Chapter 23

Introduction to the Transition Elements: Ligand Field Theory

Bonding in Transition Metals
- Crystal Field Theory (CFT)
- Ligand Field Theory (LFT)
- Molecular Orbital Theory (MO)

The power behind any theory is how well it explains properties and the spectroscopic behavior of compounds and, in the case of transition metals complexes, magnetic behavior.

Ligand Field Theory (LFT) is much simpler than MO theory (a little more sophisticated than CFT), but it is a very useful theory.

Transition Elements / Compounds

- "d block" elements/compounds

- Primarily strong, hard metals in their elemental forms that conduct electricity and heat very well.

- They form colored compounds (varies with ox. state) due to electronic transitions in the visible region from one d orbital to another (small energy gap)

- They are often paramagnetic (i.e. they contain unpaired electron(s))

Various bonding theories can explain the properties of T.M. (transition metal) compounds.

First, show (without derivation) the M.O. approach

Bonding in Transition Metal Comlexes:
Two Considerations

A. <u>Geometry</u>

ML_6 O_h (octahedral)

ML_4 T_d vs D_{4h}

       (tetrahedral vs. square planar)
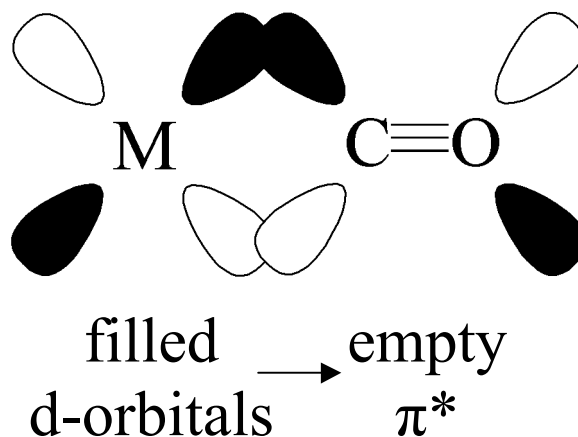
B. <u>Ligand Type</u> π – acceptors

              π – donors

              σ – donors

many ligands are a combination of donor types, but the "pure" donor diagrams can be considered
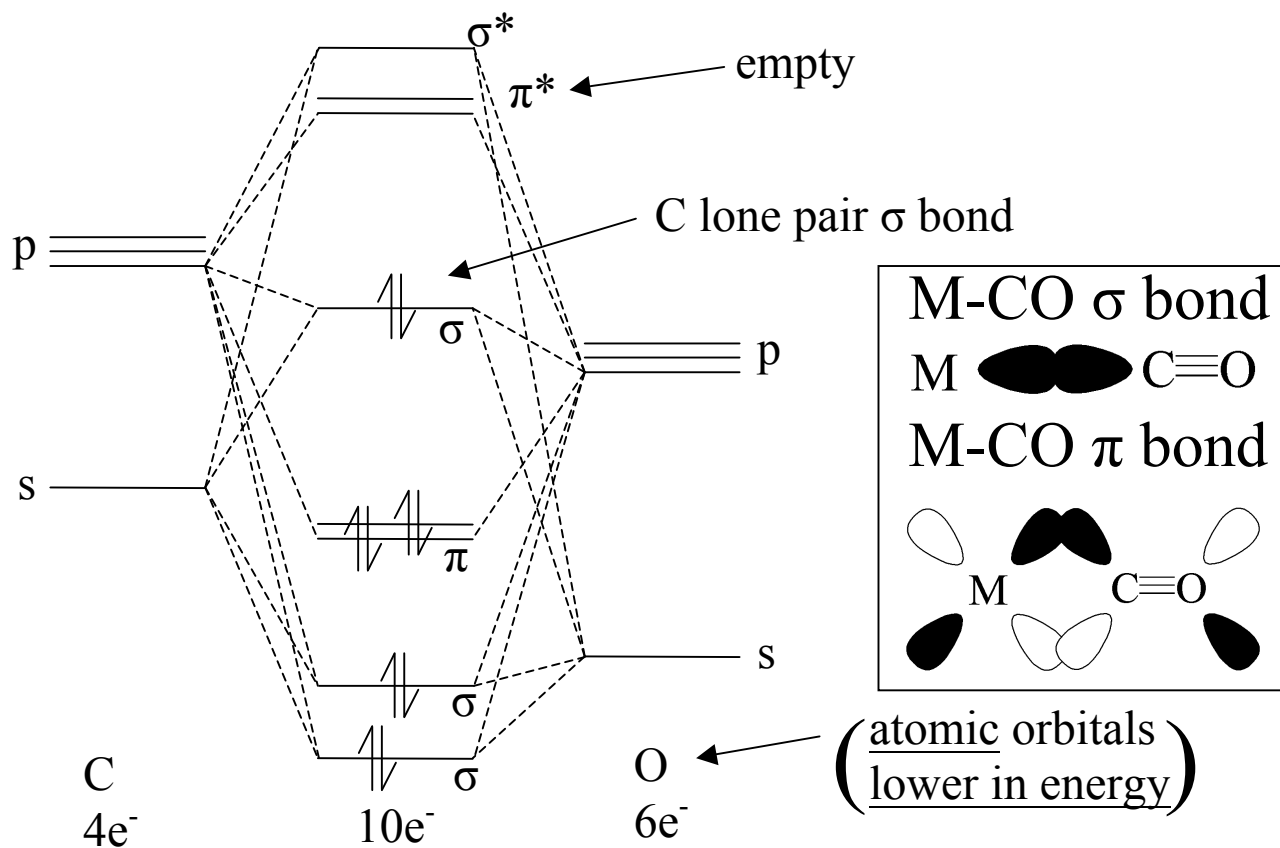
<u>π – acceptors</u>

