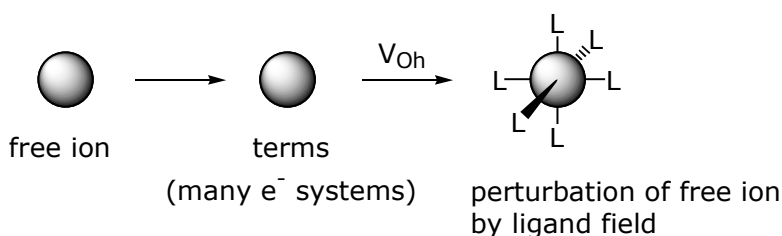


5.04, Principles of Inorganic Chemistry II  
 MIT Department of Chemistry  
**Lecture 29: Weak and Strong Field Approximations**

Weak Field

In the weak field, the  $2e^-$  energies are greater than the  $1e^-$  energies, i.e.

$Q_{ij} \left( \frac{1}{r_{ij}^5} \right) \gg V_{Oh}$ . So the strategy here is to first determine state symmetries followed by application of ligand field.



Strong field

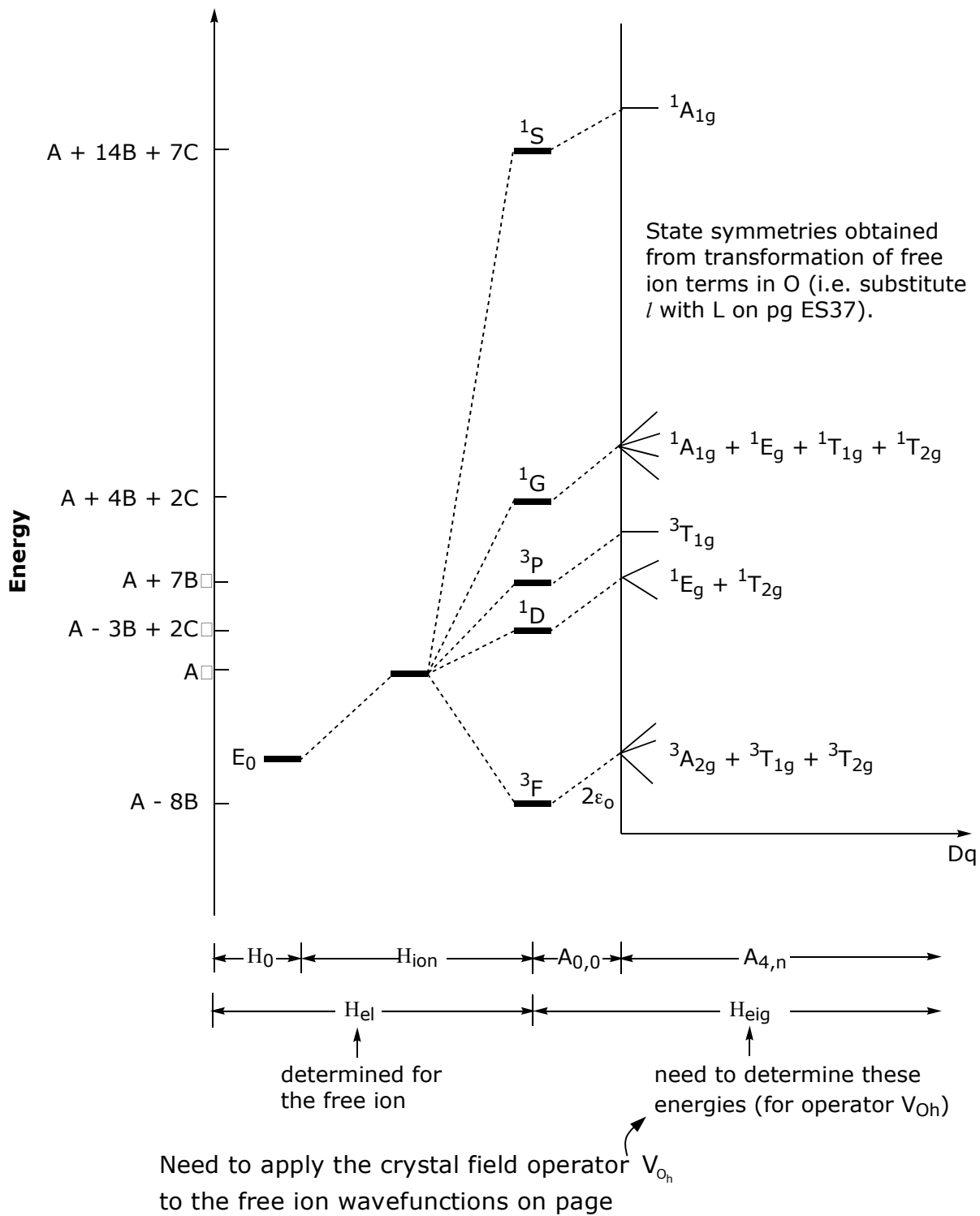
Here the  $1e^-$  energies (orbital energies) are first determined, followed by the perturbation of  $2e^-$  terms... begin with configurations and see how they are perturbed by  $Q_{ij}$ .

