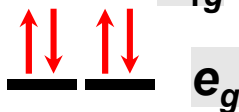
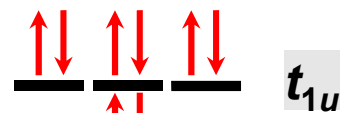
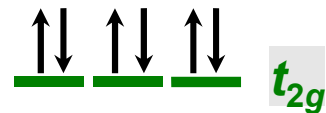
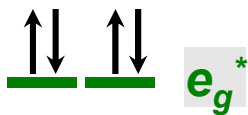


Coordination Chemistry II: Ligand Field Theory Continued

Chapter 10

Wednesday, November 25, 2015

Adding Metal Electrons



Metal ions typically have some valence electrons that can be accommodated in the **metal d orbitals**

- d^0 ions – Ti^{4+} , Zr^{4+} , V^{5+} , Ta^{5+} , Cr^{6+} , Mo^{6+} , etc.

- d^1 ions – Ti^{3+} , V^{4+} , Ta^{4+} , Cr^{5+} , Mo^{5+} , etc.

- d^2 ions – V^{3+} , Ta^{3+} , Cr^{4+} , Mo^{4+} , etc.

- d^3 ions – V^{2+} , Ta^{2+} , Cr^{3+} , Mo^{3+} , Mn^{4+} , etc.

- d^4 - d^7 – hold on

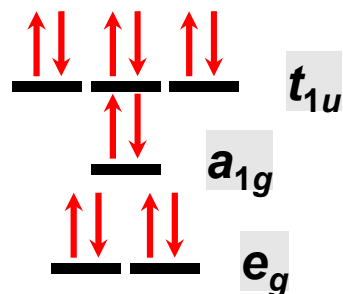
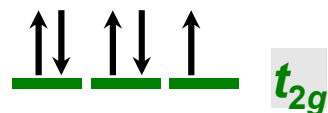
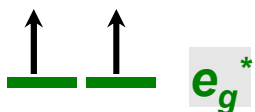
- d^8 ions – Co^{1+} , Ni^{2+} , Cu^{3+} , etc.

- d^9 ions – Ni^{1+} , Cu^{2+} , etc.

- d^{10} ions – Cu^{1+} , Zn^{2+} , etc.

Periodic Table of Elements

High Spin and Low Spin Complexes



The situation is a little more complicated for d^4 - d^7 metals:

• d^4 ions – Cr^{2+} , Mo^{2+} , Mn^{3+} , Fe^{4+} , Ru^{4+} , etc.

• d^5 ions – Mn^{2+} , Re^{2+} , Fe^{3+} , Ru^{3+} , etc.

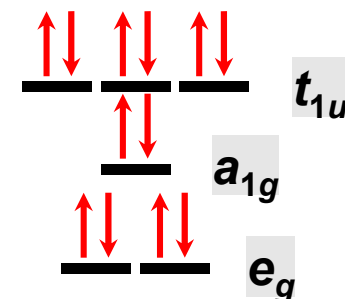
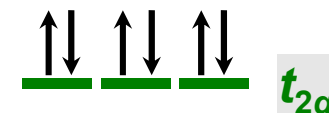
• d^6 ions – Fe^{2+} , Ru^{2+} , Co^{3+} , Rh^{3+} , Pt^{4+} , etc.

• d^7 ions – Fe^{1+} , Ru^{1+} , Co^{2+} , Rh^{2+} , Ni^{3+} , etc.

For d^4 - d^7 electron counts:

