

LECTURE 2

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

2.1 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.

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. 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:

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

The above 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.** This idea is developed in the context of d orbitals in section 2.3.

2.2 The explicit form of atomic orbital wavefunctions

The wavefunction for any atomic orbital may be written in terms of polar co-ordinates 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:

$$\begin{aligned}x &= r \sin\theta \cos\phi \\y &= r \sin\theta \sin\phi \\z &= r \cos\theta\end{aligned}$$

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.

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

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.

2.3 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.

$$\begin{array}{llll}
 \mathbf{C}_3 & x \rightarrow y & xy & \rightarrow yz \\
 & y \rightarrow z & yz & \rightarrow zx = xz \\
 & z \rightarrow x & xz & \rightarrow yx = xy \\
 & & x^2 - y^2 & \rightarrow y^2 - z^2 \\
 & & 3z^2 - (x^2 + y^2 + z^2) & \rightarrow 3x^2 - (y^2 + z^2 + x^2)
 \end{array}$$

But:

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

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:

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

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?

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

$$\begin{array}{lllll}
 \mathbf{C}_2 & x \rightarrow -x & xy & \rightarrow +xy & +1 \\
 & y \rightarrow -y & yz & \rightarrow -yz & -1 \\
 & z \rightarrow z & xz & \rightarrow -xz & -1 \\
 & & x^2 - y^2 & \rightarrow x^2 - y^2 & +1 \\
 & & 3z^2 - (x^2 + y^2 + z^2) & \rightarrow 3z^2 - (x^2 + y^2 + z^2) & +1 \\
 & & & & \chi(\mathbf{C}_2) = +1
 \end{array}$$

$$\begin{array}{lllll}
 \mathbf{S}_4 & x \rightarrow -y & xy & \rightarrow -xy & -1 \\
 & y \rightarrow +x & yz & \rightarrow -xz & 0 \\
 & z \rightarrow -z & xz & \rightarrow yz & 0 \\
 & & x^2 - y^2 & \rightarrow y^2 - x^2 & -1 \\
 & & 3z^2 - (x^2 + y^2 + z^2) & \rightarrow 3z^2 - (x^2 + y^2 + z^2) & +1 \\
 & & & & \chi(\mathbf{S}_4) = -1
 \end{array}$$

$$\begin{array}{llllll}
 \sigma_d & x \rightarrow -y & xy & \rightarrow & xy & +1 \\
 & y \rightarrow -x & yz & \rightarrow & -xz & 0 \\
 & z \rightarrow z & xz & \rightarrow & -yz & 0 \\
 & & x^2-y^2 & \rightarrow & y^2-x^2 & -1 \\
 & & 3z^2-(x^2+y^2+z^2) & \rightarrow & 3z^2-(x^2+y^2+z^2) & +1 \\
 & & & & & \chi(\sigma_d) = +1
 \end{array}$$

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

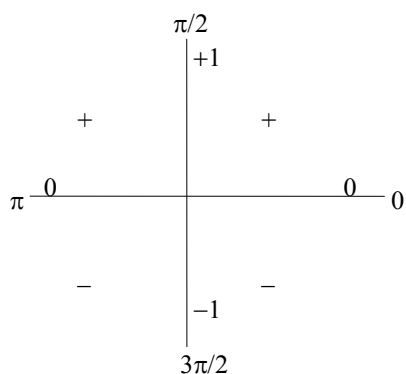
Hence by inspection or by application of the reduction formula we see that the d orbitals transform as $T_2 + E$ in T_d . Symmetry considerations do not allow us to predict whether e or t_2 orbital will be lower in energy in a T_d environment.

2.4 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 $\alpha=2\pi/3$.

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

	$p \quad \ell=1$	$d \quad \ell=2$	$f \quad \ell=3$
$C_2 \quad \alpha=\pi$	-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


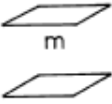
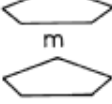
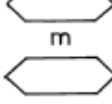





By inspection or by application of the reduction formula we see that:

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

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

2.5 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}	D_{4h}	D_{5h}	D_{6h}
				
d_{z^2}	 a_1'	a_{1g}	a_1'	a_{1g}
d_{yz}		e_g	e_1''	e_{1g}
d_{xz}	 e''			
d_{xy}		b_{2g}	e_2'	e_{2g}
$d_{x^2-y^2}$	 e'	b_{1g}		

2.6 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

2.7 Jahn-Teller Theorem

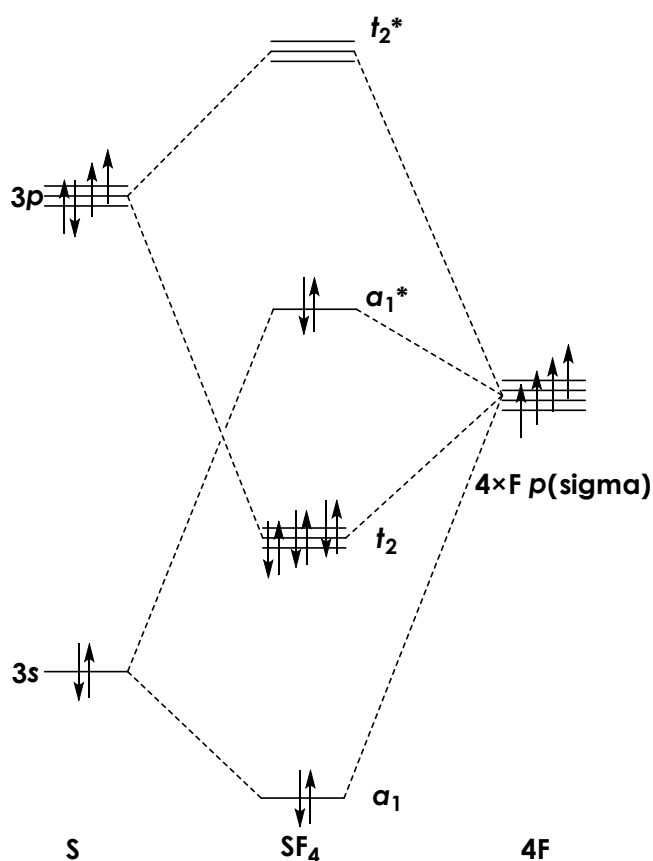
A system with an orbitally degenerate ground state must distort so as to relieve the degeneracy.

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

2.8 "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 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 orbital (the HOMO) can mix with one of the t_2 components (the LUMO). 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	$B_2 + E$	$A_1 + E$	$A_1 + B_1 + B_2$

PROBLEMS

1. Using the expression $\chi(\alpha) = \sin\{(\ell+1/2)\alpha\}/\sin\{\alpha/2\}$, evaluate the character of d orbitals under the rotational operations of D_3 , D_4 and D_5 . By application of the reduction formula, deduce the pattern of ligand field splitting of the d orbitals in these point groups. Comment on your results.
2. 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.