Correlation Diagrams

C734b 2008

Spin Postulate

An electron possesses an intrinsic angular momentum in addition to its normal orbital angular momentum $\mathbf{L} \equiv \mathbf{S}$

Electrons exhibit a magnetic moment $\vec{\mu}$ where

$$\vec{\mu} = -g_e \vec{S}\left(\frac{\mu_B}{\hbar}\right) = -g_e \vec{S}\left(\frac{e}{2m_e}\right)$$

where m_e ≡ mass of the electron and μ_B ≡ Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e} = 0.9274 \times 10^{-23} \, \text{JT}^{-1}$$

s = ½ for electrons and g_e =2.00232

S is an angular momentum like **L** with components S_x, S_y and S_z and associated self-adjoint operators:

$\hat{S}_x, \hat{S}_y, \hat{S}_z, \hat{S}^2$ which obey similar commutation relationships as $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$

$\hat{S}_x, \hat{S}_y, \hat{S}_z$ all commute with $\hat{S}^2$ but not with each other

Only one component, say $\hat{S}_z$ can have a common set of eigenfunctions with $\hat{S}^2$

Note: $\hat{S}_x, \hat{S}_y, \hat{S}_z, \hat{S}^2$ ≠ f(x, y, z) which means they commute with $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$

Total angular momentum of electrons ≡ $\vec{J} = \vec{L} + \vec{S}$ where $\hat{J}_i, \hat{J}^2$ obey similar

commutation relationships as $\hat{L}_i, \hat{L}^2$

For *any* angular momentum $\vec{A}$

Can define raising and lowering operators $\hat{A}^+, \hat{A}^-$ as

$$\hat{A}^+ = \hat{A}_x + i\hat{A}_y$$

$$\hat{A}^- = \hat{A}_x - i\hat{A}_y$$

Let the eigenfunctions of $\hat{A}^2$ and $\hat{A}_z$ be $|j_a, m_a\rangle$ with eigenvalues $j_a(j_a + 1)\hbar^2$ and $m_a\hbar$ respectively.

m_a ranges from $-j_a$ to $+j_a$ in integer steps.

Can show that: $\hat{A}^\pm |j_a, m_a\rangle = \hbar\sqrt{j_a(j_a + 1) - m_a(m_a \pm 1)}|j_a, m_a \pm 1\rangle$

Since $\vec{s} = \dfrac{1}{2}$ for electrons $\left\langle s^2 \right\rangle = s(s+1)\hbar^2 = \dfrac{3}{4}\hbar^2$ and $\left\langle m_s \right\rangle = m_s\hbar = \pm\dfrac{1}{2}\hbar$

The two spin eigenvectors are: $\left| s, m_s \right\rangle = \left| \dfrac{1}{2}, \dfrac{1}{2} \right\rangle \equiv \alpha$ (spin up)

and $\left| s, m_s \right\rangle = \left| \dfrac{1}{2}, -\dfrac{1}{2} \right\rangle \equiv \beta$ (spin down)

$$\left\langle \dfrac{1}{2}, \pm\dfrac{1}{2} \middle| \dfrac{1}{2}, \pm\dfrac{1}{2} \right\rangle = 1 \qquad \text{and} \qquad \left\langle \dfrac{1}{2}, \pm\dfrac{1}{2} \middle| \dfrac{1}{2}, \mp\dfrac{1}{2} \right\rangle = 0$$

Spin functions are orthonormal: normalized and orthogonal.

Spherical Symmetry for many electron atoms (N)

Hamiltonian is given by: $\hat{H} = \hat{H}_o + \hat{H}_{ee} + \hat{H}_{\vec{L}\cdot\vec{S}}$

$\hat{H}_o \equiv$ kinetic energy of electrons and the e$^-$ - nucleus interactions

If $\hat{H} = \hat{H}_o$ alone $\Rightarrow \psi(1,2,\cdots,N) = \psi(1)\psi(2)\cdots\psi(N)$

with each one e$^-$ state characterized by 4 quantum numbers, n, ℓ, m_ℓ, m_s

$\hat{H}_{ee} \equiv$ electron – electron interaction which couples angular momenta of the individual electrons in 2 possible ways

Low "Z" elements (Z ~< 40)

$$\vec{L} = \sum_i \vec{\ell}_i \qquad \vec{S} = \sum_i \vec{s}_i$$

Spin-orbit interactions couples $\vec{L}$ and $\vec{S}$ to form $\vec{J} = \vec{L} + \vec{S}$

$\equiv$ **Russell-Saunders coupling**

High "Z" elements (Z > 40)

Orbital and spin angular momenta of each electron couples first:

$\vec{j}_i = \vec{\ell}_i + \vec{s}_i$ $\equiv$ total angular momenta of each individual electron.

