i = \sum_k r_{ik} \psi_k$$

where the summation extends over the k members of the degenerate set.

Provided that this equation is satisfied a symmetry operation does not alter the energy E because:

$$\hat{H}\psi_i = E\psi_i$$

where \hat{H} is the Hamiltonian and:

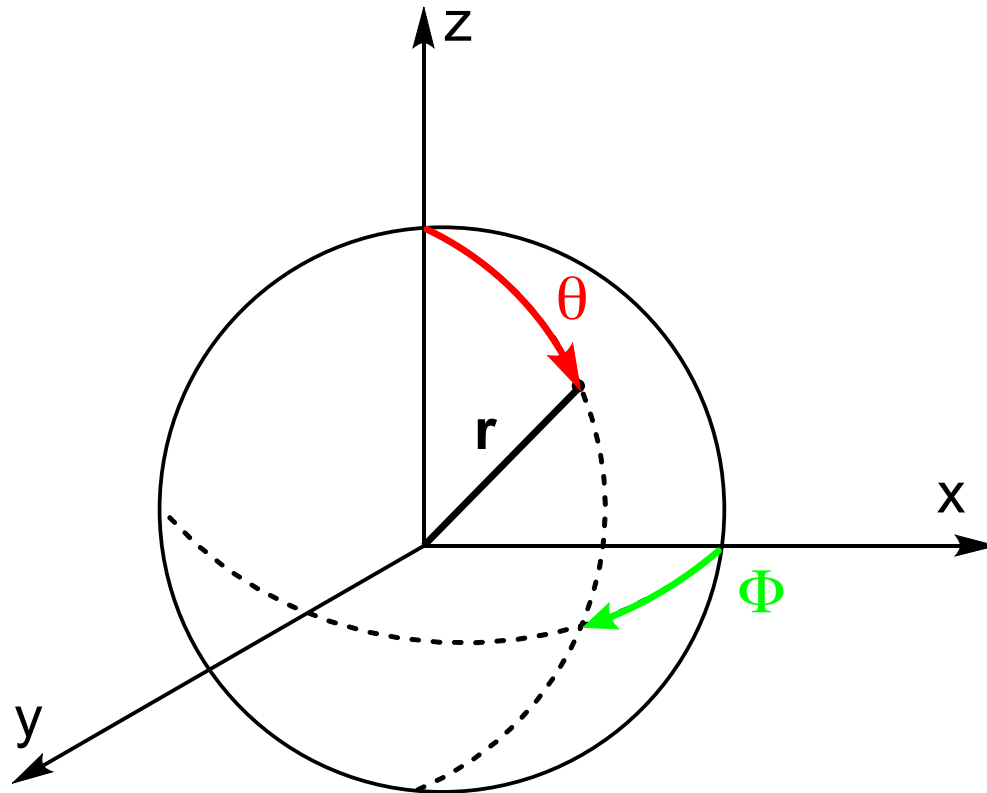
$$\hat{H}(R\psi_i) = \sum_k r_{ik} E\psi_k = E \sum_k r_{ik} \psi_k = E(R\psi_i)$$

These equations express the important qualitative idea that **symmetry operations may interconvert (mix up) members of a degenerate set. Indeed a powerful qualitative approach to identification of degeneracy is to look for interconversion under symmetry operations.**

The explicit form of atomic orbital wavefunctions

The wavefunction for any atomic orbital may be written in terms of polar coordinates r , θ and ϕ and is then separable into radial (R) and angular (A) parts.

$$\psi(r, \theta, \phi) = R(r)A(\theta, \phi)$$



Cartesian co-ordinates x , y and z are related to polar co-ordinates r , θ and ϕ through the relationships:

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

Hence associated with the angular functions $A(\theta, \phi)$ for s, p and d orbitals we have Cartesian functions $f(x, y, z)$, where $f(x, y, z) = r A(\theta, \phi)$ for p orbitals and $f(x, y, z) = r^2 A(\theta, \phi)$ for d orbitals.

These considerations provide the justification for treating the p orbitals as x , y and z vectors and at the same time introduce the explicit form of the wavefunctions for the d orbitals.

Orbital	$A(\theta, \phi)$	Normalisation for $A(\theta, \phi)$	$f(x, y, z)$
s	1	$\frac{1}{2}(1/\sqrt{\pi})$	1
p_x	$\sin\theta \cos\phi$	$\frac{1}{2}(\sqrt{3/\pi})$	x
p_y	$\sin\theta \sin\phi$	$\frac{1}{2}(\sqrt{3/\pi})$	y
p_z	$\cos\theta$	$\frac{1}{2}(\sqrt{3/\pi})$	z
d_{z^2}	$3 \cos^2\theta - 1$	$\frac{1}{4}(\sqrt{5/\pi})$	$3z^2 - (x^2 + y^2 + z^2)$
d_{xz}	$\sin\theta \cos\theta \cos\phi$	$\frac{1}{2}(\sqrt{15/\pi})$	xz
d_{yz}	$\sin\theta \cos\theta \sin\phi$	$\frac{1}{2}(\sqrt{15/\pi})$	yz
$d_{x^2-y^2}$	$\sin^2\theta \cos 2\phi$	$\frac{1}{4}(\sqrt{15/\pi})$	$x^2 - y^2$
d_{xy}	$\sin^2\theta \sin 2\phi$	$\frac{1}{4}(\sqrt{15/\pi})$	xy

Splitting of d orbitals in tetrahedral symmetry

Having introduced the explicit form of the d orbital radial wavefunctions we can consider the problem of degeneracy of d orbitals in various ligand field environments, using the point group T_d as our first example.

We consider the effects of symmetry operations (C_3 , C_2 , S_4 and σ_d) on the x, y and z vectors and then use the explicit algebraic dependence of the d functions on (x,y,z) to determine their transformation properties. As in previous examples it is only necessary to look at one operation of each class.