CO, NO^+, CNR, CN^-

filled $\longrightarrow$ empty
d-orbitals π^*

<u>π – donors</u> halides (X^- = Cl, Br, I)
NH_2^- (amide)
NR_2^-
O_2^-
OR^-, SR^-

<u>σ – donors</u> H^-, NH_3

Molecular Orbital Treatment

Without going into the group theory considerations of how to set up symmetry adapted atomic orbitals on the metals and the ligands. First, recall MO diagram for CO.

$\boxed{\text{ML}_n}$ How would one go about trying to build a molecular orbital diagram for a coordination complex?

- Assume central atom has s, p, d orbitals in valence shell = 9 orbitals
- Assume each ligand atom, L, has s and p orbitals
    4 x n ligands = 4n orbitals

Octahedral ML_6

metal   9 orbitals

ligands   4x6 = 24 orbitals

$\left.\phantom{\begin{array}{c}a\\b\\c\end{array}}\right\}$ Total number of orbitals in the "basis set" is 33.

Thirty – three orbitals sounds like a lot!

Actually, it is not as bad as it sounds, because the orbitals can be grouped according to special rules dictated by the shape of the molecules

$\longrightarrow$ symmetry adapted linear combinations (SALC'S)

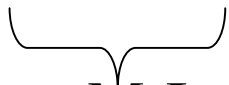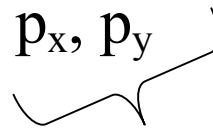# Electronic Structure of Transition Metal Complexes

Q. What are we trying to accomplish?

A. An understanding of how d orbitals are affected by bringing "n" ligands around the metal center.

ML_n n = 6   Octahedral   } basic
        n = 4   Tetrahedral   } geometry

The d orbitals on M change energy according to the types of orbitals on L (σ, π, π^*)

σ – Donor Only Case

Metal   d   s   p   Energy-wise d < s < p
          (5) (1) (3)   highest occupied are d
                                 as s and p are empty for M^{n+}

Ligands   s, p_z, p_x, p_y

       along M-L   these form
       axis so used in   π - bonds
       σ - bonding

∴ on the ligands, if only σ – bonding is possible for an
ML_6 compound:

Metal   Ligand
d, s, p = 9 orbitals   s + p_z → sp

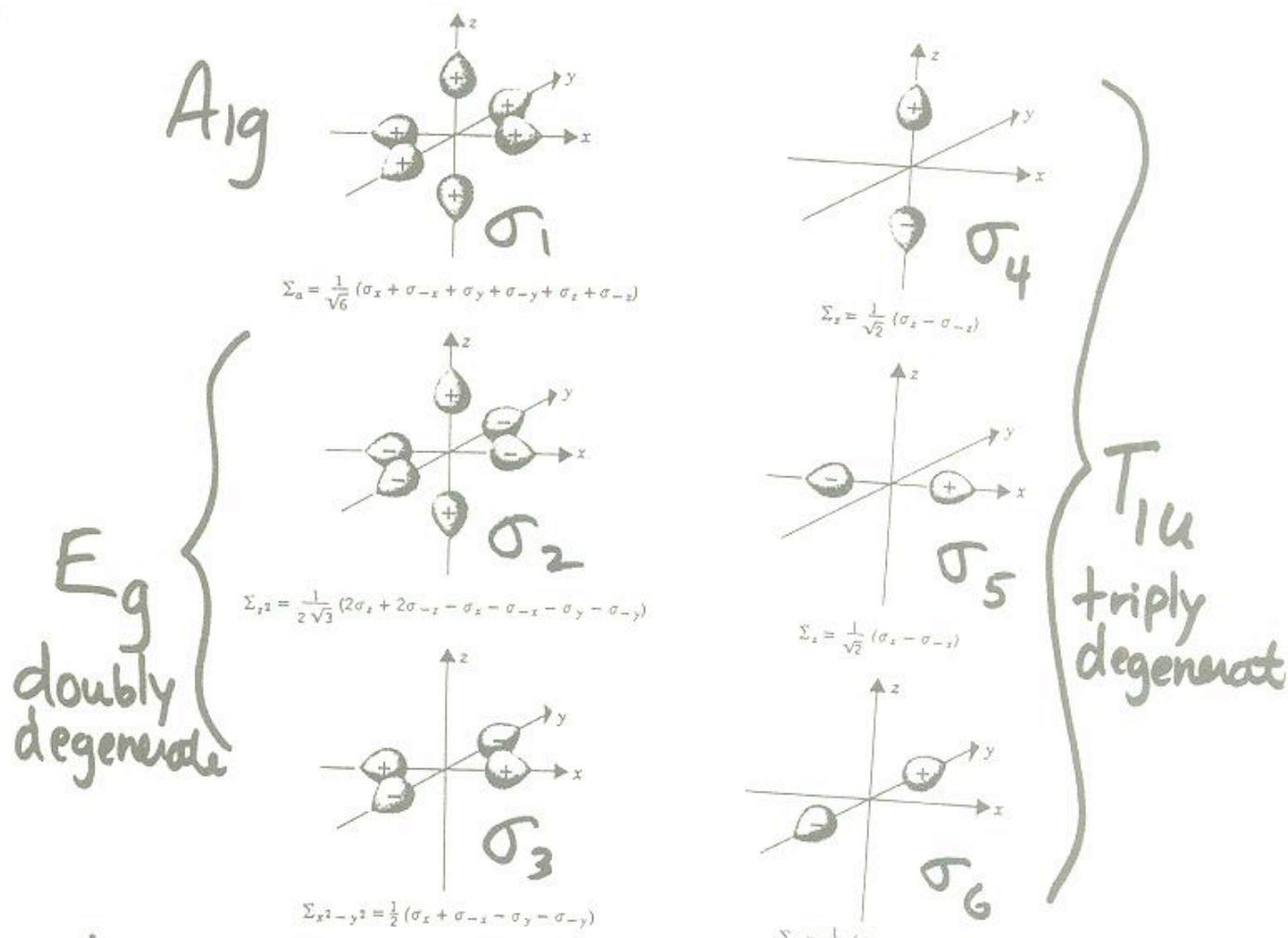   6 x   orbitals
             we use these to make SALC's
          symmetry adapted linear combinations

Six SALC's

The Ligand Group Orbitals for :L donating a lone pair to a M-L sigma bond look like this:

A_{1g} σ_1

$\Sigma_a = \frac{1}{\sqrt{6}}(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})$

σ_4

$\Sigma_z = \frac{1}{\sqrt{2}}(\sigma_z - \sigma_{-z})$

E_g doubly degenerate

σ_2

$\Sigma_{z^2} = \frac{1}{2\sqrt{3}}(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$

σ_3

$\Sigma_{x^2-y^2} = \frac{1}{2}(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$

σ_5

$\Sigma_x = \frac{1}{\sqrt{2}}(\sigma_x - \sigma_{-x})$

σ_6

T_{1u} triply degenerate

Now, we need to match these symmetries with the same symmetries from the metal valence orbitals. These will be the only combinations to produce overlap!