These then couple to total $\vec{J} = \sum_i \vec{j}_i$

$\equiv$ **j-j coupling**

Note: can have intermediate coupling for intermediate Z although L-S (Russell-Saunders) scheme is often used as a first approximation.

Note: For low Z $\hat{H}_{ee} > \hat{H}_{\vec{L}.\vec{S}}$

For high Z $\hat{H}_{ee} < \hat{H}_{\vec{L}.\vec{S}} \because \vec{L} \cdot \vec{S} \sim \alpha^2 Z^2$

$\alpha^2 \equiv$ fine-structure constant $= 7.29735 \times 10^{-3} \sim 1/137$

Coupled energy states in Russell-Saunders coupling are called **multiplets** and these are described by spectral terms of the form ^{2S+1}L

$$L = \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad \cdots$$
$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$
$$S \quad P \quad D \quad F \quad G \quad \cdots$$

spin multiplicity $\equiv 2S+1$

How to get L or S?

Given any angular momenta $\vec{A}_1$ and $\vec{A}_2$

$$\vec{A} = A_1 + A_2,\, A_1 + A_2 - 1, \cdots \left| A_1 - A_2 \right|$$

$$m_a = -A, -A + 1, \cdots, +A$$

If there are > 2 angular momenta, couple A_1 and $A_2 \rightarrow A_{12}$, then $A_{12} + A \rightarrow A_{123}$, etc.

The effect of spin-orbit interactions is to split the multiplets into their components with term symbols: $^{2S+1}L_J$

Spin-orbit splitting: $\Delta E_{\bar{L}\cdot\bar{S}} = \dfrac{1}{2}\xi(L,S)\left[J(J+1)-L(L+1)-S(S+1)\right]$

where $\xi(L,S)$ ≡ spin-orbit coupling constant > 0 for < ½-filed shells

$\rightarrow$ smallest J lies lowest in energy

If ξ < 0 for > ½-filled shells $\rightarrow$ largest J lies lowest in energy

≡ Hund's third rule

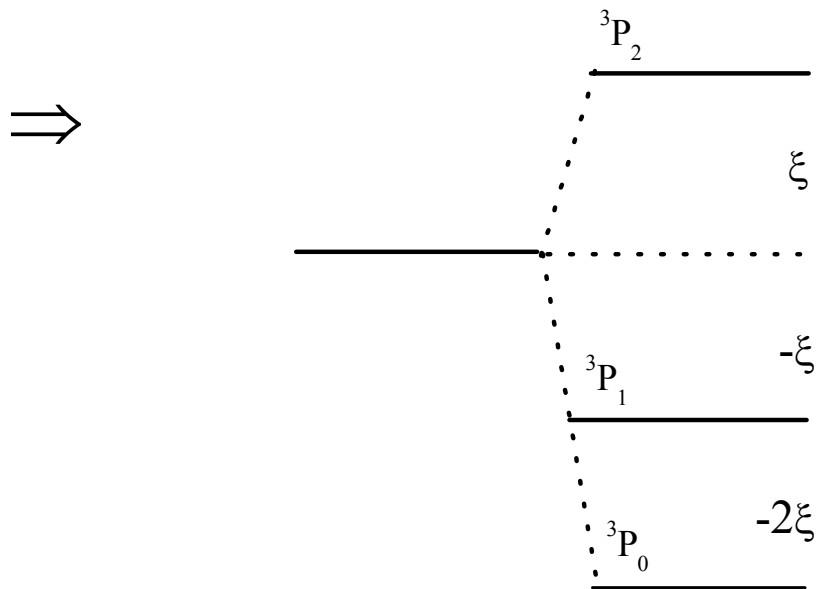**Example:** (ns)^1(np)^1 configuration $\quad \ell_1 = 0;\ \ell_2 = 1 \quad \Rightarrow \quad L = 1$

