

5.03, Inorganic Chemistry
 Prof. Daniel G. Nocera
Lecture 2 May 11: Ligand Field Theory

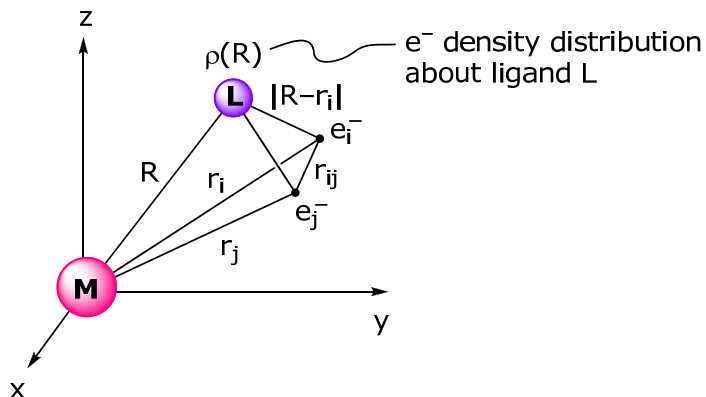
The ligand field problem is defined by the following Hamiltonian,

$$H = -\frac{\hbar^2}{2m} \nabla^2 \quad \text{with} \quad E_n = KE = \frac{p^2}{2m} \quad \text{where} \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\begin{array}{l} \swarrow \\ \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right] \\ \searrow \\ \text{hydrogen atom} \\ \text{(1e}^- \text{ problem)} \end{array}$$

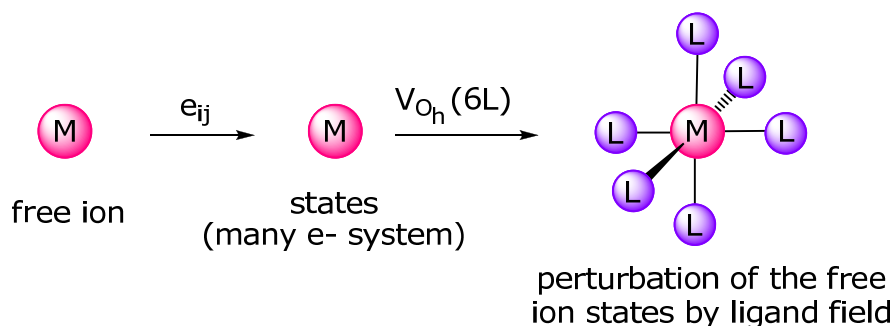
$$\underbrace{\sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z^* e^2}{r_i} \right]}_{\text{free ion or atom}} + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \frac{e^2}{r_{ij}} + \underbrace{\sum_{i=1}^N \frac{\rho(R)}{|R-r_i|}}_{\text{ligand field}} d\tau_R$$

The Hamiltonian contains three types of terms arising from the electrons interacting with the positively charged nucleus of the atom (defined by $1e^-$ interactions, r_i), $2e^-$ interactions arising from e^-e^- repulsions (r_{ij}), the interaction of electrons with electron cloud of the ligands ($|R-r_i|$ where R is the position of the ligand),

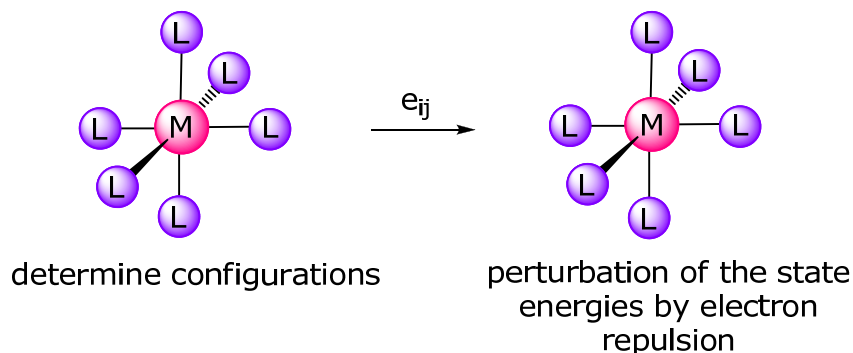


The electronic part of the Hamiltonian is spectroscopically probed in two regimes, depending on the strength of the ligand field.