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

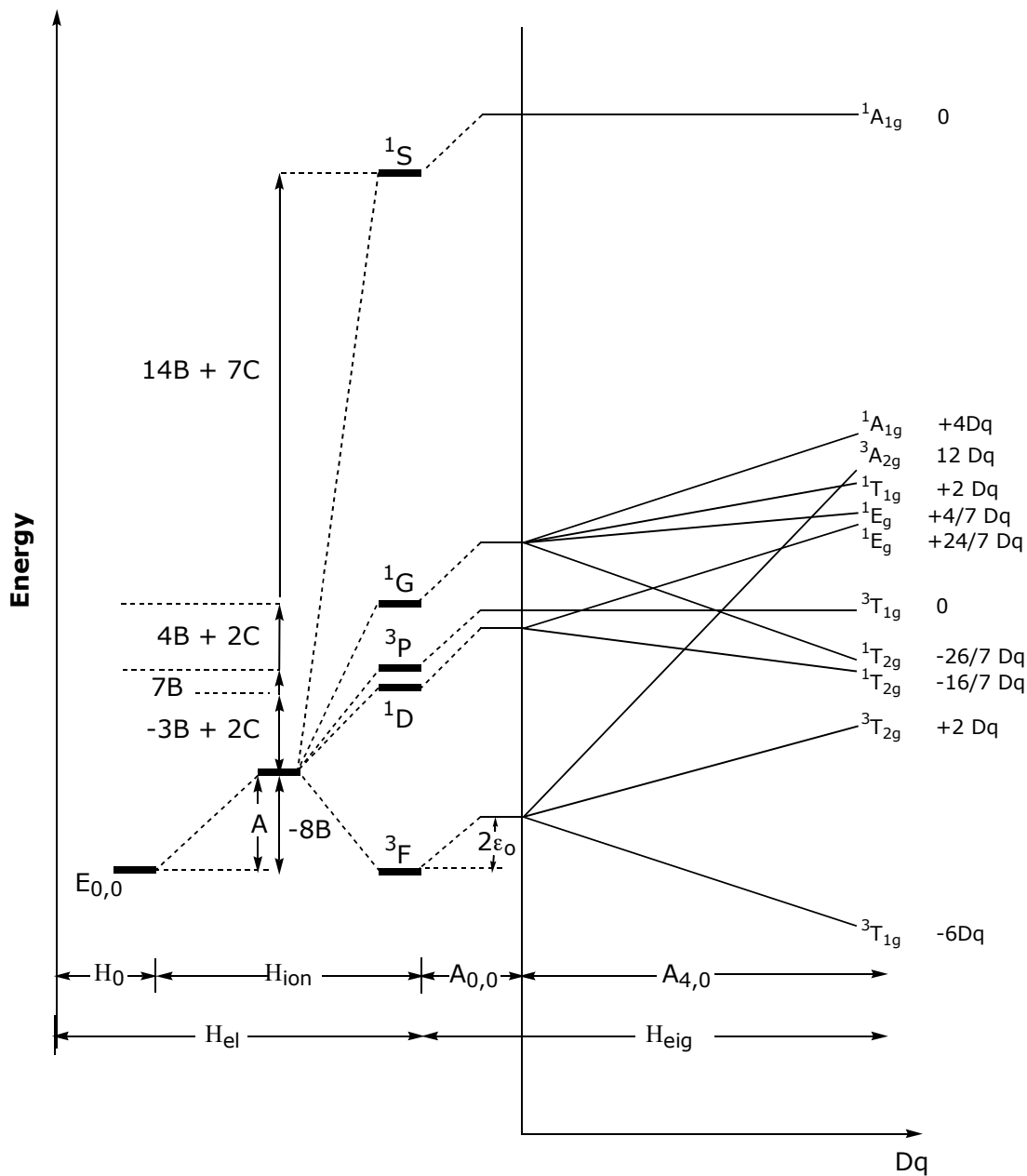
1. determine free ion states
2. determine how atomic states are split in a weak field limit ( $PE \gg 10Dq$ )
3. determine states arising from configurations in a strong field limit ( $PE \ll 10 Dq$ )
4. correlate between strong and weak fields (TS diagrams)

The results of the weak field approximation for a  $d^2$  ion are as follows...