C_3

$$x \rightarrow y$$

$$y \rightarrow z$$

$$z \rightarrow x$$

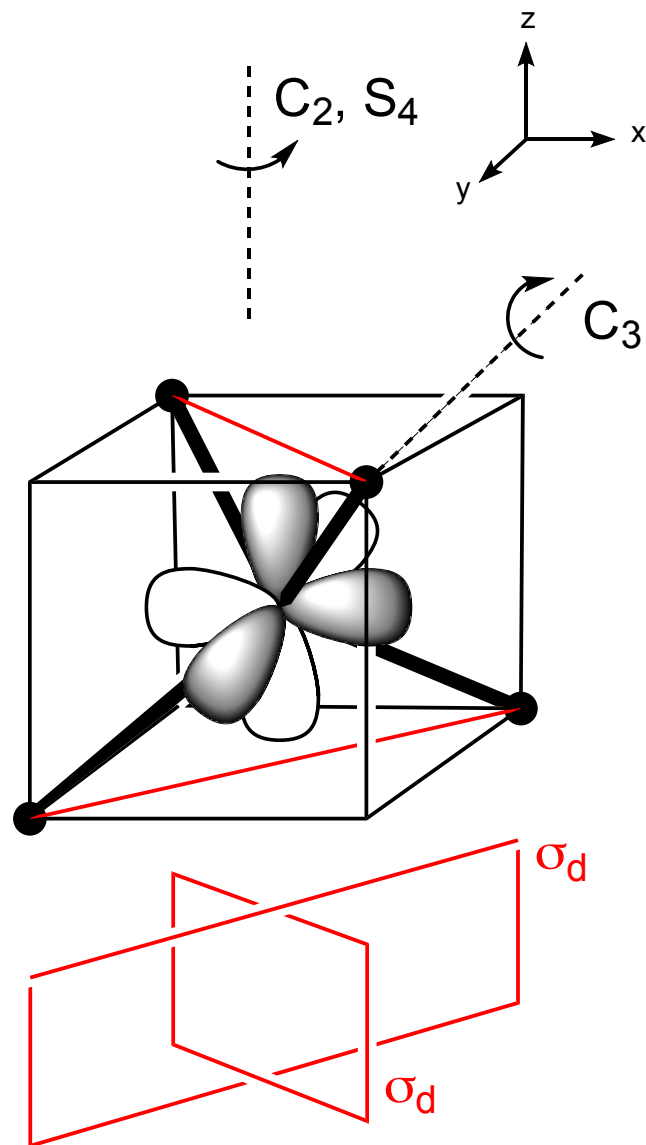
$$xy \rightarrow yz$$

$$yz \rightarrow zx = xz$$

$$xz \rightarrow yx = xy$$

$$x^2 - y^2 \rightarrow y^2 - z^2$$

$$3z^2 - (x^2 + y^2 + z^2) \rightarrow 3x^2 - (y^2 + z^2 + x^2)$$



$$\begin{aligned}
 y^2-z^2 &= -(1/2)\{x^2-y^2\} - (1/2)\{3z^2-(x^2+y^2+z^2)\} \\
 3x^2-(x^2+y^2+z^2) &= +(3/2)\{x^2-y^2\} - (1/2)\{3z^2-(x^2+y^2+z^2)\}
 \end{aligned}$$

Hence we see that the trio $[d_{xy}, d_{yz}, d_{xz}]$ are interconverted and $[d_{x^2-y^2}, d_{z^2}]$ are converted into linear combinations of each other under the C_3 operation. This is a sure indication of degeneracy within these two sets of orbitals. Taking account of the normalisation constants we can represent the effects of the 3-fold rotation in terms of a (5×5) matrix:

$$C_3 \begin{pmatrix} d_{xy} \\ d_{yz} \\ d_{xz} \\ d_{x^2-y^2} \\ d_{z^2} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 & -\sqrt{3}/2 \\ 0 & 0 & 0 & \sqrt{3}/2 & -1/2 \end{pmatrix} \begin{pmatrix} d_{xy} \\ d_{yz} \\ d_{xz} \\ d_{x^2-y^2} \\ d_{z^2} \end{pmatrix}$$

$$\begin{aligned} y^2-z^2 &= -(1/2)\{x^2-y^2\} - (1/2)\{3z^2-(x^2+y^2+z^2)\} \\ 3x^2-(x^2+y^2+z^2) &= +(3/2)\{x^2-y^2\} - (1/2)\{3z^2-(x^2+y^2+z^2)\} \end{aligned}$$

Hence we see that the trio $[d_{xy}, d_{yz}, d_{xz}]$ are interconverted and $[d_{x^2-y^2}, d_{z^2}]$ are converted into linear combinations of each other under the C_3 operation. This is a sure indication of degeneracy within these two sets of orbitals. Taking account of the normalisation constants we can represent the effects of the 3-fold rotation in terms of a (5×5) matrix:

Note the block diagonal form of the transformation matrices. The sum of the diagonal elements is -1 , so the character of the set of d functions is $\chi(C_3) = -1$.

For the other operations it is not necessary to consider the full form of the transformation matrix because only diagonal elements contribute to the character and we can identify these by simply asking: does the function remain unchanged or does it change sign?

C_2

Contribution to $\chi(\mathbf{R})$

$$x \rightarrow -x \qquad xy \qquad \rightarrow \qquad xy \qquad +1$$

$$y \rightarrow -y \qquad yz \qquad \rightarrow \qquad -yz \qquad -1$$

$$z \rightarrow z \qquad xz \qquad \rightarrow \qquad -xz \qquad -1$$

$$x^2 - y^2 \rightarrow x^2 - y^2 \qquad +1$$

$$3z^2 - (x^2 + y^2 + z^2) \rightarrow 3z^2 - (x^2 + y^2 + z^2) \qquad +1$$

$$\chi(C_2) = +1$$

S_4

Contribution to $\chi(\mathbf{R})$

$$x \rightarrow -y \qquad xy \qquad \rightarrow \qquad -xy \qquad -1$$

$$y \rightarrow +x \qquad yz \qquad \rightarrow \qquad -xz \qquad 0$$

$$z \rightarrow -z \qquad xz \qquad \rightarrow \qquad yz \qquad 0$$

$$x^2 - y^2 \rightarrow y^2 - x^2 \qquad -1$$

$$3z^2 - (x^2 + y^2 + z^2) \rightarrow 3z^2 - (x^2 + y^2 + z^2) \qquad +1$$

$$\chi(S_4) = +1$$

σ_d *Contribution to $\chi(\mathbf{R})$*

$$x \rightarrow -y \qquad xy \qquad \rightarrow \qquad xy \qquad +1$$

$$y \rightarrow -x \qquad yz \qquad \rightarrow \qquad -xz \qquad 0$$

$$z \rightarrow z \qquad xz \qquad \rightarrow \qquad -yz \qquad 0$$

$$x^2 - y^2 \rightarrow y^2 - x^2 \qquad -1$$

$$3z^2 - (x^2 + y^2 + z^2) \rightarrow 3z^2 - (x^2 + y^2 + z^2) \qquad +1$$

$$\chi(\sigma_d) = +1$$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
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
$\Gamma(d)$	5	-1	+1	-1	+1

Hence by inspection or by application of the reduction formula we see that the d orbitals transform as **$T_2 + E$** in T_d . Symmetry considerations do not allow us to predict whether e or t_2 orbital will be lower in energy in a T_d environment.

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)

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

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

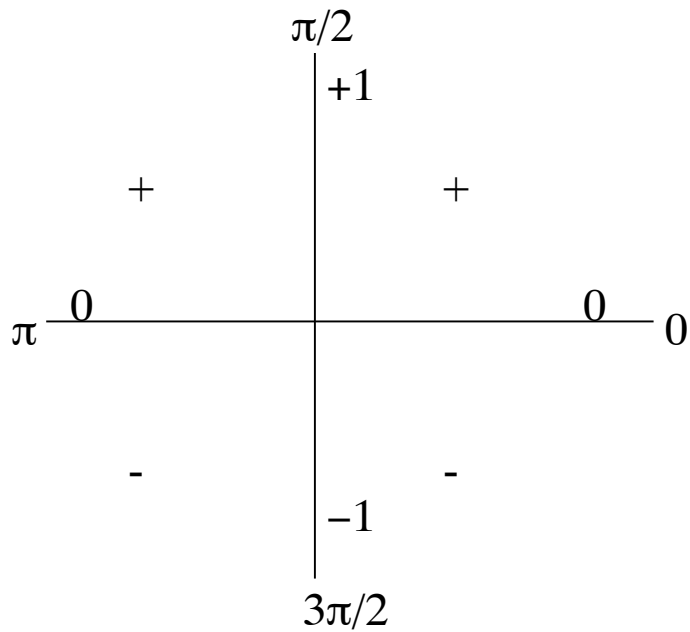
A general expression for $\chi(\alpha)$ for atomic wavefunctions under rotation by angle α and ligand field splitting in octahedral fields

It would be extremely tedious to have to apply the approach outlined above to all problems concerned with atomic orbitals in molecular systems.

Fortunately there exists a general expression for the character of a set of atomic orbitals with an arbitrary angular momentum ℓ under rotation by a general angle α :

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

Remembering the sign of the sine function in the four different quadrants we can write down expressions for the character of p, d and f orbitals under C_2 , C_3 and C_4 rotations.



e.g. for an f orbital with $\ell=3$ under a C_3 rotation where $\alpha=2\pi/3$.