• when $\Delta_o > \Pi_{total} \rightarrow$ low spin

• when $\Delta_o < \Pi_{total} \rightarrow$ high spin

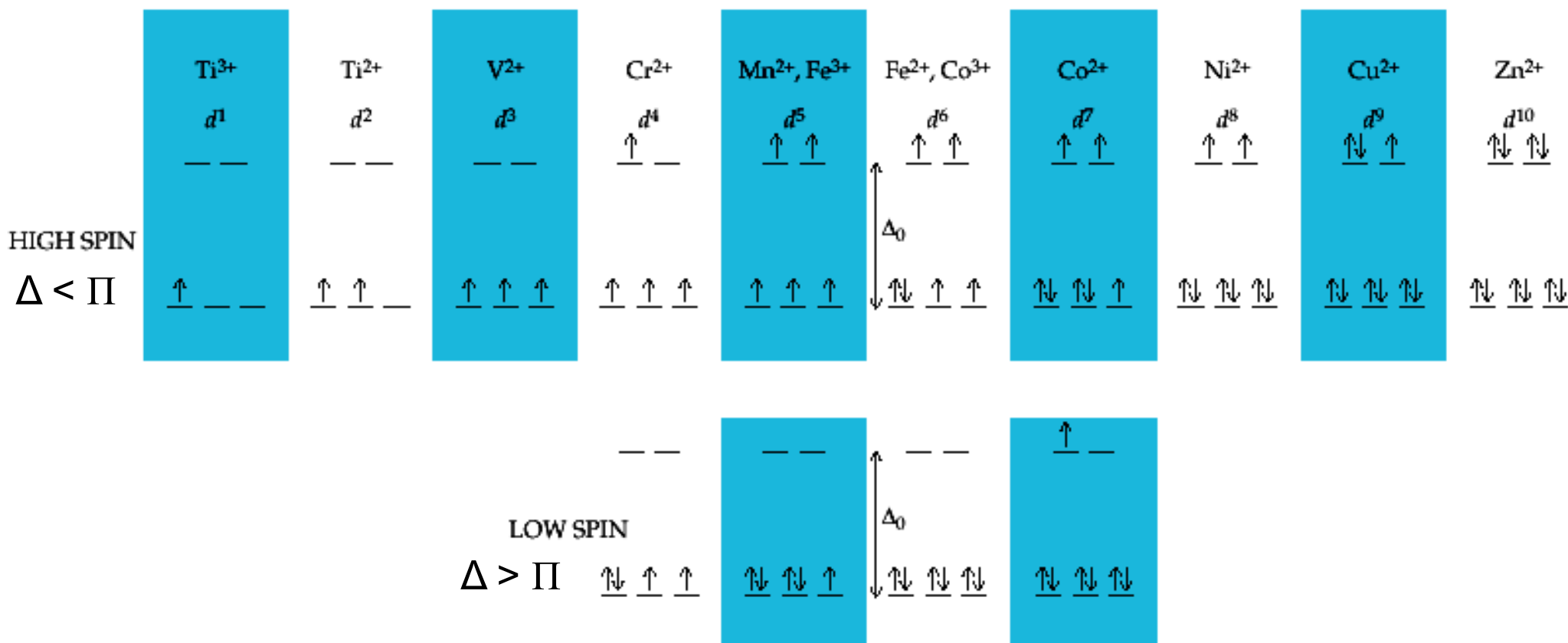


HIGH SPIN

LOW SPIN

High Spin and Low Spin

Electron configurations for octahedral complexes, e.g. $[M(H_2O)_6]^{n+}$.
 Only the d^4 through d^7 cases can be either high-spin or low spin.



Weak-field ligands:

- Small Δ , High spin complexes

Strong-field ligands:

- Large Δ , Low spin complexes

Electron Pairing Energy

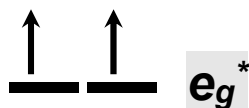
The total electron pairing energy, Π_{total} , has two components, Π_c and Π_e

- Π_c is a destabilizing energy for the Coulombic repulsion associated with putting two electrons into the same orbital
- Π_e is a stabilizing energy for electron exchange associated with two degenerate electrons having parallel spin

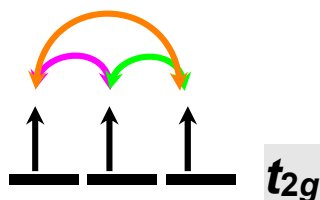
d^4 HS



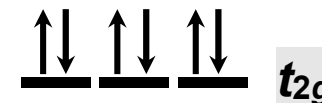
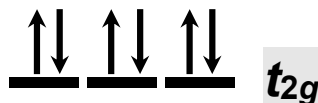
d^8



d^6 LS



Π_e only counts for electrons at the same energy!