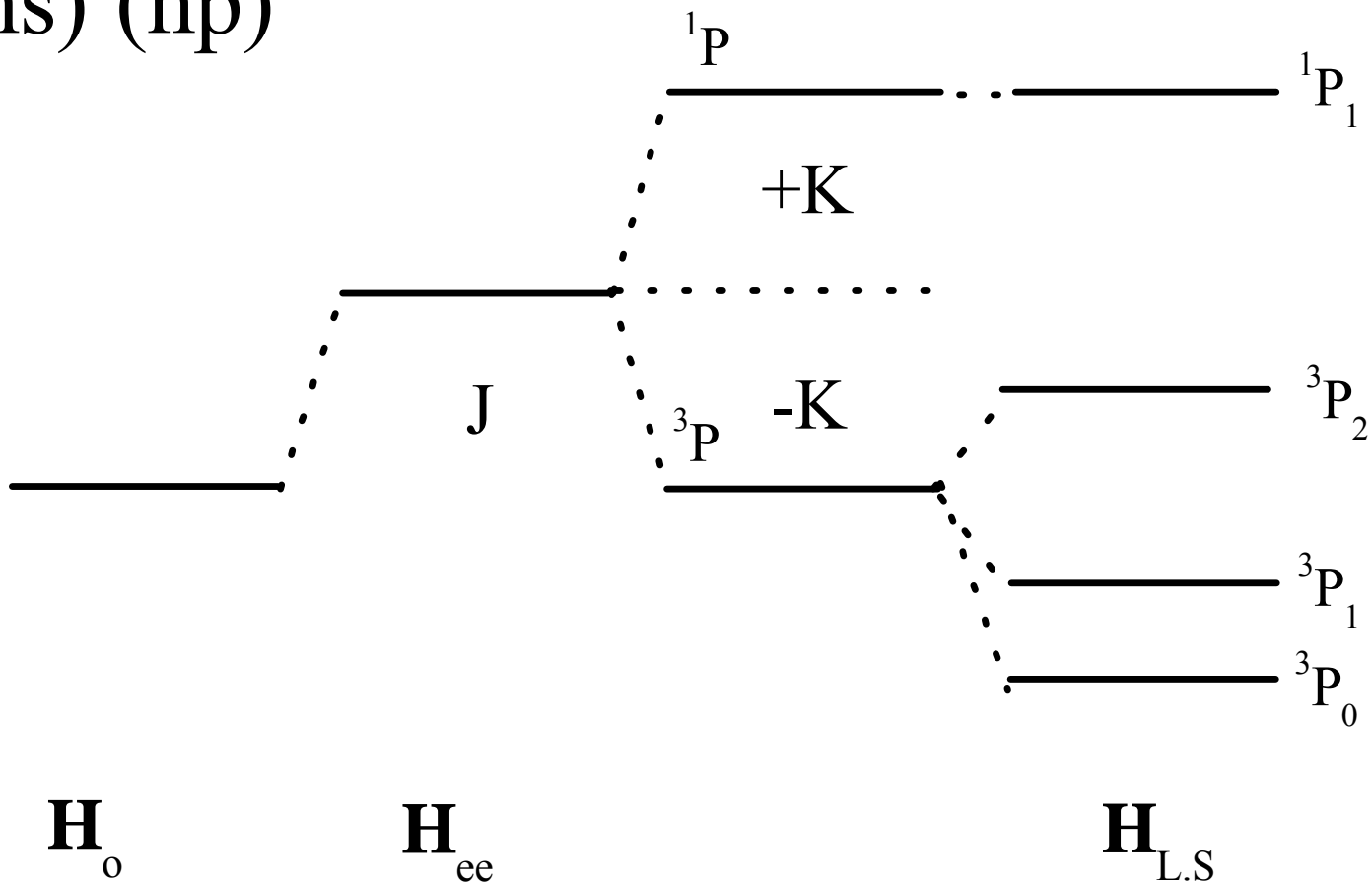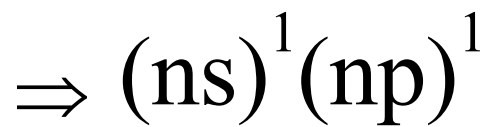$s_1 = \frac{1}{2};\ s_2 = \frac{1}{2} \quad \Rightarrow \quad S = 1, 0$

$\Rightarrow$ terms are ^3P, ^1P

When S = 0, L = 1, J = 1 $\quad \Rightarrow \quad ^1P_1$

When S = 1, L = 1, J = 2,1,0 $\quad \Rightarrow \quad ^3P_{2,1,0}$

$\Rightarrow$

$^3P_2$ ξ

$^3P_1$ $-\xi$

$^3P_0$ -2ξ

-$\mathbf{H}_{ee}$ has 2 parts: a Coulomb repulsion J and an exchange interaction $\pm K$ which is non-classical and is a consequence of the Pauli-Exclusion Principle which requires the total wave function to be antisymmetric with respect to the interchange of two spin ½ particles (electrons which are fermions).

$\Rightarrow (ns)^1(np)^1$

^1P

$^1P_1$

$+K$

J

^3P $-K$

$^3P_2$

$^3P_1$

$^3P_0$

$\mathbf{H}_o$ $\mathbf{H}_{ee}$ $\mathbf{H}_{L.S}$

Intermediate Crystal Fields (low Z elements)

Let $\mathbf{H}_{CF} \equiv$ term in the Hamiltonian which describes the electrostatic interaction with the surrounding ions or ligands.

if $\quad \hat{H}_{CF} > \hat{H}_{ee} \Rightarrow \quad$ strong crystal field

if $\quad \hat{H}_{ee} > \hat{H}_{CF} > \hat{H}_{\vec{L}\cdot\vec{S}} \Rightarrow \quad$ intermediate crystal field

if $\quad \hat{H}_{CF} < \hat{H}_{\vec{L}\cdot\vec{S}} \Rightarrow \quad$ weak crystal field

-Consider an atomic term with angular momentum $\mathbf{L}$. A representation, D_L, for any group of proper rotations can be found using angular momentum eigenfunctions: spherical harmonics $\{Y_L^M\}$ as a 2L+1 degenerate basis set.