As it stands, the correlation diagram is:

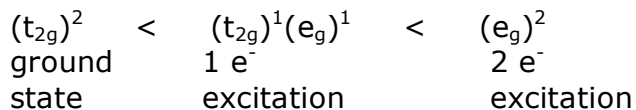


Summarizing the state energies for the  $d^2$  ion under the influence of  $V_{oh}$  in the weak field approximation,



## Correlation of Strong Field Configurations to Terms at Zero Field

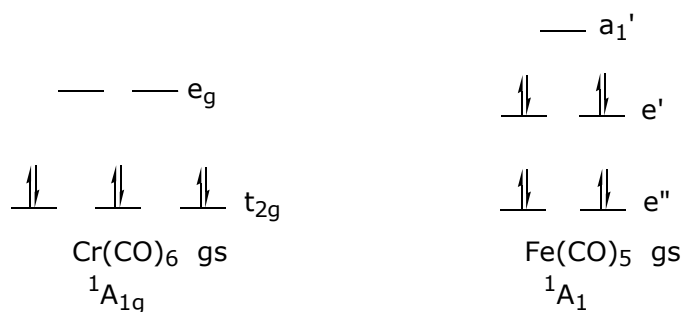
In the strong field, two electrons give rise to three configurations:



Must now determine what states from  $d^2$  weak field correlate to these configurations. Described below is a general procedure for various cases... the  $d^2$  problem is considered as an example

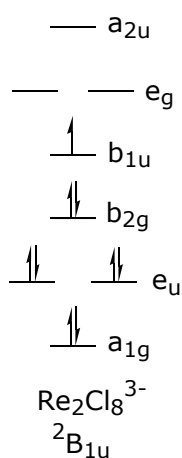
Case 1: all orbitals are fully occupied

State symmetry:  ${}^1A_{1(g)}$



Case 2: a non degenerate orbital of symmetry X that is singly occupied

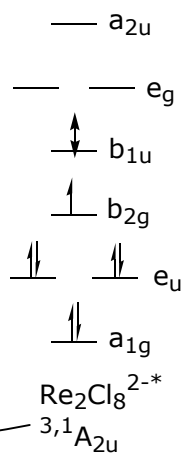
State symmetry:  ${}^2X$



Case 3: Two singly occupied, nondegenerate orbitals of symmetry X and X'

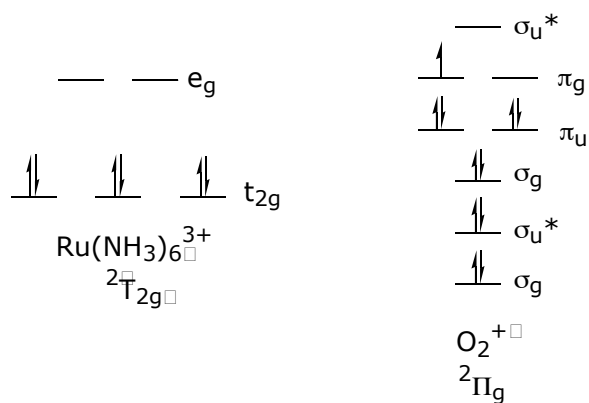
State symmetry:  $^1(X \cdot X')$  and  $^3(X \cdot X')$

the  $\delta\delta^*$  excited state



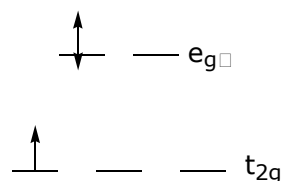
Case 4: A degenerate orbital of symmetry X lacking a single  $e^-$  or occupied by a single  $e^-$

State symmetry,  $^2X$



Case 5: Two degenerate orbitals of X and X' symmetry that are each singly occupied

State symmetry,  $^1(X \cdot X')$  and  $^3(X \cdot X')$



$t_{2g} \times e_g = T_{1g} + T_{2g}$   
 States : singlet and triplet, so...  
 $^1T_{1g} + ^1T_{2g} + ^3T_{1g} + ^3T_{2g}$

Case 6: n electrons in n degenerate orbitals of X and X' symmetry. The direct product will give X·X' orbital symmetries. But there is a problem, some of these states will violate the Pauli exclusion principle. Can use group theory to discern the Pauli forbidden states... a singlet wavefunction is antisymmetric with respect to electron exchange, ∴ orbital part of the wavefunction must be symmetric. Conversely, a triplet wavefunction is symmetric with respect to spin, ∴ orbital angular momentum must be antisymmetric.

