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 $\bar{\mu}$ where

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

where $m_e \equiv$ mass of the electron and $\mu_B \equiv$ Bohr magneton

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

$s = \frac{1}{2}$ 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 \( \hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2 \)

\[
\hat{S}_x, \hat{S}_y, \hat{S}_z, \hat{S}^2
\]

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

Total angular momentum of electrons \( \equiv \mathbf{J} = \hat{L} + \hat{S} \) 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: $\hat{A}^\pm|j_a, m_a\rangle = \hbar\sqrt{j_a(j_a+1) - m_a(m_a\pm1)}|j_a, m_a \pm 1\rangle$
Since $\bar{s} = \frac{1}{2}$ for electrons $\langle s^2 \rangle = s(s+1)\hbar^2 = \frac{3}{4} \hbar^2$ and $\langle m_s \rangle = m_s \hbar = \pm \frac{1}{2} \hbar$

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

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

$$\left\langle \frac{1}{2}, \pm \frac{1}{2} \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle = 1 \quad \text{and} \quad \left\langle \frac{1}{2}, \pm \frac{1}{2} \left| \frac{1}{2}, \mp \frac{1}{2} \right\rangle = 0 \right.$$  

Spin functions are orthonormal: normalized and orthogonal.
Spherical Symmetry for many electron atoms (N)

Hamiltonian is given by: \( \hat{H} = \hat{H}_o + \hat{H}_{ee} + \hat{H}_{L\cdot\mathbf{S}} \)

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

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, \( n, \ell, m_\ell, m_s \)

\( \hat{H}_{ee} \equiv \text{electron – electron interaction which couples angular momenta of the individual electrons in 2 possible ways} \)
Low “Z” elements \((Z \ll 40)\)

\[
\vec{L} = \sum_i \vec{\ell}_i, \quad \vec{S} = \sum_i \vec{s}_i
\]

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:

\[
\vec{j}_i = \vec{\ell}_i + \vec{s}_i \quad \equiv \text{total angular momenta of each individual electron.}
\]

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

\(\equiv\) **j-j coupling**

\textbf{Note:} can have intermediate coupling for intermediate \(Z\) although L-S (Russell-Saunders) scheme is often used as a first approximation.
For low $Z$ \( \hat{H}_{ee} > \hat{H}_{L,S} \)

For high $Z$ \( \hat{H}_{ee} < \hat{H}_{L,S} \) \( \therefore \vec{L} \cdot \vec{S} \sim \alpha^2 Z^2 \)

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

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

\[
\begin{align*}
&L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad \cdots \\
&\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \\
&S \quad P \quad D \quad F \quad G \quad \cdots 
\end{align*}
\]

\textit{spin multiplicity} \( \equiv 2S+1 \)
How to get L or S?

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

$$\tilde{A} = A_1 + A_2, \quad A_1 + A_2 - 1, \cdots |A_1 - A_2|$$

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

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: \[ \Delta E_{L-S} = \frac{1}{2} \xi(L,S)[J(J+1) - L(L+1) - S(S+1)] \]

where \( \xi(L,S) \equiv \text{spin-orbit coupling constant} > 0 \) for < \( \frac{1}{2} \)-filled shells

\( \rightarrow \) smallest J lies lowest in energy

If \( \xi < 0 \) for > \( \frac{1}{2} \)-filled shells \( \rightarrow \) largest J lies lowest in energy

\( \equiv \text{Hund’s third rule} \)

Example: \((n{s}^1)(n{p}^1)\) configuration \(\ell_1 = 0; \ell_2 = 1 \Rightarrow L = 1\)

\(s_1 = \frac{1}{2}; s_2 = \frac{1}{2} \Rightarrow S = 1, 0\)

\( \Rightarrow \) terms are \(3P, 1P\)

When \(S = 0, L = 1, J = 1 \Rightarrow 1P_1\)

When \(S = 1, L = 1, J = 2,1,0 \Rightarrow 3P_{2,1,0}\)
-H_{ee} has 2 parts: a Coulomb repulsion J and an exchange interaction ±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).
⇒ (ns)\(^{(1)}\) (np)\(^{(1)}\)
Intermediate Crystal Fields  (low Z elements)

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

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

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

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

-Consider an atomic term with angular momentum $L$. 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 $\Gamma_L$ is used for historical reasons.
Can show: \( \hat{R}(\alpha)Y^M_L(\theta, \varphi) = Y^M_L(R^{-1}\{\theta, \varphi\}) \)

\[ = Y^M_L(\theta, \varphi - \alpha) = e^{-iM\alpha}Y^M_L(\theta, \varphi) \]