Note: here D_L instead of Γ_L is used for historical reasons.

Can show:
$$\hat{R}(\alpha)Y_L^M(\theta,\varphi) = Y_L^M\left(R^{-1}\{\theta,\varphi\}\right)$$

$$= Y_L^M(\theta, \varphi - \alpha) = e^{-iM\alpha}Y_L^M(\theta,\varphi)$$

This means each member is transformed into itself multiplied by a numerical coefficient $e^{-iM\alpha}$

$$\therefore D_L(\alpha) = \begin{pmatrix} e^{-iL\alpha} & 0 & \cdots & 0 \\ 0 & e^{-i(L-1)\alpha} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & e^{iL\alpha} \end{pmatrix}$$

$$\Rightarrow \chi(D_L(\alpha)) = e^{-iL\alpha}\sum_{p=0}^{2L} e^{i\alpha\alpha} \qquad = e^{-iL\alpha}\frac{\left(e^{i(2L+1)\alpha}-1\right)}{e^{i\alpha}-1} \qquad \times \frac{e^{-\frac{i\alpha}{2}}}{e^{-\frac{i\alpha}{2}}}$$

a geometric progression

$$\Rightarrow \chi(D_L(\alpha)) = \frac{\sin\left[\dfrac{(2L+1)\alpha}{2}\right]}{\sin\left(\dfrac{\alpha}{2}\right)}$$

Can calculate the character system for any group of rotations for any L, and if reducible, can do this in the usual way into a direct sum of IRs

Note: for $\chi(E)$ As $\alpha \to 0$ $\displaystyle\lim_{\alpha\to0} \frac{\sin\dfrac{[(2L+1)\alpha]}{2}}{\sin\left(\dfrac{\alpha}{2}\right)} = \lim_{\alpha\to0}\frac{(2L+1)\alpha}{\alpha} = 2L+1$

Splitting of states of angular momentum L
in an intermediate crystal field

$$\chi\left[D_L(\alpha)\right] = \frac{\sin\left[(L+\tfrac{1}{2})\alpha\right]}{\sin\left(\tfrac{1}{2}\alpha\right)}$$

Therefore :-

$$\chi(C_2) = \frac{\sin\left[(L+\tfrac{1}{2})\pi\right]}{\sin\left(\tfrac{1}{2}\pi\right)} = (-1)^L$$

$$\chi(C_3) = \frac{\sin\left[(L+\tfrac{1}{2})\tfrac{2}{3}\pi\right]}{\sin(\pi/3)} = \begin{cases} 1 & \text{for } L = 0, 3, \cdots \\ 0 & \text{for } L = 1, 4, \cdots \\ -1 & \text{for } L = 2, 5, \cdots \end{cases}$$

$$\chi(C_4) = \frac{\sin\left[(L+\tfrac{1}{2})\tfrac{\pi}{2}\right]}{\sin(\pi/4)} = \begin{cases} 1 & \text{for } L = 0, 1, 4, 5, \cdots \\ -1 & \text{for } L = 2, 3, 6, 7, \cdots \end{cases}$$

$$\chi(E) = 2L + 1$$

State	D_L	Direct sum in cubic field
S	D_0	A_1
P	D_1	T_1
D	D_2	$E \oplus T_2$
F	D_3	$A_2 \oplus T_1 \oplus T_2$
G	D_4	$A_1 \oplus E \oplus T_1 \oplus T_2$

The splitting of states in lower symmetries is
given in correlation tables an example of which
is in Table

16

Table shows $\chi(D_L)$ for $\alpha = \pi/2$, $2\pi/3$, and π and the splitting of the free ion states in O_h symmetry for $L \geq 2$

Splittings in lower symmetries deduced from correlation tables, or
by finding direct sums using common classes in both groups.

Parity

If inversion, i, is a group operation then the wave function ψ will have definite parity.