O_h character table

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2'$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(x^2-y^2), z^2$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, yz, zx)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

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The metal orbitals are grouped by symmetry labels just like the ligand SALC'S

$s \rightarrow A_{1g}$ (one orbital)

$p \rightarrow T_{1u}$ (three orbitals so triply degenerate)

In an octahedral environment, the five d orbitals split:

$d \nearrow$ E_g (two orbitals so doubly degenerate) $d_{x^2-y^2}$, d_{z^2}

↘ T_{2g} (three orbitals so triply degenerate)

$$d_{xy}, d_{xz}, d_{yz}$$

since d < s < p in energy, the M.O. diagram arranges them

$\equiv T_{1u}$

——— A_{1g}

$\equiv E_g$

$\equiv T_{2g}$

Six metal and Six Sigma Ligand Orbitals

Metal	Ligand	Metal	Ligand

① A_{1g}

s

σ_1

$$\Sigma_a = \tfrac{1}{\sqrt{6}}(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})$$

② (a)

E_g

(b)

dz^2

σ_2

$$\Sigma_{z^2} = \tfrac{1}{2\sqrt{3}}(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$$

dx^2-y^2

σ_3

$$\Sigma_{x^2-y^2} = \tfrac{1}{2}(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$$

T_{1u}

Pz

Px

Py

σ_4 (a)

$$\Sigma_z = \tfrac{1}{\sqrt{2}}(\sigma_z - \sigma_{-z})$$

③ σ_5 (b)

$$\Sigma_x = \tfrac{1}{\sqrt{2}}(\sigma_x - \sigma_{-x})$$

σ_6 (c)

$$\Sigma_y = \tfrac{1}{\sqrt{2}}(\sigma_y - \sigma_{-y})$$
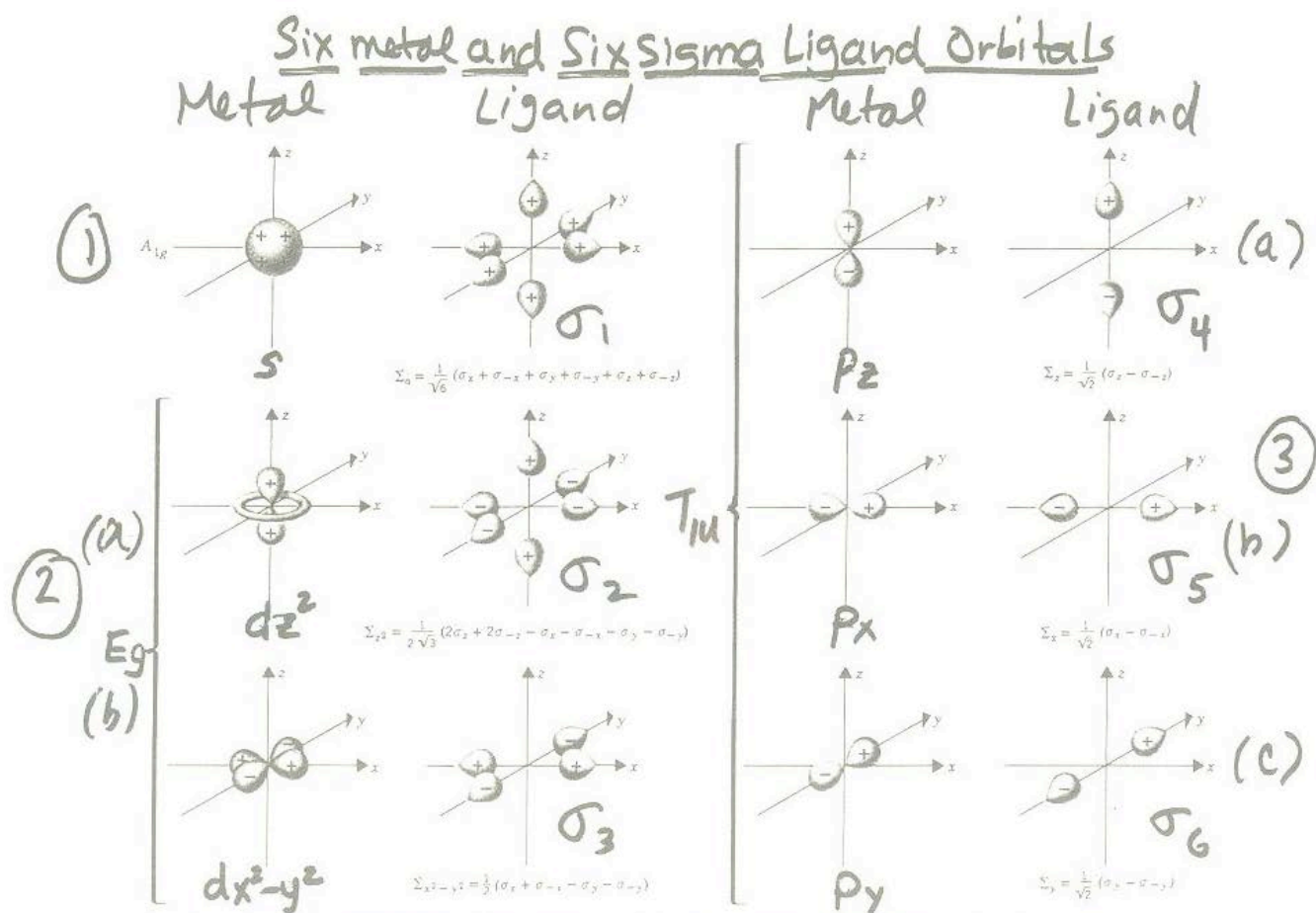
Figure 23-8 The six metal orbitals with σ symmetry and the ligand group orbitals (Σ) that overlap properly with these metal orbitals to form σ-type MO's in an ML$_6$ complex. Each ligand group orbital (Σ, with subscripts to designate the matching d orbital) is shown adjacent to the metal orbital with which it overlaps. The resulting MO's are listed in Fig. 23-9. The E_g set is doubly degenerate and the T_{1u} set is triply degenerate.