In the **weak field**, the $2e^-$ energies are greater than the $1e^-$ energies, i.e. $Q_{ij} \left(\frac{1}{r_{ij}} \right) \gg V_{O_h}$ of which Δ_o is a measure of V_{O_h} . So the strategy here is to first determine state symmetries followed by applications of ligand field.



In the **strong field**, the $1e^-$ energies (orbital energies) are first determined, followed by the perturbation of $2e^-$ terms... begin with configurations and see how they are perturbed by Q_{ij} .



The overall approach to determining the energy levels of a molecule is:

- ❖ determine free ion states
- ❖ determine how atomic states are split in a weak field limit ($PE \gg \Delta_o$)
- ❖ determine states arising from configurations in a strong field limit ($PE \ll \Delta_o$)
- ❖ correlate between strong and weak fields (Tanabe-Sugano diagrams).

The Weak Field

The problem begins by considering a free ion (K_h symmetry). Different atomic configurations give rise to different **terms** or **energy levels**. The many e^- system is characterized by a total orbital and total spin angular momentum,

total orbital angular momentum, L

$$L = \sum_i^n \ell_i \quad L = 0, 1, 2, 3, \dots$$

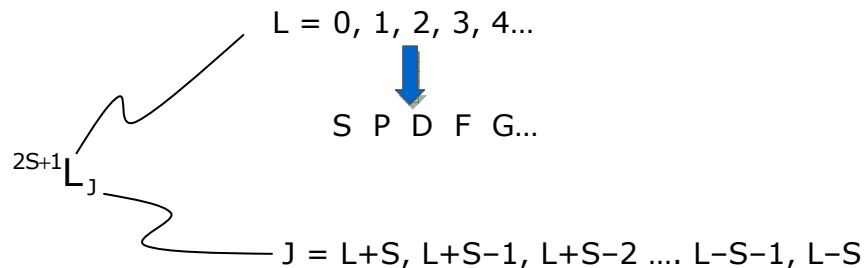
$$M_L = \sum_i^n m_{\ell_i} \quad M_L = L, L-1, \dots, 1-L, -L$$

total spin angular momentum, S

$$S = \sum_i^n s_i \quad S = \frac{1}{2}, 1, \frac{3}{2}, \dots$$

$$M_S = \sum_i^n m_{s_i} \quad M_S = S, S-1, \dots, 1-S, -S$$

A term is symbolized by



We will therefore need to

- 1) determine terms of a given configuration
- 2) determine the eigenfunction of these terms
- 3) calculate terms energies

As an illustrative example, consider the p^2 configuration,

$$\begin{array}{cccc}
 M_L & +1 & 0 & -1 \\
 & \uparrow & \downarrow & _ \\
 & _ & _ & _
 \end{array}$$

A shorthand notation for this configuration is $(\overset{+}{1} \bar{0})$, which is a **Slater determinant**

$$(\overset{+}{1} \bar{0}) = \frac{1}{\sqrt{2}} \begin{vmatrix} (\overset{+}{1})^1 & (\overset{+}{1})^2 \\ (\bar{0})^1 & (\bar{0})^2 \end{vmatrix} = \frac{1}{\sqrt{2}} \left[(\overset{+}{1}, \bar{0}) - (\bar{0}, \overset{+}{1}) \right]$$

All the possible configurations are summarized in the following table which defines the configurations in terms of M_L and M_S

$M_S \backslash M_L$	1	0	-1
2		(1, 1)	
1	$(\overset{+}{1}, \overset{+}{0})$	$(\overset{+}{1}, \bar{0}) (\bar{0}, \overset{+}{0})$	$(\bar{1}, \bar{0})$
0	$(\overset{+}{1}, \bar{1})$	$(\overset{+}{0}, \bar{0})$ $(\overset{+}{1}, \bar{1})$ $(\bar{1}, \bar{1})$	$(\bar{1}, \bar{1})$
-1	$(\bar{0}, \bar{1})$	$(\bar{0}, \bar{1}) (\bar{0}, \bar{1})$	$(\bar{0}, \bar{1})$
-2		$(\bar{1}, \bar{1})$	

The table summarizing the number of constituent configurations in terms of M_L and M_S ,

$M_S \backslash M_L$	1	0	-1
2		1	
1	1	2	1
0	1	3	1
-1	1	2	1
-2		1	

Considering the definitions of L and S, begin with highest M_L wavefunction and eliminate $1e^-$ wavefunctions from $+L$ to $-L$ and $+S$ to $-S$. The highest M_L is 2, $M_S = 0$