Parity $\equiv$ eigenvalue of the inversion operator.

$$\hat{i}\,\psi = \lambda\psi = \pm\psi$$

If $\qquad \hat{i}\,\psi = +\psi \implies$ even or gerade $\equiv$ g-parity

If $\qquad \hat{i}\,\psi = -\psi \implies$ odd or ungerade $\equiv$ u-parity

The parity of $\quad Y_\ell^m(\theta, \varphi) = (-1)^\ell$

$$
\begin{array}{ccccc}
 & & s & p & d & f \\
\Rightarrow & \ell = & 0 & 1 & 2 & 3 \\
 & \text{parity} = & +1 & -1 & +1 & -1
\end{array}
$$

For several electrons: $\quad \psi(1, 2, 3, \ldots, N) = \psi(1)\psi(2)\cdots\psi(N)$

$$
\text{parity} = \prod_i (-1)^{\ell_i} = (-1)^{\sum_i \ell_i}
$$

This means the parity is determined by the electron configuration, **NOT** on the total orbital angular momentum, L.

Example: $\text{nsnp} \Rightarrow \text{parity} = (-1)^{0+1} = -1 \Rightarrow$ all terms are u $-$ states

$$\text{nd}^2 \Rightarrow \text{parity} = (-1)^{2+2} = +1 \Rightarrow \text{all terms are g} - \text{states}$$

$$\text{npn'p} \Rightarrow \text{parity} = (-1)^{1+1} = +1 \Rightarrow \text{all terms are g} - \text{states}$$

Now, if $i \in G$ and the parity is even $\Rightarrow \chi\left[D_L^{+}(iIR)\right] = \chi\left[D_L^{+}(IR)\right]$

If the parity is odd $\Rightarrow \chi\left[D_L^{-}(iIR)\right] = -\chi\left[D_L^{-}(IR)\right]$

Character table will have the form given by the following example for O_h

$$O_h = O \otimes C_i$$

O_h	$\{O\}$	$i\{O\}$
$\Rightarrow$ g	$\chi(O)$	$\chi(O)$
u	$\chi(O)$	$-\chi(O)$

Therefore, need only consider $\{O\}$ and work out parities later.

Example:

a) Into what states does the Russell-Saunders term d^2:^3F split in O_h symmetry?
b) What is the effect of a D_3 trigonal distortion?

a) $^3F \rightarrow L = 3, S = 1$. Since S is unaffected by electrostatic fields
(only by magnetic fields), triplet terms in the free ion remain triplets in O_h symmetry

  Parity $= (-1)^{2+2} = +1 \rightarrow$ g terms.

  From table given for D_L $L = 3$: states are $^3A_{2g}$, $^3T_{1g}$, $^3T_{2g}$

b) Select classes that are common to both groups and reduce the IR from the
group of higher symmetry in the group of lower symmetry

From character tables:

O	E	$8C_3$	$6C_2'$
A_2	1	1	-1
T_1	3	0	-1
T_2	3	0	1

D_3	E	$2C_3$	$3C_2'$
A_1	1	1	1	← actual character table
A_2	1	1	-1
E	2	-1	0

Find from reduction:

O	D_3
A_2	A_2
T_1	$A_2 \oplus E$
T_2	$A_1 \oplus E$

This is the way correlation tables are derived. Procedure can be used if such tables are not available.

This table shows how the representations of O_h are re-labelled or reduced when the symmetry is lowered. For a more extensive set see Table X-14 in Molecular Vibrations by E.B. Wilson, Jr., J.C. Decius, and P.C. Cross, McGraw Hill, New York, 1955.

O_h	O	T_d	D_{4h}	D_{2d}	C_{4v}	C_{2v}	D_{3d}	D_3	C_{2h}
A_{1g}	A_1	A_1	A_{1g}	A_1	A_1	A_1	A_{1g}	A_1	A_g
A_{2g}	A_2	A_2	B_{1g}	B_1	B_1	A_2	A_{2g}	A_2	B_g
E_g	E	E	$A_{1g}+B_{1g}$	A_1+B_1	A_1+B_1	A_1+A_2	E_g	E	A_g+B_g
T_{1g}	T_1	T_1	$A_{2g}+E_g$	A_2+E	A_2+E	$A_2+B_1+B_2$	$A_{2g}+E_g$	A_2+E	A_g+2B_g
T_{2g}	T_2	T_2	$B_{2g}+E_v$	B_2+E	B_2+E	$A_1+B_1+B_2$	$A_{1g}+E_g$	A_1+E	$2A_g+B_g$
A_{1u}	A_1	A_2	A_{1u}	B_1	A_2	A_2	A_{1u}	A_1	A_u
A_{2u}	A_2	A_1	B_{1u}	A_1	B_2	A_1	A_{2u}	A_2	B_u
E_u	E	E	$A_{1u}+B_{1u}$	A_1+B_1	A_2+B_2	A_1+A_2	E_u	E	A_u+B_u
T_{1u}	T_1	T_2	$A_{2u}+E_u$	B_2+E	A_1+E	$A_1+B_1+B_2$	$A_{2u}+E_u$	A_2+E	A_u+2B_u
T_{2u}	T_2	T_1	$B_{2u}+E_u$	A_2+E	B_1+E	$A_2+B_1+B_2$	$A_{1u}+E_u$	A_1+E	$2A_u+B_u$

Strong Crystal Fields

-one where electrostatic interactions due to ion surrounding > electron-electron interactions in ion.