σ-MOs for Octahedral Complexes

We *can* use the projection operator method to deduce the shape of the ligand group orbitals, but let's skip to the results:

$\underline{L_6}$ SALC	symmetry label
$\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$	A_{1g} (non-degenerate)
$\sigma_1 - \sigma_3 , \sigma_2 - \sigma_4 , \sigma_5 - \sigma_6$	T_{1u} (triply degenerate)
$\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 , 2\sigma_6 + 2\sigma_5 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4$	E_g (doubly degenerate)
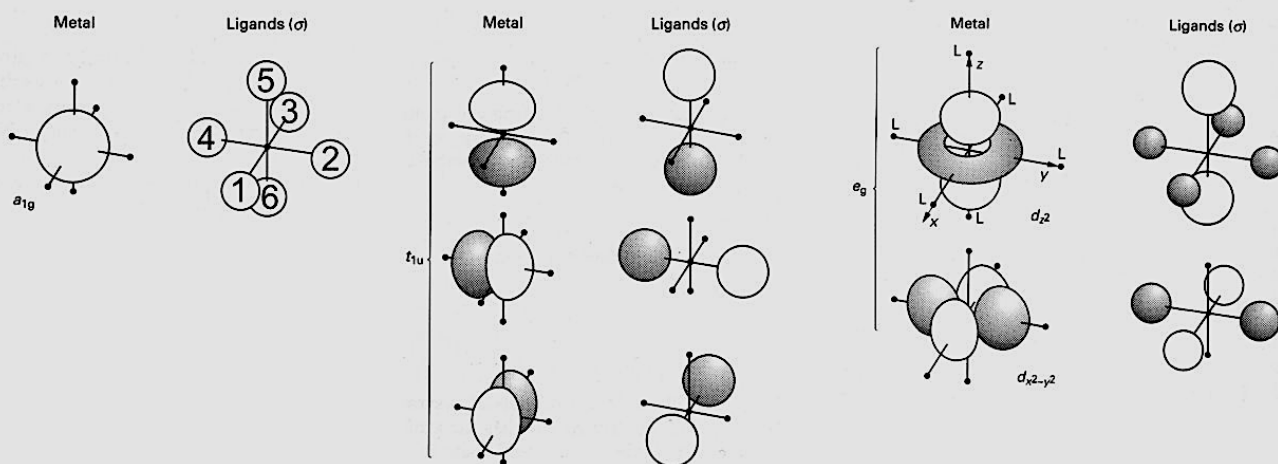
O_h M.O. Diagram $\quad$ σ-Donor $[Co(NH_3)_6]^{3+}$

metal
orbitals

molecular
orbitals

ligand
orbitals

t_{1u} (σ*)