$$\Pi_{total} = 3\Pi_e + 0\Pi_c$$

$$\Pi_{total} = 7\Pi_e + 3\Pi_c$$

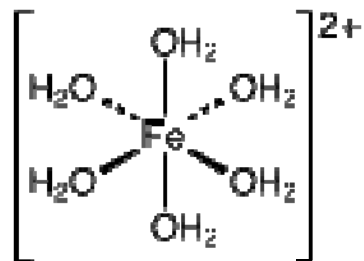
$$\Pi_{total} = 6\Pi_e + 3\Pi_c$$

$$\begin{aligned} LFSE &= 3(-0.4\Delta_o) + 1(0.6\Delta_o) \\ &= -0.6\Delta_o \end{aligned}$$

$$\begin{aligned} LFSE &= 6(-0.4\Delta_o) + 2(0.6\Delta_o) \\ &= -1.2\Delta_o \end{aligned}$$

$$\begin{aligned} LFSE &= 6(-0.4\Delta_o) + 0(0.6\Delta_o) \\ &= -2.4\Delta_o \end{aligned}$$

Using LFSE and Π



Fe^{2+}, d^6

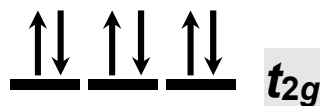
Is the complex high spin or low spin?

$$\Delta_o = 9,350 \text{ cm}^{-1}$$

$$\Pi_c = 19,600 \text{ cm}^{-1}$$

$$\Pi_e = -2,000 \text{ cm}^{-1}$$

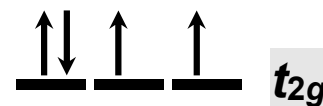
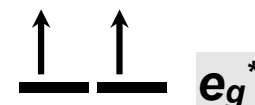
Low Spin



$$\begin{aligned} LFSE &= 6(-0.4\Delta_o) + 0(0.6\Delta_o) \\ &= -2.4(9350 \text{ cm}^{-1}) \\ &= -22,440 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} E &= 3\Pi_c + 6\Pi_e + LFSE \\ &= 3(19600) + 6(-2000) + (-22400) \\ &= 24,360 \text{ cm}^{-1} \end{aligned}$$

High Spin



$$\begin{aligned} LFSE &= 4(-0.4\Delta_o) + 2(0.6\Delta_o) \\ &= -0.4(9350 \text{ cm}^{-1}) \\ &= -3740 \text{ cm}^{-1} \end{aligned}$$

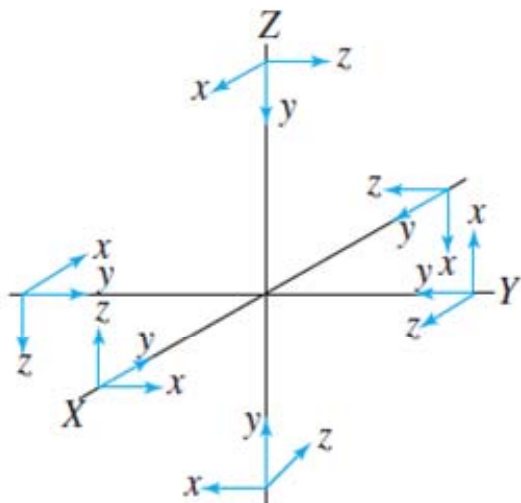
$$\begin{aligned} E &= 1\Pi_c + 4\Pi_e + LFSE \\ &= (19600) + 4(-2000) + (-3740) \\ &= 7,860 \text{ cm}^{-1} \end{aligned}$$

$$\Delta < \Pi$$

Aqua is a weak field ligand;
3d hexaaqua complexes almost always high spin

π -MOs for Octahedral Complexes

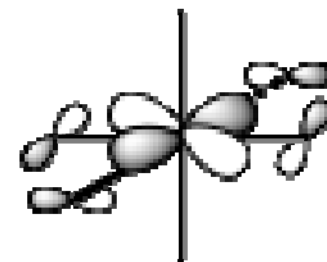
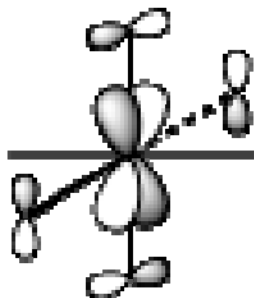
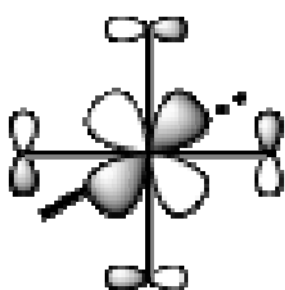
The reducible representation for the π -ligand orbitals in O_h :