$\implies$ Consider the effect on **free ion electron configurations** and deduce states and their degeneracies

Later: will correlate "strong" to "intermediate CFs.

In O_h symmetry 5d orbitals $\rightarrow$ t_{2g} (d_{xy}, d_{yz}, d_{xz}) + e_g (d_{z2}, d_{x2-y2}) and $E(t_{2g}) < E(e_g)$ since these orbitals "point" at the ligands.

Opposite scenario occurs in T_d symmetry where $E(e_g) < E(t_{2g})$

To determine states in a strong field, use **Bethe's method of Descending Symmetry**

Method based on:
(i) Electrostatic fields don't affect spin

(ii) If $\psi(1,2) = \psi^i(1)\psi^j(2)$ and $\psi^i(1)$ forms a basis for Γ_i and $\psi^j(2)$ forms a basis for Γ_j means $\psi^i(1)\psi^j(2)$ forms a basis for the direct product $\Gamma^i \otimes \Gamma^j$

Due to Pauli Exclusion Principle:
(1) 2 electrons in the same orbital generates a singlet state only.
(2) 2 electrons in different orbitals generates a singlet and a triplet state.

Example:

Find all states that forma d^2 configuration in a strong field of O_h symmetry. Correlate with those of the free ion and those of an ion in an intermediate field.

Configurations are $(t_{2g})^2$, $(t_{2g})^1(e_g)^1$ and $(e_g)^2$

Parity of d^2 terms $\equiv g$.
Simply use O character table to reduce direct products

O character table:

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

Consider $(e_g)^2 \rightarrow 6$ states:
2 singlets when the 2 electrons in the same e_g orbital, and 1 singlet and 1 triplet when they are in different e_g orbitals

6 state functions are contained in the direct product of $e_g \otimes e_g$

$e_g \otimes e_g$ reduces in O to $a_1 \oplus a_2 \oplus e$

Don't know which are singlets and triplets.

Bethes's method is to lower the symmetry until all representations **in the direct product** are one-dimensional

Examine the Correlation Tables

In D_{4h} symmetry: $A_{1g} \rightarrow A_{1g}$; $A_{2g} \rightarrow B_{1g}$; $E_g \rightarrow A_{1g} + B_{1g}$

$\therefore$ $e_{1g} \rightarrow a_{1g} + b_{1g}$ orbitals; that is, they split.

$$\therefore e_g^2 \rightarrow a_{1g}^2 \rightarrow {}^1A_{1g}$$

$$\rightarrow a_{1g}^1 b_{1g}^1 \rightarrow {}^1B_{1g}, {}^3B_{1g}$$

$$\rightarrow b_{1g}^2 \rightarrow {}^1A_{1g}$$

Since the electrostatic field does not affect spin means that the ${}^3B_{1g}$ state in D_{4h} must have come from ${}^3A_{2g}$ state in O_h.
All other states must be singlets.

$\Longrightarrow$ in O_h $d^2 \rightarrow {}^1A_{1g}, {}^3A_{2g}, {}^1E_g$

Total degeneracy = 6 as expected (= (2S+1)x state degeneracy = 1x1 + 3x1 +1x2)

Next: do t_{2g}^2 configuration in O_h

Reduce in C_{2h}

$$t_{2g} \otimes t_{2g} = a_{1g} \oplus e_g \oplus t_{1g} \oplus t_{2g}$$

$$
\begin{array}{cccc}
a_g & a_g & a_g & a_g \\
 & \oplus & \oplus & \oplus \\
 & b_g & b_g & a_g \\
 & & \oplus & \oplus \\
 & & b_g & b_g
\end{array}
$$

$$\therefore t_{2g} \otimes t_{2g} \left(O_h\right) \rightarrow \left(a_g \oplus a_g \oplus b_g\right) \otimes \left(a_g \oplus a_g \oplus b_g\right) \left(C_{2h}\right)$$

Put in 2 electrons:

$$a_g^2(1) \to {}^1A_g$$

$$a_g^1(1)a_g^1(2) \to {}^1A_g, {}^3A_g$$

$$a_g^1(1)b_g^1 \to {}^1B_g, {}^3B_g$$

$$a_g^1(2)b_g^1 \to {}^1B_g, {}^3B_g$$

$$a_g^2(2) \to {}^1A_g$$

$$b_g^2 \to {}^1A_g$$

We are looking for triplet state(s) in C_{2h} that transform as ${}^3A_g \oplus {}^3B_g \oplus {}^3B_g$

In O_h this **must** be the T_{1g} state

Therefore, states are: ${}^1A_{1g} \oplus {}^1E_g \oplus {}^3T_{1g} \oplus {}^1T_{2g}$ in O_h

Total degeneracy = 1x1 + 1x2 + 3x3 + 1x3 = 15

Lastly: $t_{2g}^1 e_g^1$.