$M_L = 2, M_S = 0$, which is a 1D term

Removing the count of configurations arising from a 1D term (i.e., from $M_L = 2, 1, 0, -1, -2$ and $M_S = 1, 0, -1$), leaves

$M_L \backslash M_S$	1	0	-1
2			
1	1	1	1
0	1	2	1
-1	1	1	1
-2			

The highest M_L is 1 and highest M_S of this M_L value is also 1, thus giving rise to a 3P term

Again, eliminating states of the 3P term,

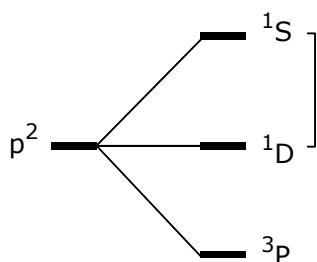
$M_L \backslash M_S$	1	0	-1
2			
1			
0		1	
-1			
-2			

This leaves only one configuration of $M_L = 0$ and $M_S = 0$, which is a 1S term

Thus the terms arising from a p^2 configuration are: 1D , 3P , and 1S . May predict the ground state from Hund's rule:

- 1) state with maximum M_S is lowest in energy
- 2) for states of the same spin multiplicity, the state with largest M_L will be lowest in energy
- 3) note, Hund's rule does not address excited state ordering

Hund's rule identifies 3P as the ground state. Summarizing the energy (term) levels



this ordering must be determined from spectroscopy

How about the d ion states?

d^1 ion

... is straightforward. There are 10 permutations of an electron in 5 d orbitals, $s = 1/2$ or $s = -1/2$ in orbitals of m_ℓ of 2 to -2

$M_L \backslash M_S$	1	0	-1
2			
1	1	1	1
0	1	2	1
-1	1	1	1
-2			

This gives $M_L = 2, 1, 0, -1, -2$ and $M_S = 1, 0, -1$, thus giving values of $L = 2$ and $S = 1$ or a 2D state. This is the only term for the d^1 configuration