*x and y axes
on each ligand*

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2'$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	irreducible representations
Γ_π	12	0	0	0	-4	0	0	0	0	0	$T_{1g} + T_{2g} + T_{1u} + T_{2u}$

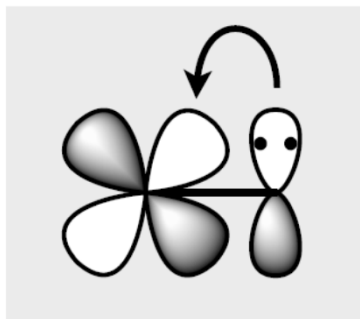
The non-bonding t_{2g} orbitals of an octahedral metal complex are oriented perfectly to form π -bonds with ligands



π Donor vs π Acceptor Ligands

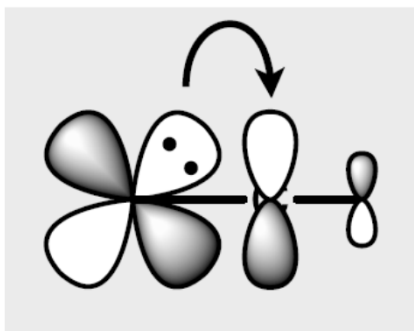
The nature of the metal ligand π interaction is dependent on the type of ligand.

- π -donor ligands are ligands with one or more lone pairs of electrons in p orbitals on the donor atom that can donate to empty orbitals on the metal.
 - preferred for metals with high oxidation states and low d electron count (d^0 - d^3)



Examples:
 Cl^- , Br^- , I^- , OR^- , SR^- ,
 NR_2^- , O^{2-} , NR^{2-} , N^{3-}

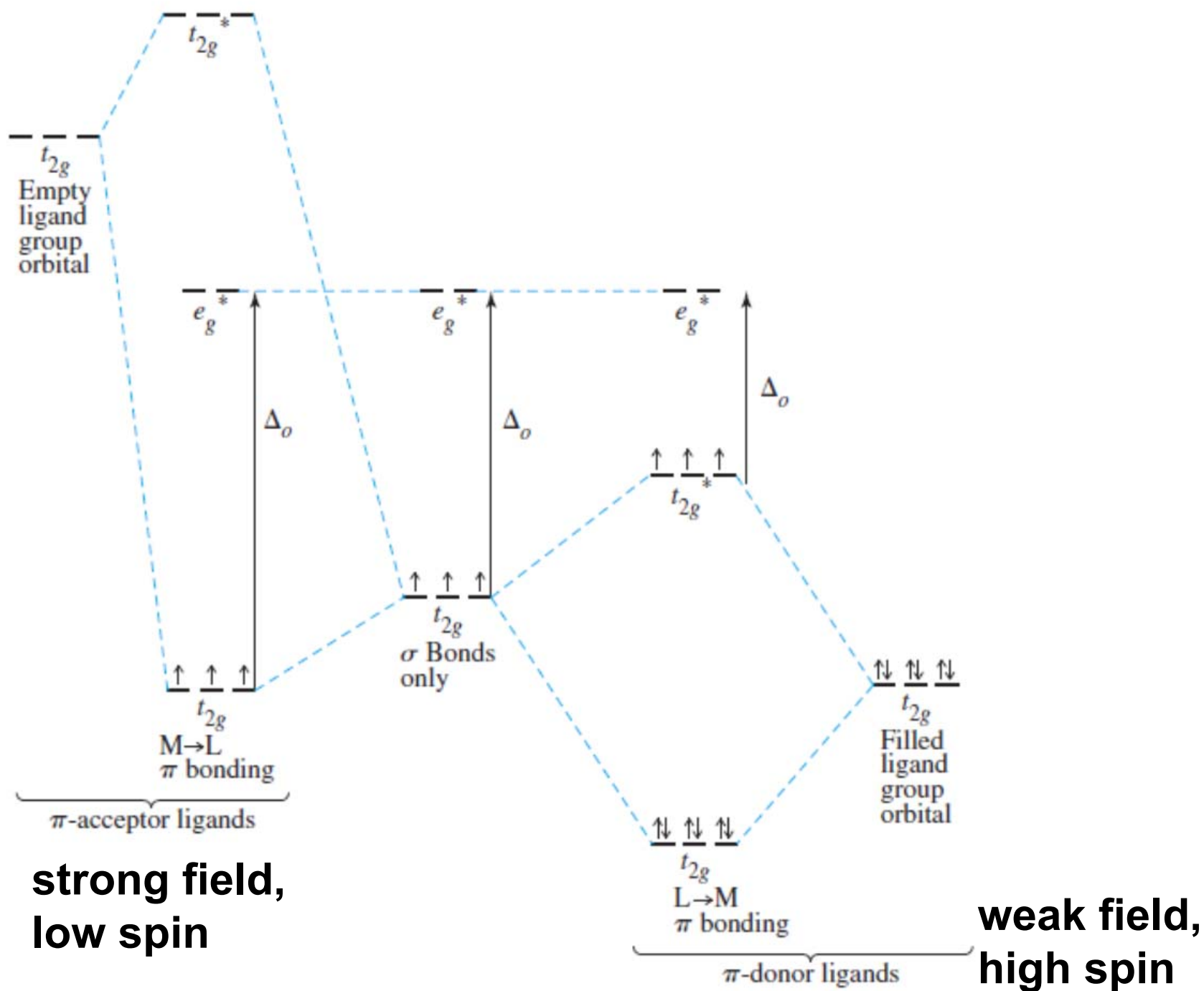
- π -acceptor ligands (π -acidic ligands) are ligands with empty π^* orbitals on the donor atom that can accept electrons from the metal.
 - preferred for metals with low oxidation states and high d electron count (d^6 or higher)
 - donation of electron density from the metal to the ligand π^* orbital results in weakening of the multiple ligand bond