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

	p $\ell=1$	d $\ell=2$	f $\ell=3$
$C_2 \quad \alpha=\pi$	-1	+1	-1
$C_3 \quad \alpha=2\pi/3$	0	-1	+1
$C_4 \quad \alpha=\pi/2$	+1	-1	-1

We can use this result to write down the characters of p, d and f orbitals under the rotational operations of the octahedron:

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

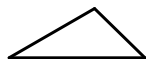
By inspection or by application of the reduction formula we see that:

$$\begin{aligned}
 \mathbf{p} &\rightarrow T_1 \\
 \mathbf{d} &\rightarrow E + T_2 \\
 \mathbf{f} &\rightarrow A_2 + T_1 + T_2
 \end{aligned}$$

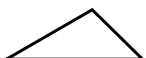
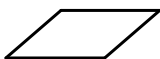
In full octahedral symmetry we simply need add u subscripts for p and f orbitals and a g subscript for d orbitals.

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

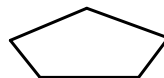
Extension of the ideas above to deal with axial fields is left as a problem. An important qualitative result is that in D_{3h} , D_{5h} and D_{6h} , there is a 2:2:1 splitting pattern. d_{z^2} is unique, but (d_{xz}, d_{yz}) and $(d_{x^2-y^2}, d_{xy})$ convert into linear combinations of each other under rotational operations and therefore form two degenerate pair. D_{4h} forms an exception to this pattern. (d_{xz}, d_{yz}) interconvert under the C_4 operation, but $d_{x^2-y^2}$ and d_{xy} simply convert into 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 to the D_{4h} point group.

D_{3h} 

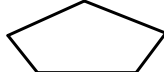
M

 D_{4h} 

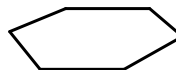
M

 D_{5h} 

M

 D_{6h} 

M

 d_{z^2} a_1' a_{1g} a_1' a_{1g} d_{yz} e'' e_g e_1'' e_{1g} d_{xz} e' b_{2g} e_2' e_{2g} d_{xy} $d_{x^2-y^2}$ b_{1g}

Tables of descent in symmetry

These tables summarise results of the sort we have been discussing. They show how functions corresponding to a given irreducible representation in a group of high symmetry behave in sub-groups of lower symmetry.

R_3 (The group of a sphere)	O	D_4	D_3
S	A_1	A_1	A_1
P	T_1	$A_2 + E$	$A_2 + E$
D	$E + T_2$	$A_1 + B_1 + B_2 + E$	$A_1 + 2E$
F	$A_2 + T_1 + T_2$	$A_2 + B_1 + B_2 + 2E$	$A_1 + 2A_2 + 2E$
G	$A_1 + E + T_1 + T_2$	$2A_1 + A_2 + B_1 + B_2 + 2E$	$2A_1 + A_2 + 3E$
H	$E + 2T_1 + T_2$	$A_1 + 2A_2 + B_1 + B_2 + 3E$	$A_1 + 2A_2 + 4E$

Jahn-Teller Theorem

A system with an orbitally degenerate ground state must distort so as to relieve the degeneracy.

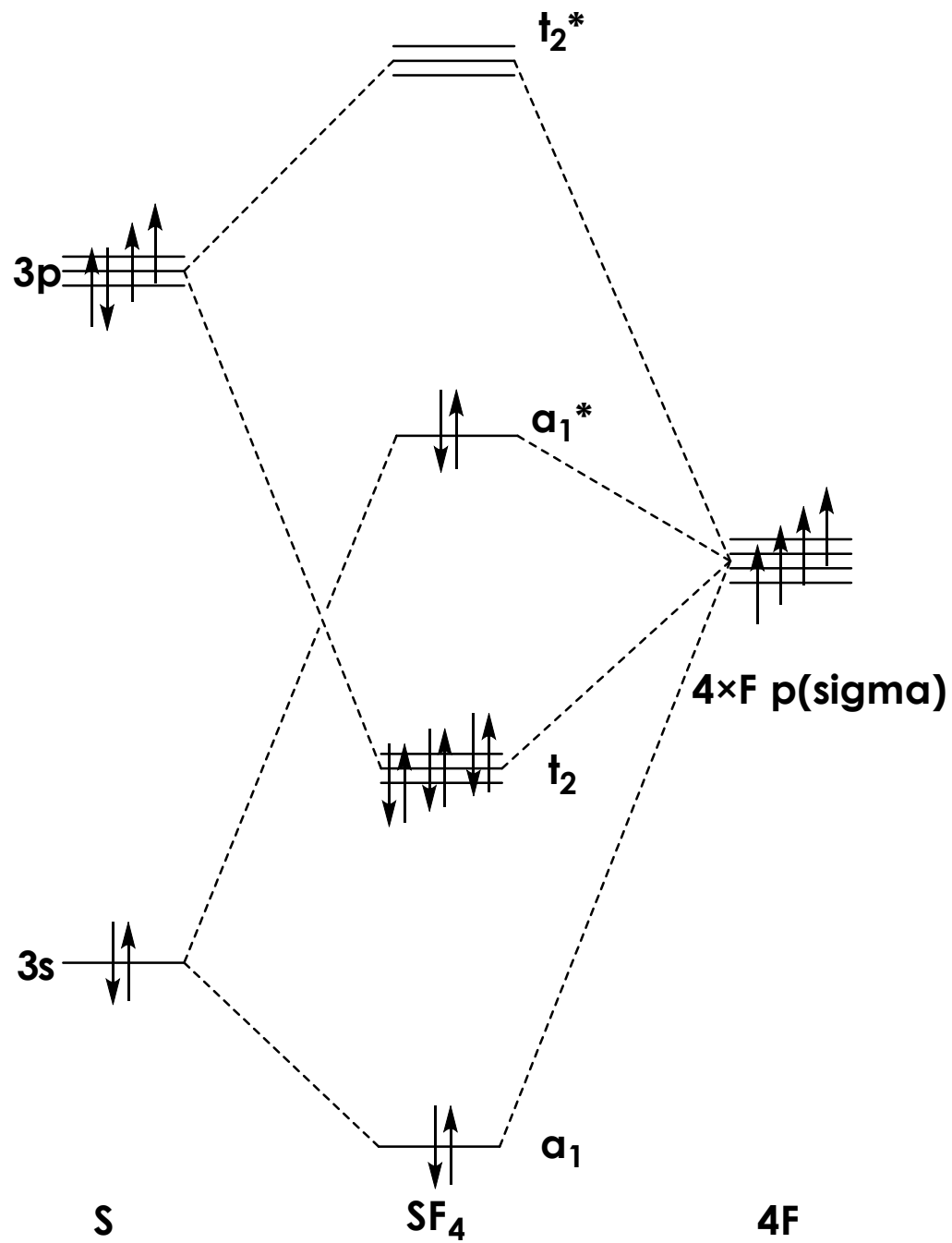
Tables of descent in symmetry are useful in deciding which sort of distortion will lift the symmetry as required by this theorem. Consider for example an octahedral system. Squashing or elongation along one of the C_4 axes takes us into the D_{4h} point group. Squashing or elongation along one of the 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.

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}	$B_{2u} + E_u$	$A_{1u} + E_u$

“2nd order” Jahn-Teller effects

Group theoretical arguments provide an alternative approach to the VSEPR model for rationalising the structures of simple polyatomic molecules.

Consider for example the σ bonding in SF_4 . An MO diagram constructed in a hypothetical tetrahedral geometry has occupied bonding t_2 and a_1 levels as in CF_4 , but in an addition the antibonding a_1^* level must be also occupied by two electrons. The empty t_2 antibonding level lies at higher energy and is unoccupied. Consider now a distortion to a lower symmetry. Descent of symmetry tables tells us that the a_1 wavefunction must remain totally symmetric. The threefold degeneracy of the t_2 level will be lifted. Provided that one component of t_2 is also totally symmetric, the occupied antibonding (the HOMO) can mix with one of the t_2 components. This will stabilise the lower electronic level.