Method of descending symmetry is not necessary since both singlets and triplets are allowed (t_{2g}, e_g are different orbitals)

$$t_{2g} \otimes e_g \rightarrow t_{1g} \oplus t_{2g} \text{ in } O_h$$

Therefore, states are: $^1T_{1g}, {}^3T_{1g}, {}^1T_{2g}, {}^3T_{2g}$

Total degeneracy = 1x3 + 3x3 + 1x3 + 3x3 = 24

Application of the method of descending symmetry to the configuration d^2 in O_h symmetry.

Point Group	Config-uration	Direct Product Representation	Irreducible Representations	Allowed States	Degen-eracy
O_h	e_g^2	$E_g \otimes E_g$	$A_{1g} \oplus A_{2g} \oplus E_g$		6
D_{4h}			$A_{1g} \quad B_{1g} \quad A_{1g} \oplus B_{1g}$		
	a_{1g}^2	$A_{1g} \otimes A_{1g}$	A_{1g}	$^1A_{1g}$	
	$a_{1g}b_{1g}$	$A_{1g} \otimes B_{1g}$	B_{1g}	$^1B_{1g} \quad ^3B_{1g}$	
	b_{1g}^2	$B_{1g} \otimes B_{1g}$	A_{1g}	$^1A_{1g}$	
O_h				$^1A_{1g} \quad ^3A_{2g} \quad ^1E_g$	6
O_h	t_{2g}^2	$T_{2g} \otimes T_{2g}$	$A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$		15
C_{2h}			$A_g \quad A_g \oplus B_g \quad A_g \oplus B_g \oplus B_g$ $A_g \oplus A_g \oplus B_g$		
	a_g^2	$A_g \otimes A_g$	A_g	^1A_g	
	$a_g a_g'$	$A_g \otimes A_g$	A_g	$^1A_g, ^3A_g$	
	$a_g'^2$	$A_g \otimes A_g$	A_g	^1A_g	
	$a_g b_g$	$A_g \otimes B_g$	B_g	$^1B_g \quad ^3B_g$	
	$a_g' b_g$	$A_g \otimes B_g$	B_g	$^1B_g \quad ^3B_g$	
	b_g^2	$B_g \otimes B_g$	A_g	^1A_g	
O_h				$^1A_{1g} \, ^1E_g \, ^3T_{1g} \, ^1T_{2g}$	15
O_h	$t_{2g} e_g$	$T_{2g} \otimes E_g$	$T_{1g} \oplus T_{2g}$	$^1T_{1g} \, ^3T_{1g} \, ^1T_{2g} \, ^3T_{2g}$	24