Examples:
 CO , NO , CN^- , pyridine

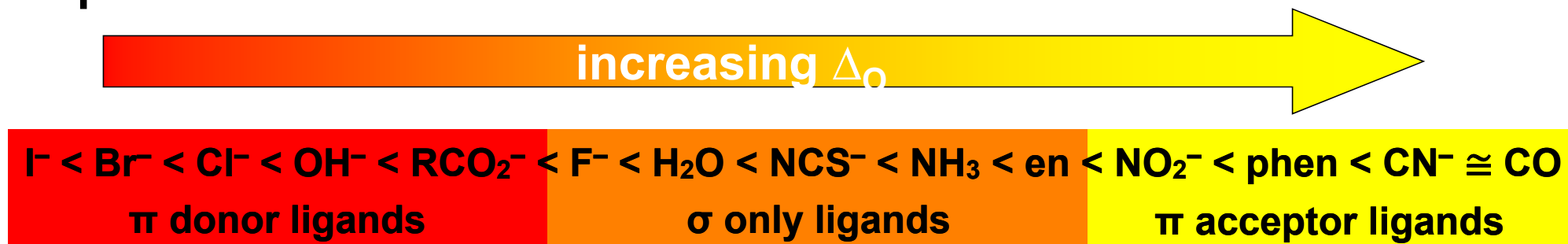
“ π back bonding”

π -Effects in Octahedral Complexes



Spectrochemical Series

The trend in Δ_o that arises from π -donor, σ -only, and π -acceptor ligands is the basis for the Spectrochemical Series. For $[ML_6]^{n+}$ complexes:



- weak-field ligands
- high-spin complexes for 3d metals*

- strong-field ligands
- low-spin complexes for 3d metals*

The value of Δ_o also depends systematically on the metal:

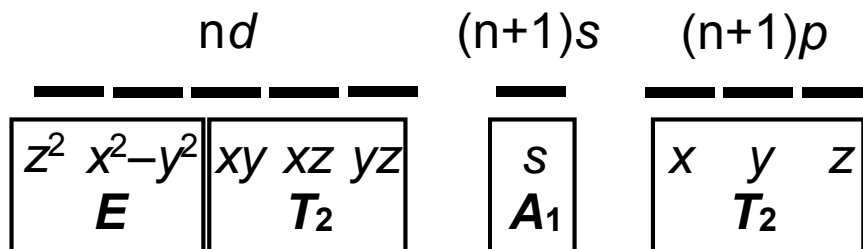
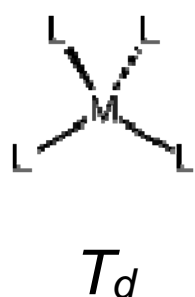
1. Δ_o increases with increasing oxidation number.
2. Δ_o increases down a group.