On this basis distortions to C_{2v} or C_{3v} symmetry would lower the electronic energy, but distortion to D_{2d} or D_{4h} would not. The former two structures are exactly those introduced in simple VSEPR arguments.

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

SYMMETRY II
LECTURE 3

**DIRECT PRODUCTS AND
SPECTROSCOPIC SELECTION
RULES**

Direct products and many electron states

Consider the problem of deciding upon the symmetry of functions formed as the product of two or more functions. This issue is of importance in determining the symmetry of many electron states from configurations when we know the symmetry of the individual one electron wavefunctions; and in formulating spectroscopic selection rules between orbitals or electronic states of known symmetry or between vibrational states.

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 large 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 spin degeneracy ($2S+1$) 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.

Non-degenerate representations

Suppose we multiply a function belonging to the irreducible representation Γ_1 by another function belonging to Γ_2 . The characters of the product function Γ_{12} must be given by:

$$\chi_{12}(\mathbf{R}) = \chi_1(\mathbf{R}) \chi_2(\mathbf{R})$$

We can thus 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	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Trivially multiplying a function of any symmetry by a function of A_1 symmetry does not alter the symmetry of the original function. In addition if we multiply together any two functions of the same symmetry we produce a function of A_1 symmetry. We also have:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$A_2 \times B_1$	1	-1	-1	1	$= B_2$
$A_2 \times B_2$	1	-1	1	-1	$= B_1$
$B_1 \times B_2$	1	1	-1	-1	$= A_2$

We can thus set up a table of *direct products*:

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. This must be 1A_1 because the electrons are spin paired in a non-degenerate level.

Groups with degenerate irreducible 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 $A_1 \times E$ or $A_2 \times E$ is simply E . The interesting case is $E \times E$, which gives a set of characters that do not correspond to one of the irreducible representations of the group.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$E \times E$	4	1	0

Application of the reduction formula allows us to deduce that this representation is reducible to $A_1 + A_2 + E$.

$$n(i) = \frac{1}{h} \sum_R \chi_r(R) \chi_i(R)$$

$$n(A_1) = 1/6\{(4 \times 1 \times 1) + (1 \times 1 \times 2) + (0 \times 1 \times 3)\} = 1$$

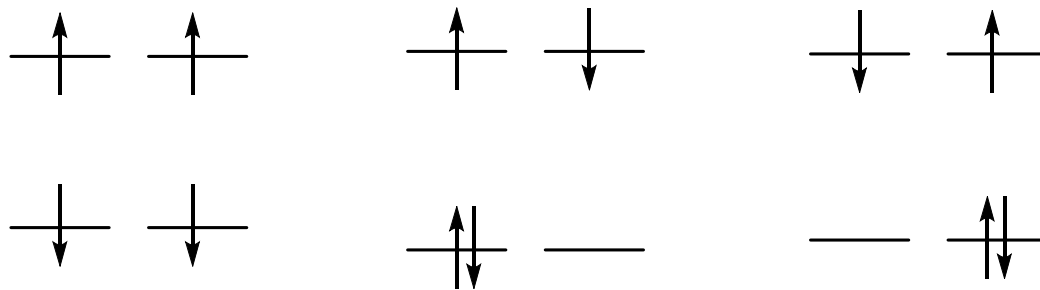
$$n(A_2) = 1/6\{(4 \times 1 \times 1) + (1 \times 1 \times 2) + (0 \times -1 \times 3)\} = 1$$

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

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			$A_1 + [A_2] + E$

There is a problem in deciding upon the electronic states that are supported by the e^2 configuration. There are only 6 ways of arranging 2 electrons in a pair of degenerate orbitals so as not to violate the Pauli exclusion principle.



Thus we cannot freely associate singlet and triplet spin wave functions with each of the A_1 , A_2 and E spatial wavefunctions. The required 6 microstates are produced either by the states ${}^3A_1 + {}^1A_2 + {}^1E$ or by ${}^1A_1 + {}^3A_2 + {}^1E$. If we use the symbols α and β to denote spin up and spin down and distinguish between electron 1 and 2 with parentheses, then the possible spin wavefunctions are:

$$\alpha(1) \beta(2) - \alpha(2) \beta(1)$$

Singlet spin wavefunction

$$\alpha(1) \alpha(2)$$

$$\beta(1) \beta(2)$$

$$\alpha(1) \beta(2) + \alpha(2) \beta(1)$$

Triplet spin wavefunctions.

$$\alpha(1)\beta(2) - \alpha(2)\beta(1)$$

Singlet spin wavefunction

Antisymmetric w/ respect to particle interchange!

$$\alpha(1)\alpha(2)$$

$$\beta(1)\beta(2)$$

$$\alpha(1)\beta(2) + \alpha(2)\beta(1)$$

Triplet spin wavefunctions.

Symmetric w/ respect to particle interchange!

Electrons are *Fermions* and therefore the overall wavefunction should be antisymmetric with respect to particle interchange. Thus the triplet spin wavefunctions must associated with that part of the direct product which is antisymmetric with respect to particle interchange. Special procedures exist for deciding which part is antisymmetric under interchange, but it suffices here to note that square brackets in the direct product tables are used to identify the antisymmetric part. Thus in the present case we see that the triplet spin wavefunction is associated with the A_2 spatial wavefunction. Hence the configuration e^2 gives terms ${}^1A_1 + {}^3A_2 + {}^1E$.

Extending these ideas to the point group T_d where we have both 2-fold and 3-fold degenerate irreducible representations, we must reduce the representations associated with the direct product $E \times E$, $E \times T_1$, $E \times T_2$, $T_1 \times T_1$, $T_1 \times T_2$ and $T_2 \times T_2$ to give the direct product table shown below.

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

Where a two-electron configuration involves occupation of two different subshells, both singlet and triplet states are allowed without restriction:

$$t_1^1 e^1 \rightarrow {}^3T_1 + {}^1T_1 + {}^3T_2 + {}^1T_2$$

$$t_2^1 e^1 \rightarrow {}^3T_1 + {}^1T_1 + {}^3T_2 + {}^1T_2$$

$$t_1^1 t_2^1 \rightarrow {}^3A_2 + {}^1A_2 + {}^3E + {}^1E + {}^3T_1 + {}^1T_1 + {}^3T_2 + {}^1T_2$$

Again problems arise in dealing with the states arising from configurations with two electrons in the same subshell. Of course the character tables give us the final answer, but in the particular case of the e^2 and t_2^2 configuration we can use a correlation approach to decide which irreducible representations support triplet states.

We know that the d^2 electron configuration gives rise to the following Russell-Saunders terms:

$$d^2 \rightarrow {}^1S + {}^3P + {}^1D + {}^3F + {}^1G$$

But tables in descent of symmetry tell us that the triplet atomic terms behave as follows in a tetrahedral field:

$$\begin{array}{ll} {}^3P & \rightarrow {}^3T_1 \\ {}^3F & \rightarrow {}^3A_2 + {}^3T_1 + {}^3T_2 \end{array}$$

The molecular terms derived from the atomic terms by descent of symmetry must correspond to the terms derived from direct products in the three possible d electron configurations in a tetrahedral field, namely e^2 , $t_2^1e^1$ and t_2^2 . The $t_2^1e^1$ configuration accounts for ${}^3T_1 + {}^3T_2$ so that the triplet term for e^2 must be 3A_2 and the triplet term for t_2^2 must be 3T_1 .

Hence we have:

$$\begin{array}{llll} e^2 & \rightarrow & {}^1A_1 + {}^3A_2 + {}^1E & \text{(gives 6 microstates in total)} \\ t_2^2 & \rightarrow & {}^1A_1 + {}^1E + {}^3T_1 + {}^1T_2 & \text{(gives 15 microstates in total)} \end{array}$$

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:

$$g \times g = g$$

$$u \times u = g$$

$$g \times u = u$$

for groups with an i
centre

$$' \times ' = '$$

$$'' \times '' = '$$

$$' \times '' = ''$$

for groups with a
 σ_h plane but no i
centre.