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

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

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

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

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 \(\alpha \to 0\) \(\lim_{\alpha \to 0} \frac{\sin\left[\frac{(2L+1)\alpha}{2}\right]}{\sin\left(\frac{\alpha}{2}\right)} = \lim_{\alpha \to 0} \frac{(2L+1)\alpha}{\alpha} = 2L + 1\)
Splitting of states of angular momentum $L$ in an intermediate crystal field

$$\chi[D_L(x)] = \frac{\sin[(L+\frac{1}{2})\pi x]}{\sin(\frac{\pi}{2} x)}$$

Therefore:

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

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

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

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

<table>
<thead>
<tr>
<th>State</th>
<th>$D_L$</th>
<th>Direct sum in cubic field</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>$D_0$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>P</td>
<td>$D_1$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>D</td>
<td>$D_2$</td>
<td>$E \oplus T_2$</td>
</tr>
<tr>
<td>F</td>
<td>$D_3$</td>
<td>$A_2 \oplus T_1 \oplus T_2$</td>
</tr>
<tr>
<td>G</td>
<td>$D_4$</td>
<td>$A_1 \oplus E \oplus T_1 \oplus T_2$</td>
</tr>
</tbody>
</table>

The splitting of states in lower symmetries is given in correlation tables, an example of which is in Table...
Table shows $\chi(D_L)$ for $\alpha = \pi/2, 2\pi/3, \text{and } \pi$ 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 $\psi$ will have definite parity.

Parity $\equiv$ eigenvalue of the inversion operator.

\[
\hat{i} \psi = \lambda \psi = \pm \psi
\]

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

If $\hat{i} \psi = -\psi \implies \text{odd or ungerade } \equiv \text{u-parity}$
The parity of \( Y_\ell^m(\theta, \varphi) = (-1)^\ell \)

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

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

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

This means the parity is determined by the electron configuration, \textbf{NOT} on the total orbital angular momentum, \( L \).
Example: \( \text{nsnp} \Rightarrow \text{parity} = (-1)^{0+1} = -1 \Rightarrow \text{all terms are u - states} \)

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

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

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

If the parity is odd \( \Rightarrow \chi[D_L^-(iIR)] = -\chi[D_L^-(IR)] \)

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

\[
\begin{array}{c|cc}
O_h & \{O\} & i\{O\} \\
\hline
\Rightarrow g & \chi(O) & \chi(O) \\
u & \chi(O) & -\chi(O) \\
\end{array}
\]

Therefore, need only consider \( \{O\} \) and work out parities later.
Example:
a) Into what states does the Russell-Saunders term $d^2\cdot{}^3F$ 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:

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>D₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E 8C₃ 6C₂</td>
<td>E 2C₃ 3C₂</td>
</tr>
<tr>
<td>A₂</td>
<td>1 1 −1</td>
<td>A₁ 1 1 1</td>
</tr>
<tr>
<td>T₁</td>
<td>3 0 −1</td>
<td>A₂ 1 1 −1</td>
</tr>
<tr>
<td>T₂</td>
<td>3 0 1</td>
<td>E 2 −1 0</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$O$</th>
<th>$T_d$</th>
<th>$D_{4h}$</th>
<th>$D_{2d}$</th>
<th>$C_{4v}$</th>
<th>$C_{2v}$</th>
<th>$D_{3d}$</th>
<th>$D_3$</th>
<th>$C_{2h}$</th>
</tr>
</thead>
<tbody>
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<td>$A_{1g}$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_{1g}$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_{1g}$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_0$</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$B_{1g}$</td>
<td>$B_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$A_{2g}$</td>
<td>$A_2$</td>
<td>$B_0$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$E$</td>
<td>$E$</td>
<td>$A_{1g} + B_{1g}$</td>
<td>$A_1 + B_1$</td>
<td>$A_1 + B_1$</td>
<td>$A_1 + A_2$</td>
<td>$E_g$</td>
<td>$E$</td>
<td>$E$</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>$T_1$</td>
<td>$T_1$</td>
<td>$A_{2g} + E_g$</td>
<td>$A_2 + E$</td>
<td>$A_2 + E$</td>
<td>$A_2 + B_1 + B_2$</td>
<td>$A_{2g} + E_g$</td>
<td>$A_2 + E$</td>
<td>$A_0 + 2B_0$</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>$T_2$</td>
<td>$T_2$</td>
<td>$B_{2g} + E_g$</td>
<td>$B_2 + E$</td>
<td>$B_2 + E$</td>
<td>$A_1 + B_1 + B_2$</td>
<td>$A_{1g} + E_g$</td>
<td>$A_1 + E$</td>
<td>$2A_0 + B_0$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$A_{1u}$</td>
<td>$B_1$</td>
<td>$A_2$</td>
<td>$A_{1u}$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_u$</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$B_{1u}$</td>
<td>$A_1$</td>
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<td>$B_0$</td>
<td>$B_u$</td>
</tr>
<tr>
<td>$E_u$</td>
<td>$E$</td>
<td>$E$</td>
<td>$A_{1u} + B_{1u}$</td>
<td>$A_1 + B_1$</td>
<td>$A_2 + B_2$</td>
<td>$A_1 + A_2$</td>
<td>$E_u$</td>
<td>$E$</td>
<td>$A_u + B_u$</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>$T_1$</td>
<td>$T_2$</td>
<td>$A_{2u} + E_u$</td>
<td>$B_2 + E$</td>
<td>$A_1 + E$</td>
<td>$A_1 + B_1 + B_2$</td>
<td>$A_{2u} + E_u$</td>
<td>$A_2 + E$</td>
<td>$A_u + 2B_u$</td>
</tr>
<tr>
<td>$T_{2u}$</td>
<td>$T_2$</td>
<td>$T_1$</td>
<td>$B_{2u} + E_u$</td>
<td>$A_2 + E$</td>
<td>$B_1 + E$</td>
<td>$A_2 + B_1 + B_2$</td>
<td>$A_{1u} + E_u$</td>
<td>$A_1 + E$</td>
<td>$2A_u + B_u$</td>
</tr>
</tbody>
</table>
Strong Crystal Fields

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

⇒ 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 $\rightarrow t_{2g} (d_{xy}, d_{yz}, d_{xz}) + e_g (d_{z^2}, d_{x^2-y^2})$ 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 $\Gamma_i$ and $\psi^j(2)$ forms a basis for $\Gamma_j$ 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 form a $d^2$ 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:

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>E</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6C_4$</th>
<th>$6C'_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
<td>$-1$</td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>$-1$</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$T_1$</td>
<td>3</td>
<td>0</td>
<td>$-1$</td>
<td>1</td>
<td>$-1$</td>
<td></td>
</tr>
<tr>
<td>$T_2$</td>
<td>3</td>
<td>0</td>
<td>$-1$</td>
<td>$-1$</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
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 \(e_g \otimes e_g\)

\[e_g \otimes e_g \text{ reduces in O to } a_1 \oplus a_2 \oplus e\]

Don’t know which are singlets and triplets.

Bethes’s method is to lower the symmetry until all representations \textbf{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.
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.

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

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

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

⇒ 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 $C_{2h}$
\[ t_{2g} \otimes t_{2g} = a_{1g} \oplus e_g \oplus t_{1g} \oplus t_{2g} \]

\[ a_g \quad a_g \quad a_g \quad a_g \]
\[ \oplus \quad \oplus \quad \oplus \]
\[ b_g \quad b_g \quad a_g \quad a_g \]
\[ \oplus \quad \oplus \]
\[ b_g \quad b_g \]

\[ \therefore t_{2g} \otimes t_{2g} \quad (O_h) \rightarrow (a_g \oplus a_g \oplus b_g) \otimes (a_g \oplus a_g \oplus b_g) \quad (C_{2h}) \]
Put in 2 electrons:

\[ a_g^2 (1) \rightarrow ^1 A_g \]
\[ a_g^1 (1) a_g^1 (2) \rightarrow ^1 A_g , ^3 A_g \]
\[ a_g^1 (1) b_g^1 \rightarrow ^1 B_g , ^3 B_g \]
\[ a_g^1 (2) b_g^1 \rightarrow ^1 B_g , ^3 B_g \]
\[ a_g^2 (2) \rightarrow ^1 A_g \]
\[ b_g^2 \rightarrow ^1 A_g \]

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

In \( O_h \) this **must** be the \( T_{1g} \) state.

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

Total degeneracy = \( 1 \times 1 + 1 \times 2 + 3 \times 3 + 1 \times 3 = 15 \)
Lastly: $t_2^1 e_g^1$.