T_{1u}

4p

a_{1g} (σ*)

important part
of the MO
diagram Δ_o
changes with
ligand

A_{1g}

4s

e_g (σ*)

Δ_o

t_{2g}
non-
bonding

E_g

T_{2g}

3d

A_{1g}

T_{1u}

E_g

note*
order of Coulomb
energies for metal &
ligand orbitals
σ(L) < nd < (n+1)s
< (n+1)p

t_{1u}

e_g

a_{1g}

6 NH$_3$
sigma bonds
12e⁻ in 6 NH$_3$
ligands

π – Donor Case

$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^{-}$

you have σ and π bonding
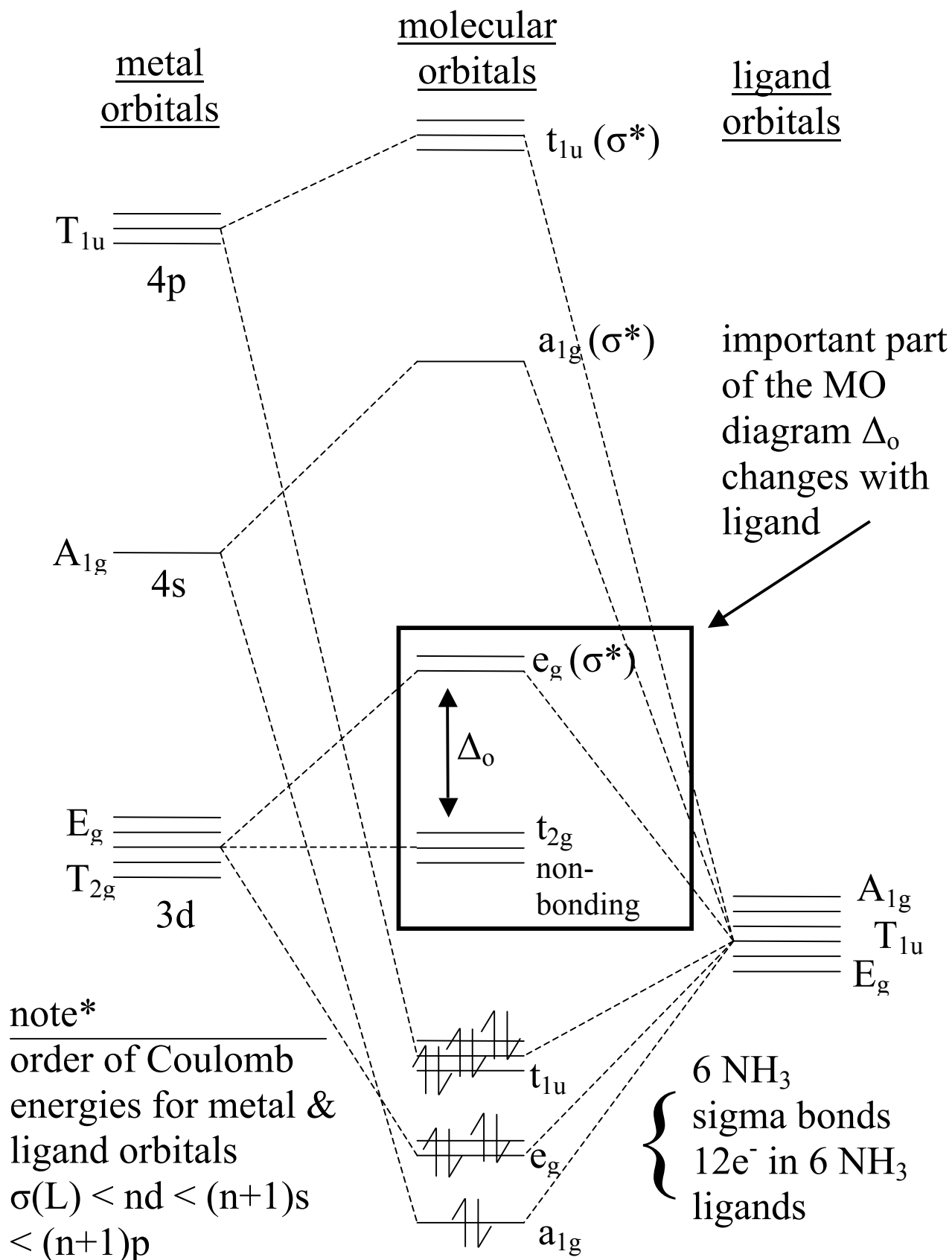
$\left(\begin{array}{c}\text{there are lone pairs that can make both types of}\\ \text{bonds as opposed to } :NH_3 \text{ which only has a lone}\\ \text{pair for } \sigma - \text{bonding}\end{array}\right)$