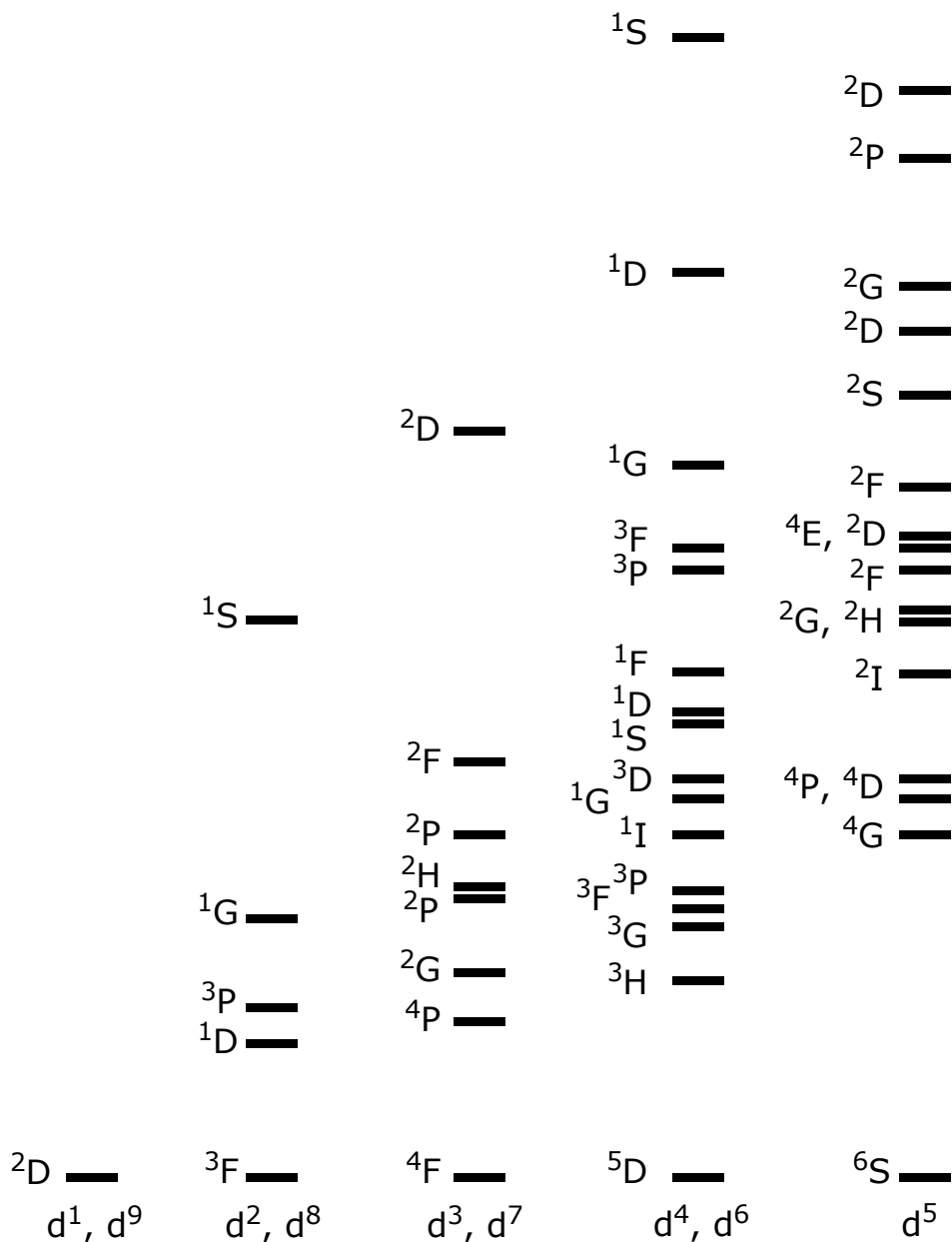
d^2 ion

... has many terms that result from the permutation of $2e^-$ in the orbital subshells derived from $\ell = 2, m_\ell = 2, 1, 0, -1, -2$

$M_L \backslash M_S$	1	0	-1
4		$({}^+{}_2, {}^+{}_2)$	
3	$({}^+{}_2, {}^+{}_1)$	$({}^+{}_2, {}^-{}_1) ({}^-{}_2, {}^+{}_1)$	$({}^-{}_2, {}^-{}_1)$
2	$({}^+{}_2, {}^+{}_0)$	$({}^+{}_2, {}^-{}_0) ({}^+{}_1, {}^-{}_1) ({}^-{}_2, {}^+{}_0)$	$({}^-{}_2, {}^-{}_0)$
1	$({}^+{}_2, {}^-{}_1) ({}^+{}_1, {}^+{}_0)$	$({}^+{}_2, {}^-{}_1) ({}^+{}_1, {}^-{}_0) ({}^-{}_1, {}^+{}_0) ({}^-{}_2, {}^-{}_1)$	$({}^-{}_2, {}^-{}_1) ({}^-{}_1, {}^-{}_0)$
0	$({}^+{}_2, {}^-{}_2) ({}^+{}_1, {}^-{}_1)$	$({}^+{}_2, {}^-{}_2) ({}^+{}_1, {}^-{}_1) ({}^-{}_2, {}^-{}_2) ({}^-{}_1, {}^+{}_1) ({}^-{}_1, {}^+{}_0)$	$({}^-{}_2, {}^-{}_2) ({}^-{}_1, {}^-{}_1)$

where the M_L terms are not shown for the convenience of space. Reducing the terms yields for a d^2 system: ${}^3F, {}^3P, {}^1G, {}^1D$ and 1S

The Russell-Saunders terms for all d^n free ions:

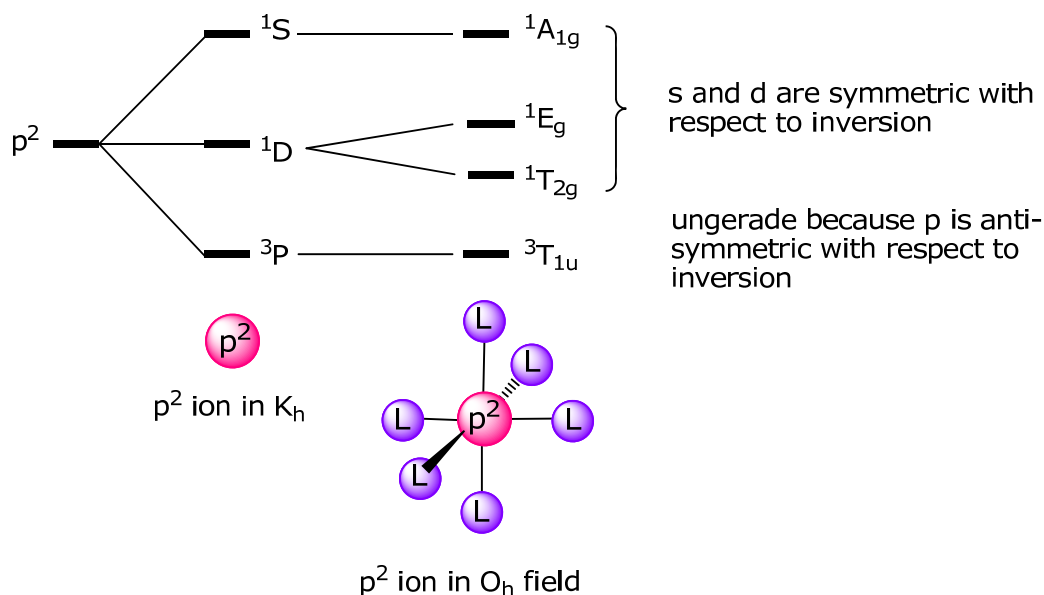


Now need to determine the states that arise from the application of an O_h field on the free ion.

The degeneracy of the wavefunction is removed upon application of the ligand field. The ligand field causes the terms to split owing to the change in symmetry from K_h to O_h . We can use the basis functions of the O_h character table to determine how the free ion states split,

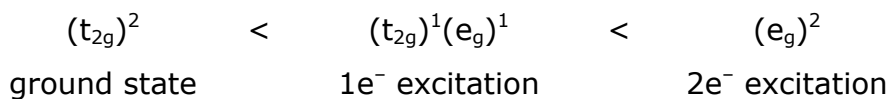
	0	E	6C ₄	3C ₂ (\equiv C ₄ ²)	8C ₃	6C ₂		
$\ell = 0$	Γ_s	1	1	1	1	1	\rightarrow	A _{1g}
$\ell = 1$	Γ_p	3	1	-1	0	1	\rightarrow	T _{1u}
$\ell = 2$	Γ_d	5	-1	1	-1	1	\rightarrow	E _g + T _{2g}
	\vdots							
	$\Gamma_f =$	A _{2u} + T _{1u} + T _{2u}						
	$\Gamma_g =$	A _{1g} + E _g + T _{1g} + T _{2g}						

Taking the terms of a p² ion in a spherical field (K_h) to an O_h ligand field leads to the further splitting,



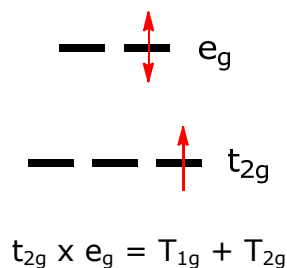
The Strong Field

The problem in the strong field begins with the electron configurations derived from the molecular orbital. As an example, consider the strong field configurations for two electrons in an octahedral ligand field. The two-electron occupancy of the ML₆(O_h) MO gives rise to three configurations:



Must now determine what states from d² weak field correlate to these configurations. Because the electrons interact differently with each other, when in different orbitals (different r_{ij}), for a given electronic configuration, many states can arise.

Let's begin with the $1e^-$ excited state, $(t_{2g})^1(e_g)^1$. The state symmetry takes the symmetry of the individually occupied orbitals, and the electrons can be singlet or triplet paired, $^1(\chi\cdot\chi')$ and $^3(\chi\cdot\chi')$



The spin can be $S = 0$ (singlet) or $S = 1$ (triplet), thus all potential states that arise from the one electron excitation of a d^2 ion in a O_h field are:

$$^1T_{1g} + ^1T_{2g} + ^3T_{1g} + ^3T_{2g}$$

The $(t_{2g})^2$ and $(e_g)^2$ configurations are more problematic because the electrons are degenerate. The direct product electrons in n degenerate orbitals of χ and χ' symmetry will give $\chi\cdot\chi'$ orbital symmetries.