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 = $1 \times 3 + 3 \times 3 + 1 \times 3 + 3 \times 3 = 24$
Application of the method of descending symmetry to the configuration $d^5$ in $O_h$ symmetry.

<table>
<thead>
<tr>
<th>Point Group</th>
<th>Configuration</th>
<th>Direct Product Representation</th>
<th>Irreducible Representations</th>
<th>Allowed States</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_h$</td>
<td>$e_g^2$</td>
<td>$E_g \otimes E_g$</td>
<td>$A_{1g} \oplus A_{2g} \oplus E_g$</td>
<td>$1^{A_{1g}}$</td>
<td>6</td>
</tr>
<tr>
<td>$D_{4h}$</td>
<td>$a_{1g}^2$</td>
<td>$A_{1g} \otimes A_{1g}$</td>
<td>$A_{1g}$</td>
<td>$1^{A_{1g}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_{1g}d_{1g}$</td>
<td>$A_{1g} \otimes B_{1g}$</td>
<td>$B_{1g}$</td>
<td>$1^{B_{1g}}, 1^{B_{1g}'}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b_{1g}^2$</td>
<td>$B_{1g} \otimes B_{1g}$</td>
<td>$A_{1g}$</td>
<td>$1^{A_{1g}}$</td>
<td></td>
</tr>
<tr>
<td>$O_h$</td>
<td>$t_{2g}^2$</td>
<td>$T_{2g} \otimes T_{2g}$</td>
<td>$A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$</td>
<td>$1^{A_{1g}}, 1^{A_{1g}'}, 1^{A_{1g}}$</td>
<td>6</td>
</tr>
<tr>
<td>$C_{2h}$</td>
<td>$a_g^2$</td>
<td>$A_g \otimes A_g$</td>
<td>$A_g$</td>
<td>$1^{A_g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_ga_g'$</td>
<td>$A_g \otimes A_g$</td>
<td>$A_g$</td>
<td>$1^{A_g}, 1^{A_g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_g^2$</td>
<td>$A_g \otimes A_g$</td>
<td>$A_g$</td>
<td>$1^{A_g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_gb_g$</td>
<td>$A_g \otimes B_g$</td>
<td>$B_g$</td>
<td>$1^{B_g}, 1^{B_g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_g'b_g$</td>
<td>$A_g \otimes B_g$</td>
<td>$B_g$</td>
<td>$1^{B_g}, 1^{B_g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b_g^2$</td>
<td>$B_g \otimes B_g$</td>
<td>$A_g$</td>
<td>$1^{A_g}$</td>
<td></td>
</tr>
<tr>
<td>$O_h$</td>
<td>$t_{2g}, e_g$</td>
<td>$T_{2g} \otimes E_g$</td>
<td>$T_{1g} \oplus T_{2g}$</td>
<td>$1^{A_{1g}}, 1^{E_g}, 1^{T_{2g}}, 1^{T_{2g}}$</td>
<td>15</td>
</tr>
<tr>
<td>$O_h$</td>
<td>$t_{2g}, e_g$</td>
<td>$T_{2g} \otimes E_g$</td>
<td>$T_{1g} \oplus T_{2g}$</td>
<td>$1^{T_{1g}}, 1^{T_{1g}}, 1^{T_{2g}}, 1^{T_{2g}}$</td>
<td>24</td>
</tr>
</tbody>
</table>
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 $d^3(O_h)$.

$H_0 + H_{ee} + H_{CF}$  
Free ion  intermediate  strong   field

$H_{ee} + H_{CF} + H_0$
**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.

\[ \therefore d^8 : \quad E(t_{2g}^6 e_g^2) < E(t_{2g}^5 e_g^3) < E(t_{2g}^4 e_g^4) \]

\[ \therefore \#e_g \text{ pairs are: } \quad 0 \quad 1 \quad 2 \]
Correlation Diagrams

# e_g pairs

\[ t_{2g}^4 e_g^4 \quad 2 \]
\[ t_{2g}^2 e_g^2 \]

\[ t_{2g}^5 e_g^3 \quad 1 \]
\[ e_g t_{2g} \]

\[ t_{2g}^6 e_g^2 \quad 0 \]

actual electron configurations

how it appears
\[ \Rightarrow E(e_g^2) < E(e_g t_{2g}) < E(t_{2g}^2) \]

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)