→ both trends are due to *stronger metal-ligand bonding*.

* Due to effect #2, octahedral 3d metal complexes can be low spin or high spin, but 4d and 5d metal complexes are always low spin.

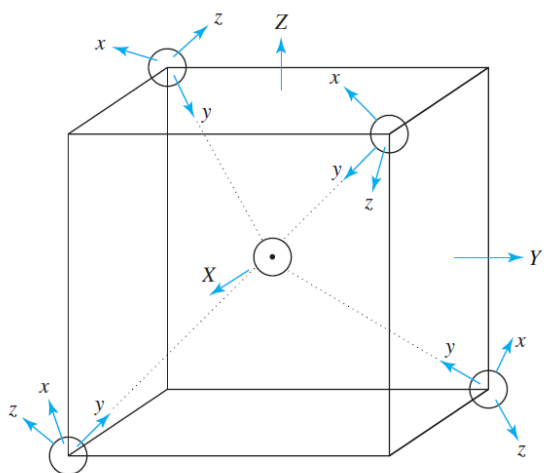
σ -MOs for Tetrahedral Complexes

Four-coordinate tetrahedral complexes are ubiquitous throughout the transition metals.

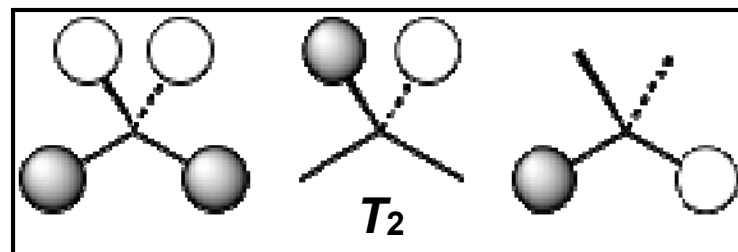
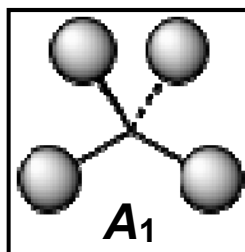


the irr. reps. of the metal valence orbitals are obtained directly from the character table

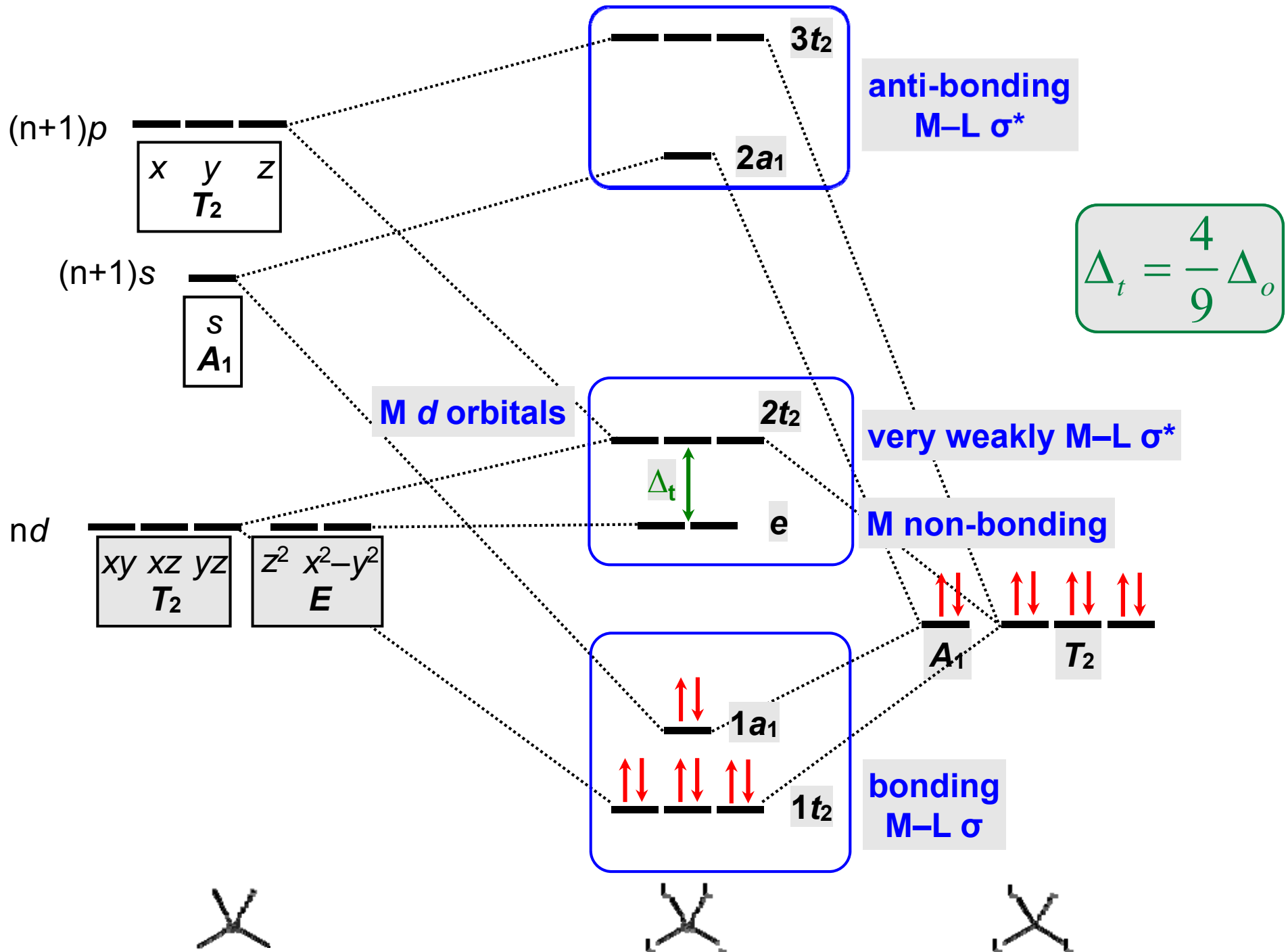
For the ligand orbitals we need to consider how the Lewis base pairs transform in the T_d point group. The result is:



$$\Gamma_{\sigma} = A_1 + T_2$$

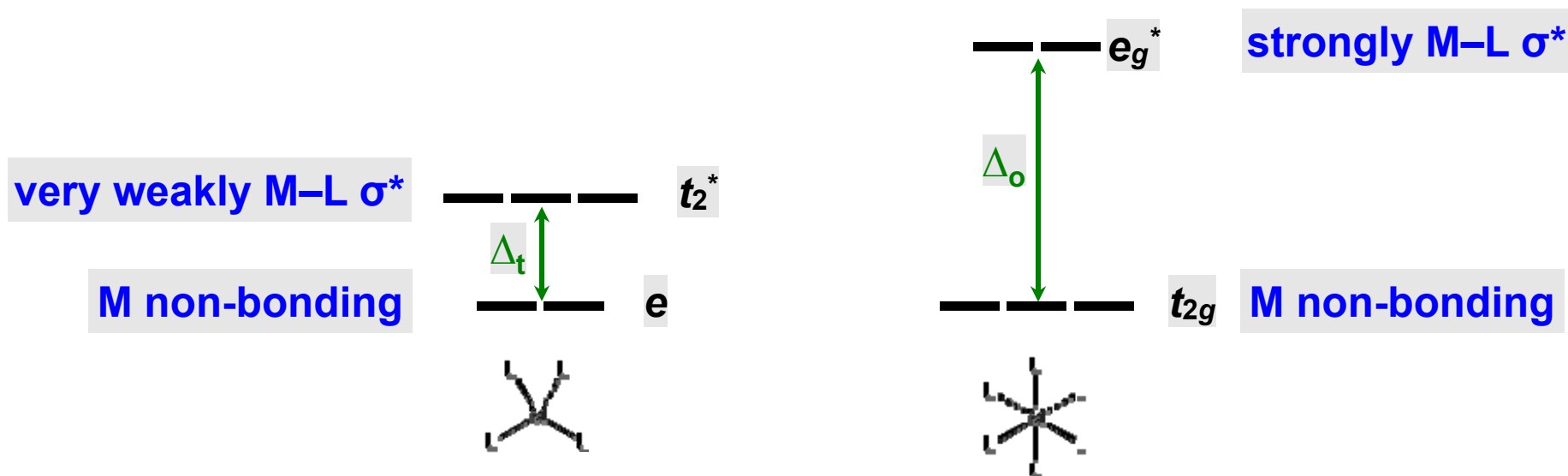


σ -ML₄ Tetrahedral MO Diagram



Tetrahedral Complexes

- Metal d orbitals are split into a non-bonding E set and a very weakly anti-bond T_2 set
- tetrahedral geometry can accommodate all d electron counts, from d^0 to d^{10}