$$(t_{2g})^2 \Rightarrow t_{2g} \times t_{2g} = A_{1g} + E_g + T_{2g} + T_{1g}$$

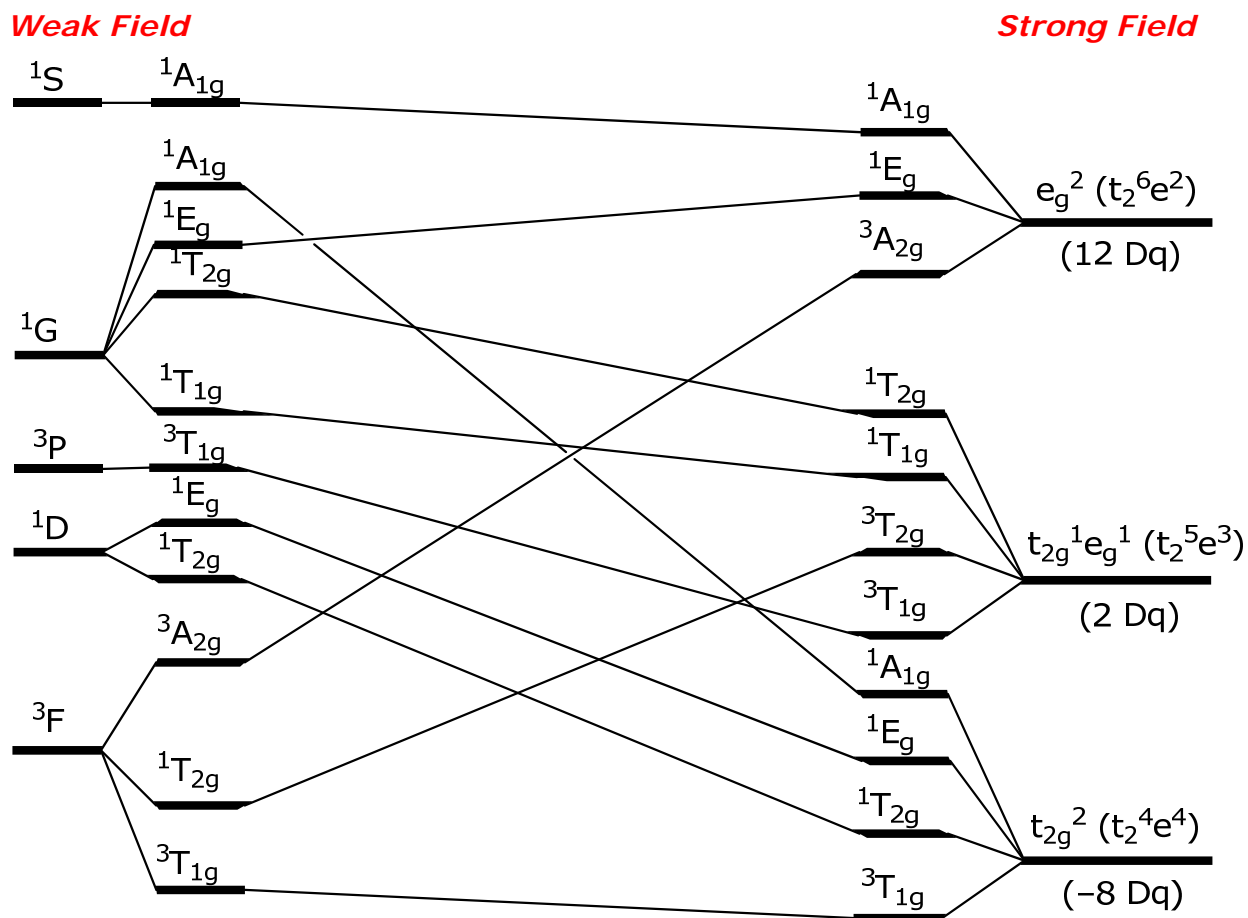
$$(e_g)^2 \Rightarrow e_g \times e_g = A_{1g} + A_{2g} + E_g$$

But there is a problem, a singlet and triplet spin pairing cannot be assigned to each state because some of these states will violate the Pauli exclusion principle. In 5.04 a procedure will be derived that shows how to eliminate these Pauli violating states. Here the result will be given:

$$(t_{2g})^2 \Rightarrow t_{2g} \times t_{2g} = ^1A_{1g} + ^1E_g + ^1T_{2g} + ^3T_{1g}$$

$$(e_g)^2 \Rightarrow e_g \times e_g = ^1A_{1g} + ^3A_{2g} + ^1E_g$$

The states created in the weak field must be the same as the states obtained in the strong field since we are dealing with the d^2 problem, just from different perspectives. We see this is the case. A correlation diagram relates the weak and strong field configurations. The d^2 correlation diagram is:



Note that for d^2 (d^n) in O_h , the same diagram is obtained for d^8 (d^{10-n}) T_d . T_d symmetry does not require the g or u subscripts.