For 2e<sup>-</sup> in ≥ 2-fold degenerate orbital

$$x(\text{singlet}) = \frac{1}{\sqrt{2}} \{ [x(R)]^2 + [x(R^2)] \}$$

$$x(\text{triplet}) = \frac{1}{\sqrt{2}} \{ [x(R)]^2 - [x(R^2)] \}$$

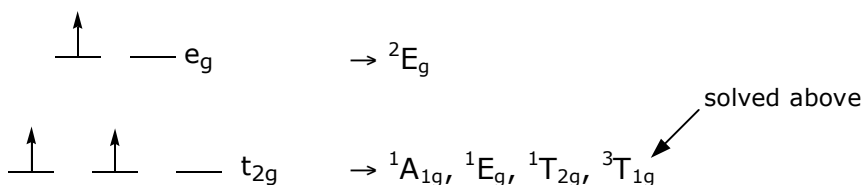
so for the (T<sub>2g</sub>)' configuration

O	E	6C <sub>4</sub>	3C <sub>2</sub> (=C <sub>4</sub> <sup>2</sup> )	8C <sub>3</sub>	6C <sub>2</sub>	
T <sub>2</sub>	3	-1	-1	0	1	
R <sup>2</sup>	E	C <sub>2</sub>	E	C <sub>3</sub> <sup>2</sup>	E	
x(R <sup>2</sup> )	3	-1	3	0	3	
[x(R)] <sup>2</sup>	9	1	1	0	1	
x <sup>+</sup>	6	0	2	0	2	→ <sup>1</sup> A <sub>1g</sub> + <sup>1</sup> E <sub>g</sub> + <sup>1</sup> T <sub>2g</sub>
x <sup>-</sup>	3	1	-1	0	-1	→ <sup>3</sup> T <sub>1g</sub>

for (e<sub>g</sub>)<sup>2</sup> configuration:

O	E	6C <sub>4</sub>	3C <sub>2</sub> (=C <sub>4</sub> <sup>2</sup> )	8C <sub>3</sub>	6C <sub>2</sub>	
T <sub>2</sub>	2	0	2	-1	0	
R <sup>2</sup>	E	C <sub>2</sub>	E	C <sub>3</sub> <sup>2</sup>	E	
x(R <sup>2</sup> )	2	2	2	-1	2	
[x(R)] <sup>2</sup>	4	0	4	1	0	
x <sup>+</sup>	3	1	3	0	1	→ <sup>1</sup> A <sub>1g</sub> + <sup>1</sup> E <sub>g</sub>
x <sup>-</sup>	1	-1	1	1	-1	→ <sup>3</sup> A <sub>2g</sub>

A more complicated case... Cr(CN)<sub>6</sub><sup>3-\*</sup>



The orbital symmetries are determined from the direct product of states. The spin multiplicity is the sum of spin vectors...  $S_i + S_j, S_i + S_j - 1, \dots |S_i - S_j|$

$${}^2E_g \times \begin{bmatrix} {}^1A_{1g} \\ {}^1E_{1g} \\ {}^1T_{2g} \\ {}^3T_{1g} \end{bmatrix} = \begin{bmatrix} E_g & S_i + S_j \dots S_i - S_j \\ A_{1g} + A_{2g} + E_g & \frac{1}{2} + 0 \dots \frac{1}{2} - 0 \\ T_{1g} + T_{2g} & \frac{1}{2} + 0 \dots \frac{1}{2} - 0 \\ T_{1g} + T_{2g} & \frac{1}{2} + 1 \dots \frac{1}{2} - 1 \end{bmatrix} \square$$

$$\therefore (t_{2g})^2(e_g)^1 = {}^2E_g + {}^2A_{1g} + {}^2A_{2g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g} + {}^4T_{1g} + {}^4T_{2g} + {}^2T_{1g} + {}^2T_{2g}$$

Thus we can now correlate the configurations on the Tanabe-Sugano diagram

$$\begin{array}{ccc} (t_{2g})^2 & < & (t_{2g})^1(e_g)^1 & < & (e_g)^2 \\ {}^3T_{1g} + {}^1A_{1g} + {}^1E_g + {}^1T_{1g} & & {}^3T_{1g} + {}^1A_{1g} + {}^1E_g + {}^1T_{1g} & & {}^3A_{2g} + {}^1A_{1g} + {}^1E_g \end{array}$$

Note: the same states, in number and symmetry, determined from the  $d^2$  configuration in the weak field approximation are obtained here... in the strong field. This has to be the case. Below is a correlation diagram relating weak and strong field configurations.

*Correlation for free-ion  $\rightarrow$  strong-field configuration for  $d^2$  in  $O_h$  and  $d^8$  in  $T_d$*   
Figure removed due to copyright considerations.