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.

For the Point Groups O and Td (and Oh)

	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					$A_1 + E + [T_1] + T_2$

Quantum mechanical integrals

Very often in quantum mechanics we need to evaluate integrals of the sort:

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

which is often abbreviated as:

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

where the symbol $d\tau$ indicates integration over all space.

In one dimension we know that when we integrate a function between $+\infty$ and $-\infty$, the integral is zero **for odd functions**:

if:
$$f_1(x) = -f_1(-x)$$

then:
$$\int_{-\infty}^{+\infty} f_1(x) = 0$$

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

if:
$$f_1(x) = f_1(-x)$$

then:
$$\int_{-\infty}^{+\infty} f_1(x) \neq 0$$

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**. 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.

Note however that even if a function is totally symmetric, this does not guarantee that the integral will be non-zero. For example a p_z orbital on oxygen in H_2O , but the integral over all space is zero.

Spectroscopic selection rules

In spectroscopy we are concerned with transitions between states each characterised by wavefunctions. 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:

$$I \propto \left| \int \Psi_1 \hat{O} \Psi_2 \right|^2$$

Hence for non-zero intensity the direct product $\Gamma_1 \times \Gamma_0 \times \Gamma_2$ 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. This has components which transform like the translations x , y and z . The irreducible representations corresponding to the three vectors always appears 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 .

When dealing with closed shell molecules in their ground vibrational state, the ground state wavefunction is totally symmetric and does not therefore affect the direct product $\Gamma_0 \times \Gamma_2$. It thus follows that **the only transitions that can be observed in IR involve vibrations of 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.

In **Raman spectroscopy** incident electric fields produce 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**, 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 simple inspection of the character table which always spells out explicitly the irreducible representations corresponding to the 6 components of the polarisability tensor.

T_d		Symmetry elements for the group					Spectroscopy active component		
		<i>E</i>	8<i>C</i>₃	3<i>C</i>₂	6<i>S</i>₄	6<i>σ</i>_d	Microwave	IR	Raman
Symmetry label	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)

Some examples of electronic transitions from transition metal spectroscopy

d¹ in a tetrahedral environment.

The ground state e¹ configuration gives a term ²E ground term and the t₂¹ excited state gives a term ²T₂. The dipole operator is T₂.

The direct product E×T₂×T₂ may be evaluated step by step as (E×T₂)×T₂ = (T₁+T₂)×T₂. The term T₂×T₂ obviously contains A₁ so that the transition ²E→²T₂ is allowed.

T _d	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 + [A₂] +E	T ₁ +T ₂	T ₁ +T ₂
T ₁				A ₁ +E+ [T₁] +T ₂	A ₂ +E+T ₁ +T ₂
T ₂					A ₁ +E+ [T₁] +T ₂

d² in a tetrahedral environment.

The e² ground configuration gives a ³A₂ ground state, whilst the excited configuration e¹t₂¹ gives triplet terms ³T₁ and ³T₂.

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

This triple direct product contains A₁ and so the transition ³A₂ → ³T₁ is allowed.

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

This triple direct product does not contain A₁ and so the transition ³A₂ → ³T₂ is not allowed.

T _d	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 + [A₂] +E	T ₁ +T ₂	T ₁ +T ₂
T ₁				A ₁ +E+ [T₁] +T ₂	A ₂ +E+T ₁ +T ₂
T ₂					A ₁ +E+ [T₁] +T ₂

d electron configurations in octahedral (O_h) symmetry.

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 $g \times u \times g = u$ and so cannot contain A_{1g} .

Hence d to d transitions are dipole forbidden in octahedral symmetry.

This does not mean that they are unobserved experimentally, *i.e.* there are means by which the selection rules can be relaxed (*e.g.* vibronic coupling)

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 $\Gamma_1 \times \Gamma_0 \times (\Gamma_2 \times \Gamma_3)$ must contain the totally symmetric irreducible representation. For closed shell molecules this effectively means that the direct product between the two vibrations involved $\Gamma_2 \times \Gamma_3$ must contain Γ_0 . 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.

Vibronic transitions

These involve a simultaneous change in electronic and vibrational state. The vibronic mechanism may allow appearance of an otherwise forbidden electronic transition by involvement of a *promoting* vibrational mode. Again we must consider a quadruple product, but here the ground wavefunction Γ_1 may not be totally symmetric if we are dealing with transition metal compounds. Γ_2 represents the excited state electronic wavefunction and Γ_3 the promoting vibration.

A very important set of transitions involving a vibronic mechanism are d to d transitions in octahedral complexes. 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 the T_{2g} ground state to the E_g excited state. This is electronically forbidden but the quadruple product:

$$t_{2g} \times t_{1u} \times (e_g \times t_{1u}) = t_{2g} \times t_{1u} \times (t_{1u} + t_{2u}) = (t_{1u} + t_{2u} + e_u + a_{2u}) \times (t_{1u} + t_{2u})$$

contains two diagonal products (and therefore a_{1g} twice) and so the transition vibronically promoted by the t_{1u} modes is allowed.

SYMMETRY II
LECTURE 4

MOLECULAR VIBRATIONS

Introduction

In general the vibration of a polyatomic molecule does not involve deformation of an individual bond or bond angle.

Instead a molecular vibration involves the excitation of a normal mode of vibration of a molecule. 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.

Basis sets for molecular vibrations

A set of $3N$ displacement vectors with 3 vectors attached to each of the N atoms in a polyatomic molecule 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 the modes may be grouped together in degenerate sets.

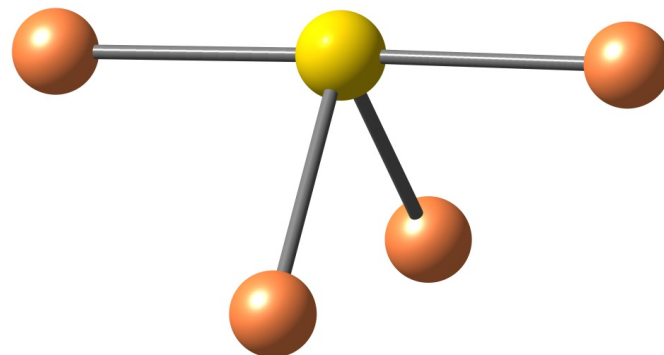
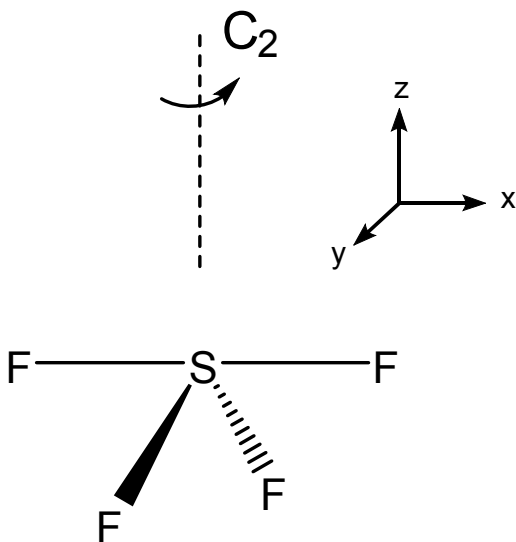
For polyatomic molecules of the sort AB_n or AB_nC_m with a unique central atom (e.g. XeF_4 , XeO_3F_2 but not B_2Cl_4) it may often be advantageous to work with a basis set of $3N-3$ vectors, omitting the 3 vectors on the central atom: these will always correspond simply to the translation of the molecule, so that with this basis set we generate vibrations plus rotations.