31

Correlation Diagrams

Connects strong field states to intermediate field states

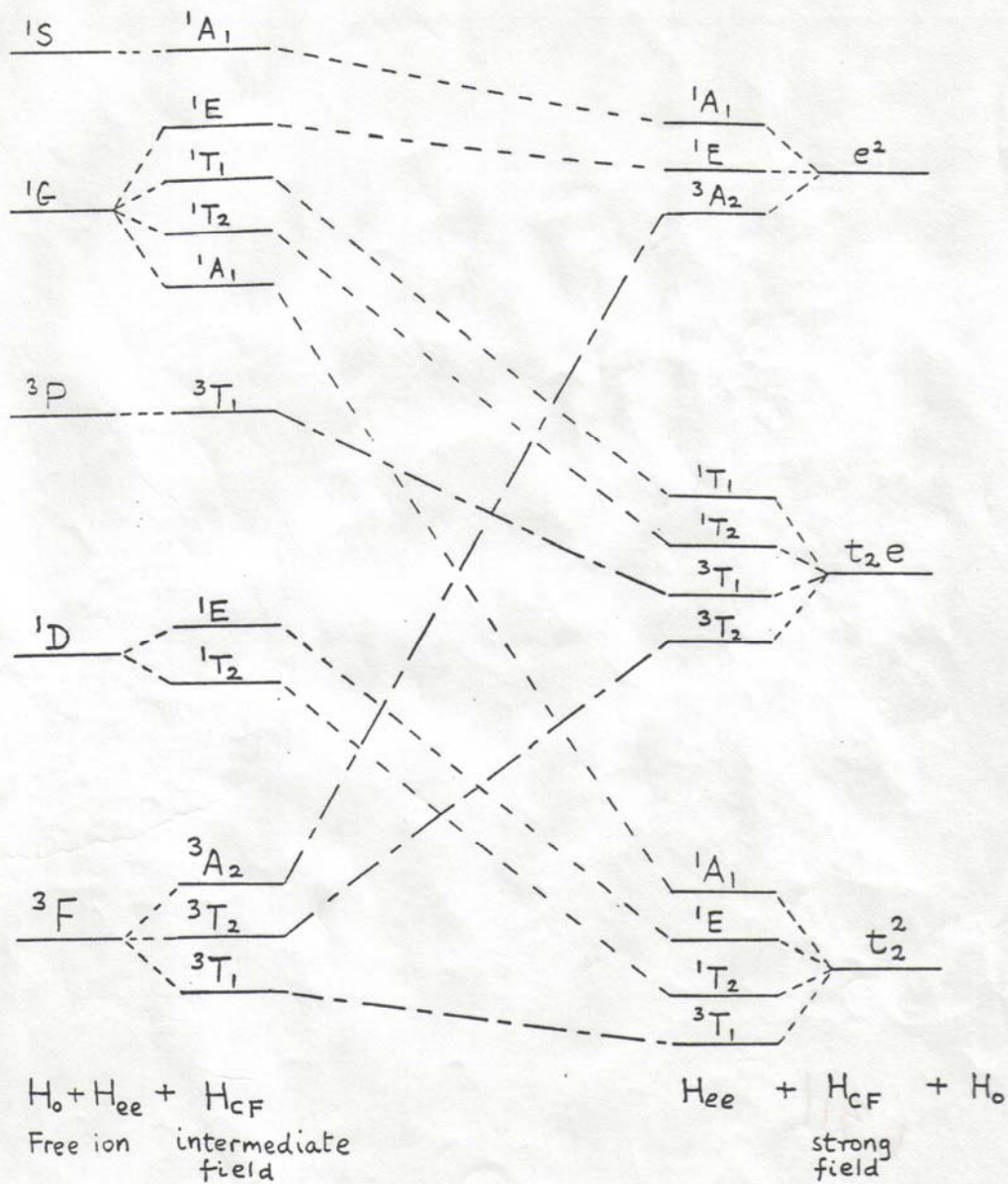**Rules:**

1.) Non-crossing rule: states of same symmetry and spin multiplicity may not cross.

2.) Hund's rules: a) states of highest spin multiplicity lie lowest in energy
   b) terms with the same S, the one with highest orbital L lies lowest.

Rule's apply strictly only to ground states.

Correlation diagram for $d^2(O_h)$.

^1S ———— $^1A_1$

$^1A_1$
^1E e^2
$^3A_2$

^1E
^1G $^1T_1$
          $^1T_2$
          $^1A_1$

^3P ———— $^3T_1$

$^1T_1$
$^1T_2$ t_2e
$^3T_1$
$^3T_2$

^1E
^1D $^1T_2$

$^1A_1$
$^3A_2$ ^1E
^3F $^3T_2$ $^1T_2$ t_2^2
          $^3T_1$ $^3T_1$

$H_o + H_{ee} + H_{CF}$

Free ion   intermediate
            field

$H_{ee} + H_{CF} + H_o$

strong
field

33

Next: consider an nd^8 configuration

Need to observe 2 new principles.

1.) doubly occupied orbitals contribute A_{1g} to direct products and 0 to S and M_S due to the Pauli Exclusion Principle.

2.) Account for spin-pairing energy. Electrons in degenerate levels tend to have unpaired spins whenever possible.

It is an empirical fact that spin-pairing in e_g orbitals requires more energy than in the t_{2g} orbitals
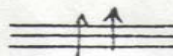
$$\therefore d^8: \qquad E\left(t_{2g}^6 e_g^2\right) < E\left(t_{2g}^5 e_g^3\right) < E\left(t_{2g}^4 e_g^4\right)$$

$$\therefore \# e_g \text{ pairs are}: \qquad 0 \qquad\qquad 1 \qquad\qquad 2$$
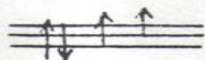
eg pairs

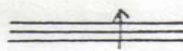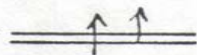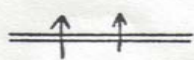$t_{2g}^4 e_g^4$ 2 t_{2g}^2

$t_{2g}^5 e_g^3$ 1 $e_g t_{2g}$

$t_{2g}^6 e_g^2$ 0 e_g^2

actual electron
configurations   how it appears

35

$$\Rightarrow E\left(e_g^2\right) < E\left(e_g t_{2g}\right) < E\left(t_{2g}^2\right)$$

Therefore d^8 behaves as if, relative to d^2, ordering of the t_{2g} and e_g levels have been inverted.

Means, the correlation diagram for d^8 is like that for d^2 but with the ordering of the high-field states inverted.

Can show: d^{10-n} (O_h) like d^n (T_d) and d^n (O_h) like d^{10-n} (T_d)