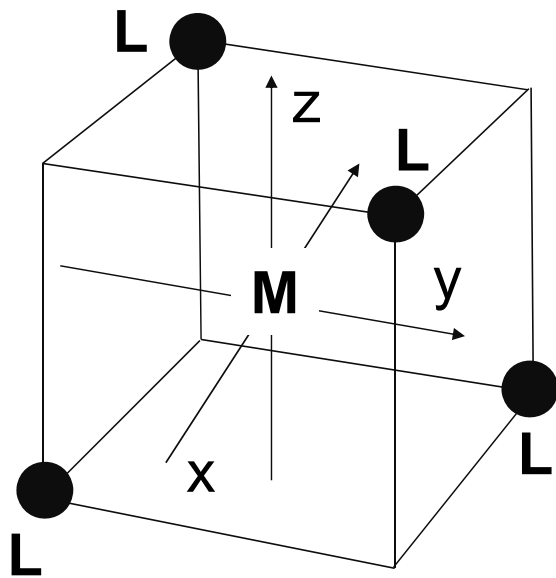
- Δ_t is small compared to Δ_o :

$$\Delta_t = \frac{4}{9} \Delta_o$$

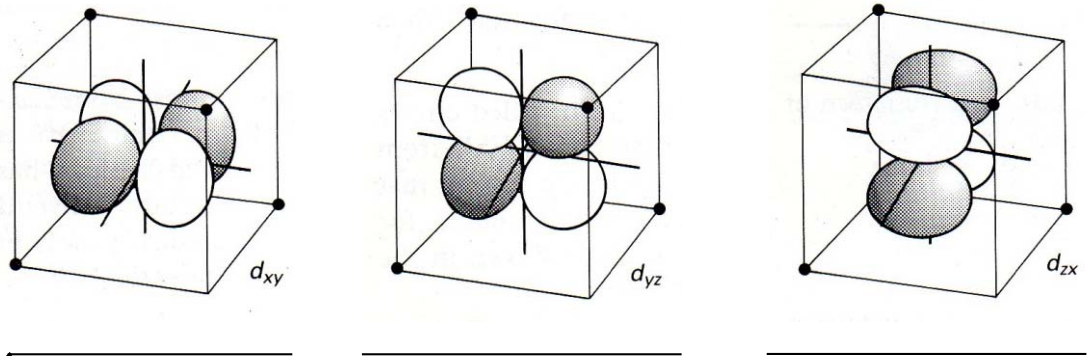
- All tetrahedral complexes of the 3d transition metals are HIGH SPIN!
- Tetrahedral complexes of the heavier transition metals are low spin.

Tetrahedral Crystal Field Splitting

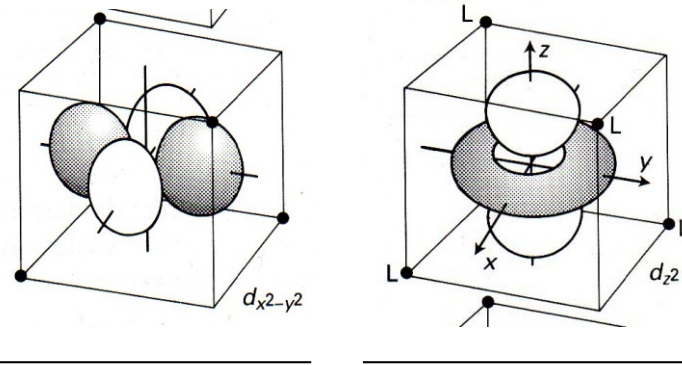
opposite splitting of
octahedral field



barycenter
(spherical field)



t_2 orbitals point more directly at
ligands and are destabilized.



e orbitals point less directly at ligands
and are stabilized.

$\Delta_t < \Delta_o$ because only 4 ligands and *d* orbitals point between ligands