Finally in many situations (especially on General Papers!) a problem will focus only on stretching vibrations. In particular we often 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. (In the AB_n species these vectors must be taken to have their origins on the B atoms, not on the A atom). This basis set will generate the n stretching vibrations without any redundancy.

Using bond stretching basis sets

In general we need to write down the characters of the transformation matrices which describe the effects of each symmetry operation in the group on the chosen basis set. **Vectors on a given atom only contribute to the diagonal sum if the atom is unshifted.** When we are dealing with the set of n bond stretching vectors in an AB_n molecule this gives us the simple rule: **Character under operation $R = \chi(R) = \text{Number of B atoms unshifted under the operation.}$** We can now apply these ideas to deduce the irreducible representations spanned by bond stretching vectors in SF_4 , CF_4 and XeF_4 .

SF₄ point group C_{2v}



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
Γ_{stretch}	4	0	2	2		

$$n(i) = \frac{1}{h} \sum_R \chi_r(R) \chi_i(R)$$

Applying the reduction formula:

$$n(A_1) = 1/4(4+0+2+2) = 2$$

$$n(A_2) = 1/4(4+0-2-2) = 0$$

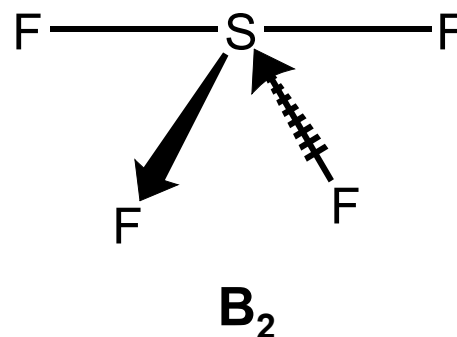
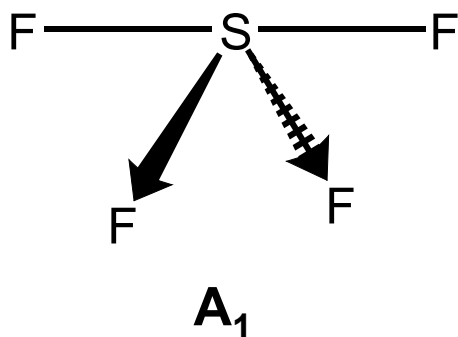
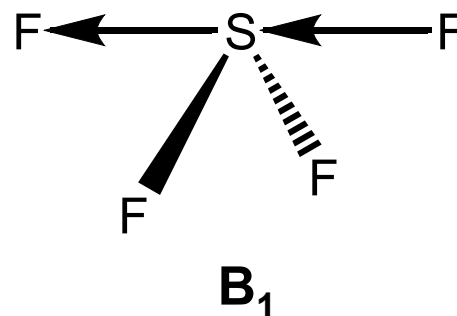
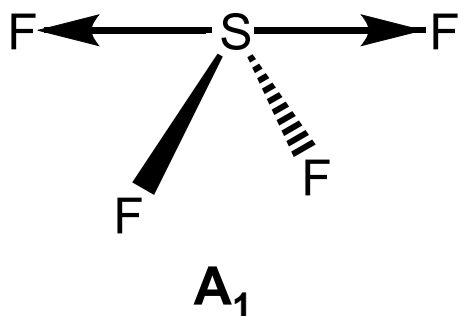
$$n(B_1) = 1/4(4+0+2-2) = 1$$

$$n(B_2) = 1/4(4+0-2+2) = 1$$

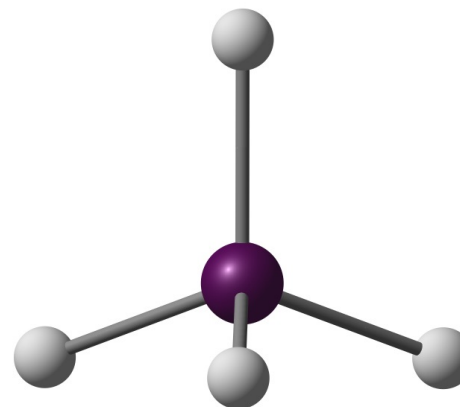
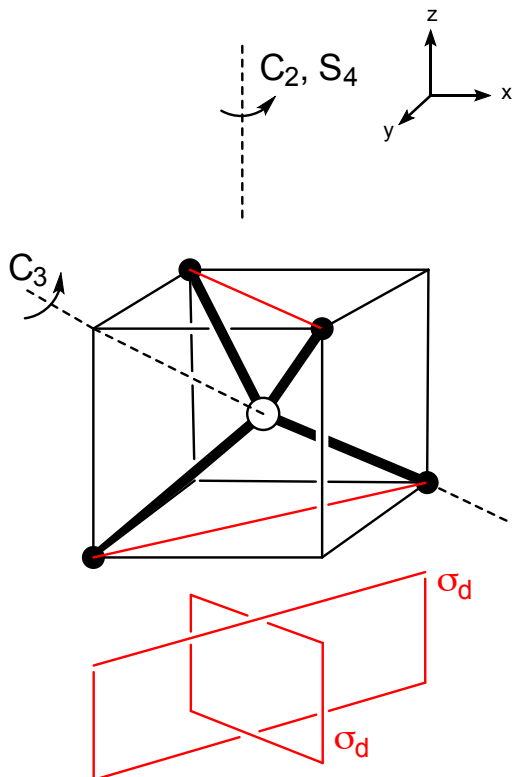
$$\Gamma_{\text{stretch}} = 2A_1 + B_1 + B_2$$

All 4 modes are both IR and Raman active. We can derive the same result by recognising that there are two different sorts of F atom.

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.



CF₄ point group T_d



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)
Γ_{stretch}	4	1	0	0	2		

$$n(i) = \frac{1}{h} \sum_R \chi_r(R) \chi_i(R)$$

Applying the reduction formula:

$$n(A_1) = 1/24 \{(4 \times 1 \times 1) + (1 \times 1 \times 8) + 0 + 0 + (2 \times 1 \times 6)\} = 1$$

$$n(A_2) = 1/24 \{(4 \times 1 \times 1) + (1 \times 1 \times 8) + 0 + 0 - (2 \times 1 \times 6)\} = 0$$

$$n(E) = 1/24 \{(4 \times 2 \times 1) - (1 \times 1 \times 8) + 0 + 0 + 0\} = 0$$

$$n(T_1) = 1/24 \{(4 \times 3 \times 1) + 0 + 0 + 0 - (2 \times 1 \times 6)\} = 0$$

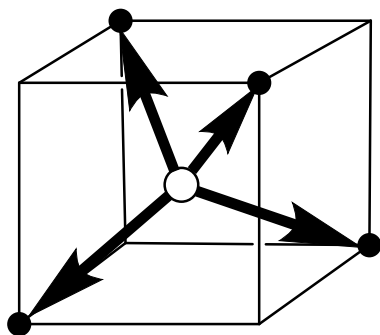
$$n(T_2) = 1/24 \{(4 \times 3 \times 1) + 0 + 0 + 0 + (2 \times 1 \times 6)\} = 1$$

$$\Gamma_{\text{stretch}} = A_1 + T_2$$

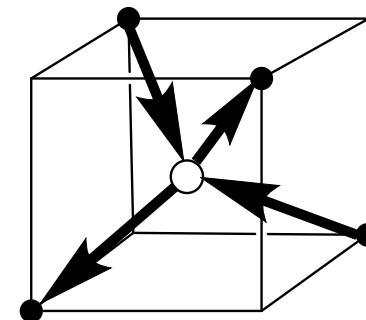
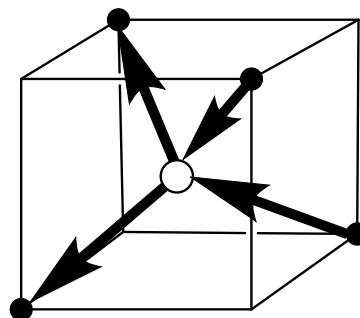
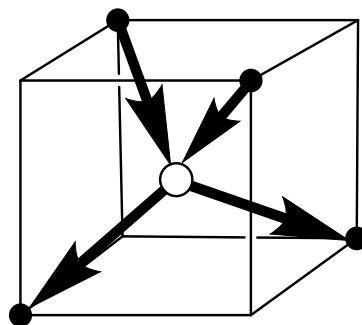
A_1 is only Raman active; T_2 is both IR and Raman active.

The form of the A_1 mode is trivially obvious.

We can sketch the form of the T_2 modes by noting that they are of the same symmetry as p orbitals on the central atom. We use a convention that the displacement vector points toward a + sign on the orbital and a way from a - sign.

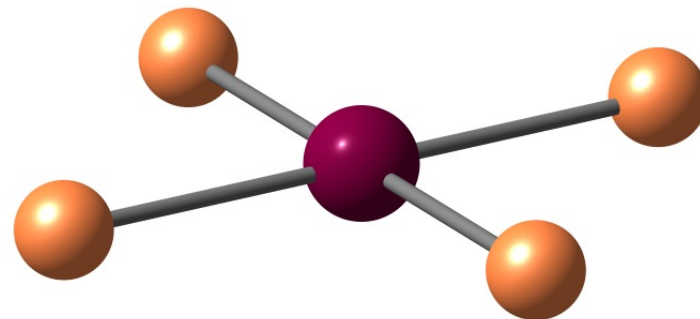
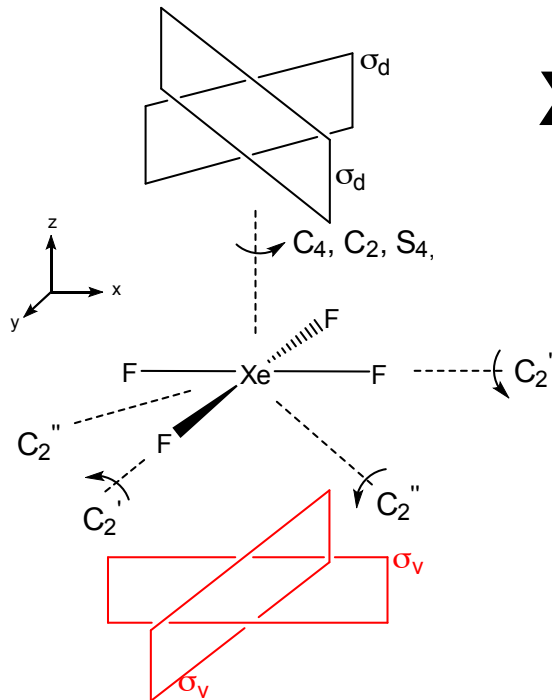


A_1 (R)



T_2 (IR + R)

XeF₄ point group D_{4h}



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	R_z	x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		x^2-y^2
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		
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	(x, y)	
E_u	2	0	-2	0	0	-2	0	2	0	0		
Γ_{stretch}	4	0	0	2	0	0	0	4	2	0		

Application of the reduction formula is tedious in this case but we simplify the calculation somewhat by recognising that the in-plane stretch vector can not possibly generate any irreducible representations that change sign under the σ_h operation. Hence we ignore E_g and the ungerade A and B representations.

$$n(A_{1g}) = 1/16\{(4 \times 1 \times 1) + 0 + 0 + (2 \times 1 \times 2) + 0 + 0 + 0 + (4 \times 1 \times 1) + (2 \times 1 \times 2) + 0\} = 1$$

$$n(A_{2g}) = 1/16\{(4 \times 1 \times 1) + 0 + 0 - (2 \times 1 \times 2) + 0 + 0 + 0 + (4 \times 1 \times 1) - (2 \times 1 \times 2) + 0\} = 0$$

$$n(B_{1g}) = 1/16\{(4 \times 1 \times 1) + 0 + 0 + (2 \times 1 \times 2) + 0 + 0 + 0 + (4 \times 1 \times 1) + (2 \times 1 \times 2) + 0\} = 1$$

$$n(B_{2g}) = 1/16\{(4 \times 1 \times 1) + 0 + 0 - (2 \times 1 \times 2) + 0 + 0 + 0 + (4 \times 1 \times 1) - (2 \times 1 \times 2) + 0\} = 0$$

$$n(E_u) = 1/16\{(4 \times 2 \times 1) + 0 + 0 + 0 + 0 + 0 + 0 + (4 \times 2 \times 1) + 0 + 0\} = 1$$

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

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.

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	R_z	x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
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	(R_x, R_y)	xy
E_g	2	0	-2	0	0	2	0	-2	0	0		
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)	

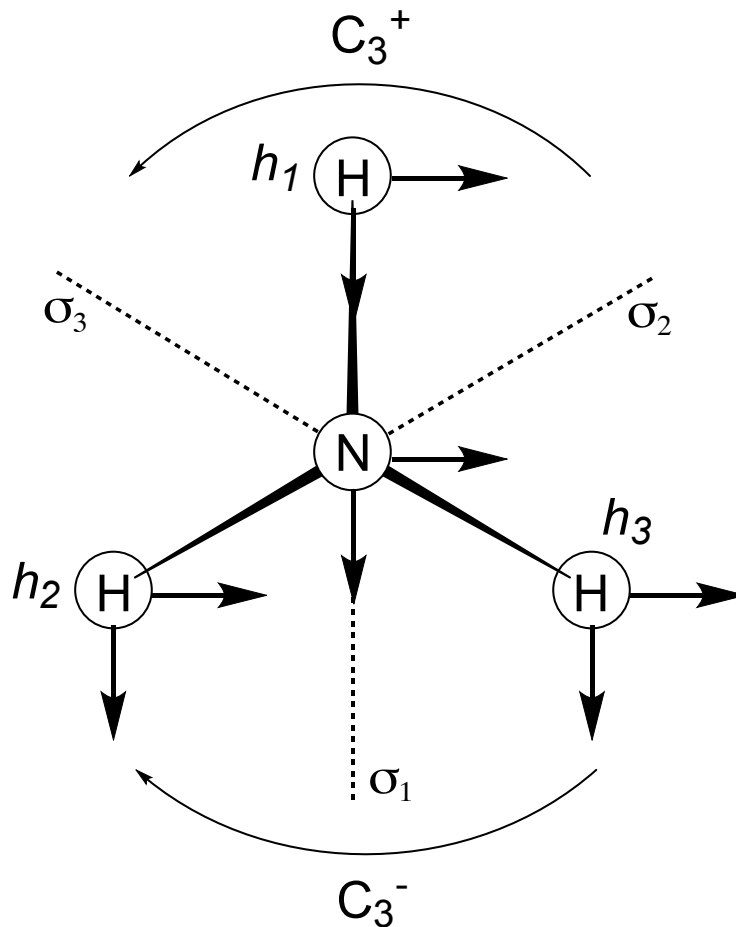
The mutual exclusion rule

In a molecule with inversion symmetry **infrared active** modes transform as x , y and z and are therefore **ungerade**. **Raman active** modes transform as x^2 , xy etc. and are therefore **gerade**.

In a molecule with a centre of symmetry no mode can be active in both infrared and Raman spectroscopy.

The vibrations of NH_3

NH_3 belongs to the point group C_{3v} and 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 4 atoms.



Plan view of the NH_3 with a complete basis set of 3 displacement vectors on each atom. Besides the two vectors seen for each atom, a “z” vector points upward from each atom.

The major new problem encountered with this basis set is the effect of the 3-fold rotation on the vectors (x, y, z) on the N atom. In general if we use $R(\alpha)$ to indicate rotation by an angle α :

$$R(\alpha) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Thus the character for a trio of vectors (x,y,z) under rotation by α is $1+2\cos\alpha$. (If we are dealing with an S type improper rotation, the z vector changes direction so that the character is instead $-1+2\cos\alpha$)

For C_3^+ , $\alpha = 120^\circ$ so that $\cos \alpha = -1/2$ and the trace of the transformation matrix for C_3^+ is $\chi(120^\circ) = 0$. Similarly for C_3^- $\alpha = 240^\circ$ and again $\cos \alpha = -1/2$ and $\chi(240^\circ) = 0$. This illustrates the general point that the character is always the same for two operations of the same class. Thus when dealing with reflections we can choose for convenience the σ_1 mirror plane where two vectors on H_1 and the N atom are unshifted under σ and one changes sign so that the contribution from each atom to $\chi(\sigma)$ is +1. Thus we derive the set of characters shown below:

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	$(x,y) (R_x, R_y)$	$(x^2-y^2, xy) (xz, yz)$
Unshifted atoms	4	1	2		
$\chi(3N)$	12	0	2		

Application of the reduction formula gives:

$$n(a_1) = 1/6\{(12 \times 1 \times 1) + 0 + (2 \times 1 \times 3)\} = 3$$

$$n(a_2) = 1/6\{(12 \times 1 \times 1) + 0 + (2 \times -1 \times 3)\} = 1$$

$$n(e) = 1/6\{(12 \times 2 \times 1) + 0 + 0\} = 4$$

hence:

$$\Gamma(3N) = 3a_1 + 1a_2 + 4e$$

$$\Gamma(\text{trans}) = 1a_1 + 1e$$

$$\Gamma(\text{rot}) = 1a_2 + 1e$$

$$\Gamma(\text{vib}) = 2a_1 + 2e$$

Using a set of 3 stretching vectors it can be quickly shown that:

$$\Gamma(\text{Stretch}) = a_1 + e$$

therefore:

$$\Gamma(\text{Bend}) = a_1 + e$$

Where stretching and bending modes are of the same symmetry, mixing between them is allowed.

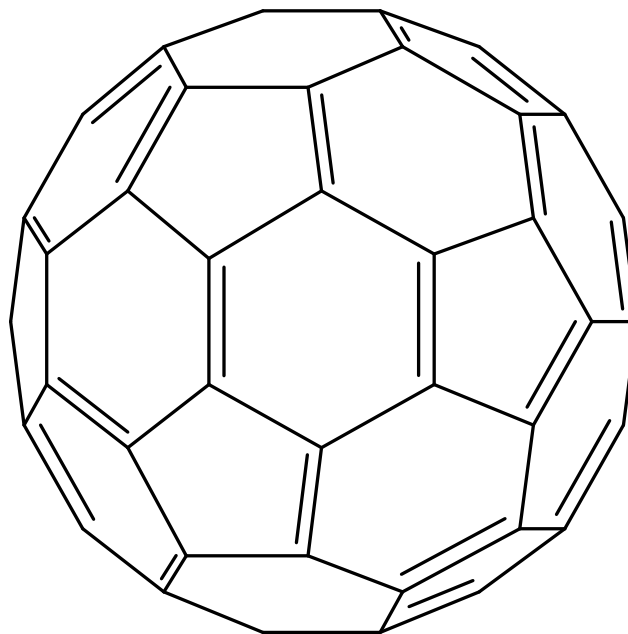
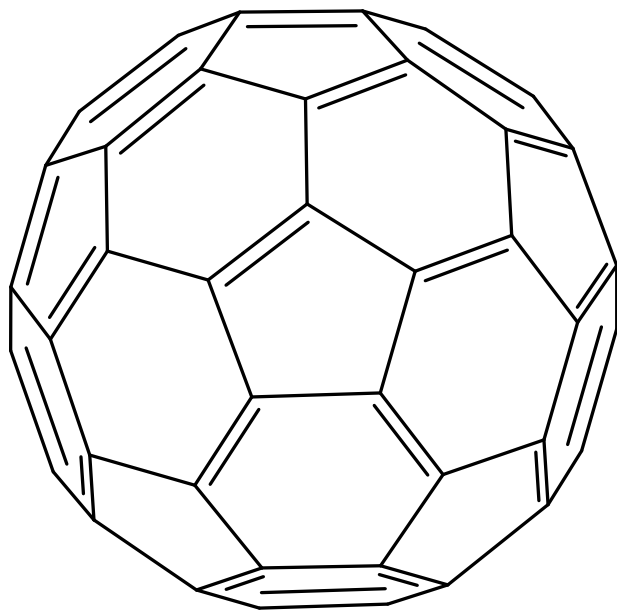
The vibrations of C_{60}

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 of C_{60} by making the simple prediction that the molecule should have only 4 infrared active vibrations.

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 looks particularly unfriendly and contains characters such as $\frac{1}{2}(1 \pm \sqrt{5})$!

The group order is $h=120$ and there are 10 irreducible representations including 4-fold degenerate G representations and five fold degenerate H representations. These degeneracies are not encountered in other molecular point groups.

Nonetheless it turns out to be very easy to derive the normal modes of vibration. This is because **none** of the rotational symmetry axes passes through an atomic position and the character of the basis set of 180 displacement vectors under the rotational operations is zero. The character under inversion i is also zero. The 15 mirror planes each contains 4 atoms so that the character under σ is $[(4 \times 2) - (4 \times 1)] = 4$. The only other operation where a non-zero character appears is under the identity operation, where $\chi(E)=180$. Application of the reduction formula is therefore much less problematic than expected. It transpires that 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	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ	$\eta^{\pm} = 1/2(1\pm\sqrt{5})$	
A_g	1	1	1	1	1	1	1	1	1	1	(R_x, R_y, R_z)	$x^2+y^2+z^2$
T_{1g}	3	η^+	η^-	0	-1	3	η^-	η^+	0	-1		
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		
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	(x, y, z)	$(2z^2-x^2-y^2, x^2-y^2, xy, yz, xz)$
T_{1u}	3	η^+	η^-	0	-1	-3	$-\eta^-$	$-\eta^+$	0	1		
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		
Γ_{3N}	180	0	0	0	0	0	0	0	0	4		

$$\begin{aligned}
 n(A_g) &= 1/120\{(1 \times 180) + (4 \times 15)\} = 2 \\
 n(T_{1g}) &= 1/120\{(3 \times 180) - (4 \times 15)\} = 4 \\
 n(T_{2g}) &= 1/120\{(3 \times 180) - (4 \times 15)\} = 4 \\
 n(G_g) &= 1/120\{(4 \times 180) + (0 \times 15)\} = 6 \\
 n(H_g) &= 1/120\{(5 \times 180) + (4 \times 15)\} = 8
 \end{aligned}$$

$$\begin{aligned}
 n(A_u) &= 1/120\{(1 \times 180) - (4 \times 15)\} = 1 \\
 n(T_{1u}) &= 1/120\{(3 \times 180) + (4 \times 15)\} = 5 \\
 n(T_{2u}) &= 1/120\{(3 \times 180) + (4 \times 15)\} = 5 \\
 n(G_u) &= 1/120\{(4 \times 180) + (0 \times 15)\} = 6 \\
 n(H_u) &= 1/120\{(5 \times 180) - (4 \times 15)\} = 7
 \end{aligned}$$

$$\text{No. of g functions} = 2 + 4 \times 3 + 4 \times 3 + 6 \times 4 + 8 \times 5 = 90$$

$$\text{No. of u functions} = 1 + 5 \times 3 + 5 \times 3 + 6 \times 4 + 7 \times 5 = 90$$

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

$$\Gamma_{\text{trans}} = T_{1u}$$

$$\Gamma_{\text{rot}} = T_{1g}$$

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

FOUR IR ACTIVE MODES: $4T_{1u}$

TEN RAMAN ACTIVE MODES: $2A_g + 8H_g$