(sp hybrid)

L   s, p$_z$,   p$_x$, p$_y$

$\underbrace{}$ $\underbrace{}$

σ - bonds π - bonds

for ML$_6$:

M: (same as before)

9 orbitals   A$_{1g}$, T$_{1u}$, T$_{2g}$ E$_g$

s   p   d
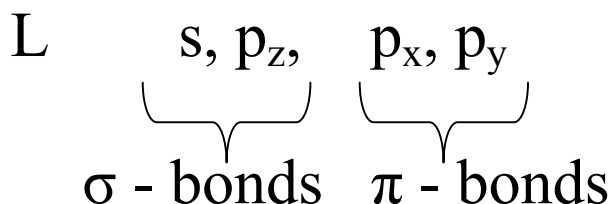
L: 6 σ orbitals (A$_{1g}$, T$_{1u}$, E$_g$)

6 x 2 (p$_x$,p$_y$) = 12 π orbitals

(T$_{1g}$, T$_{2g}$, T$_{1u}$, T$_{2u}$)

What are ligands that use π – bonds?

(π – donors like halides for example)

metal

dxz

ligands

$\Pi_{zx} = \frac{1}{2} | p_x(1) - p_x(2) + p_z(3) - p_z(4) |$
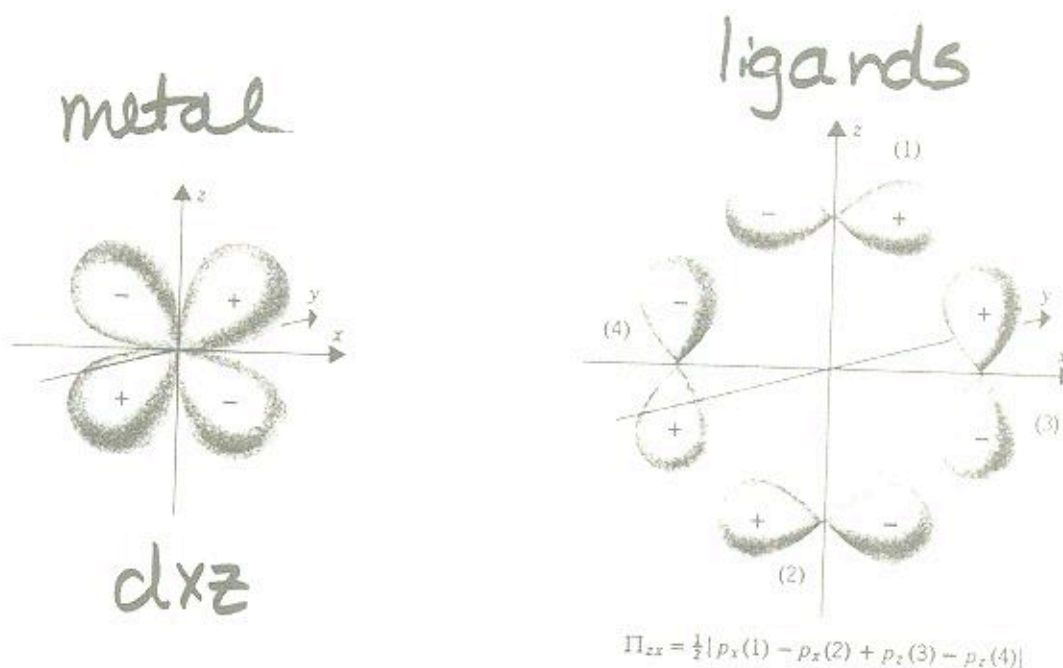
Group orbital made up of combinations of p_x and p_z orbitals on four of the atoms
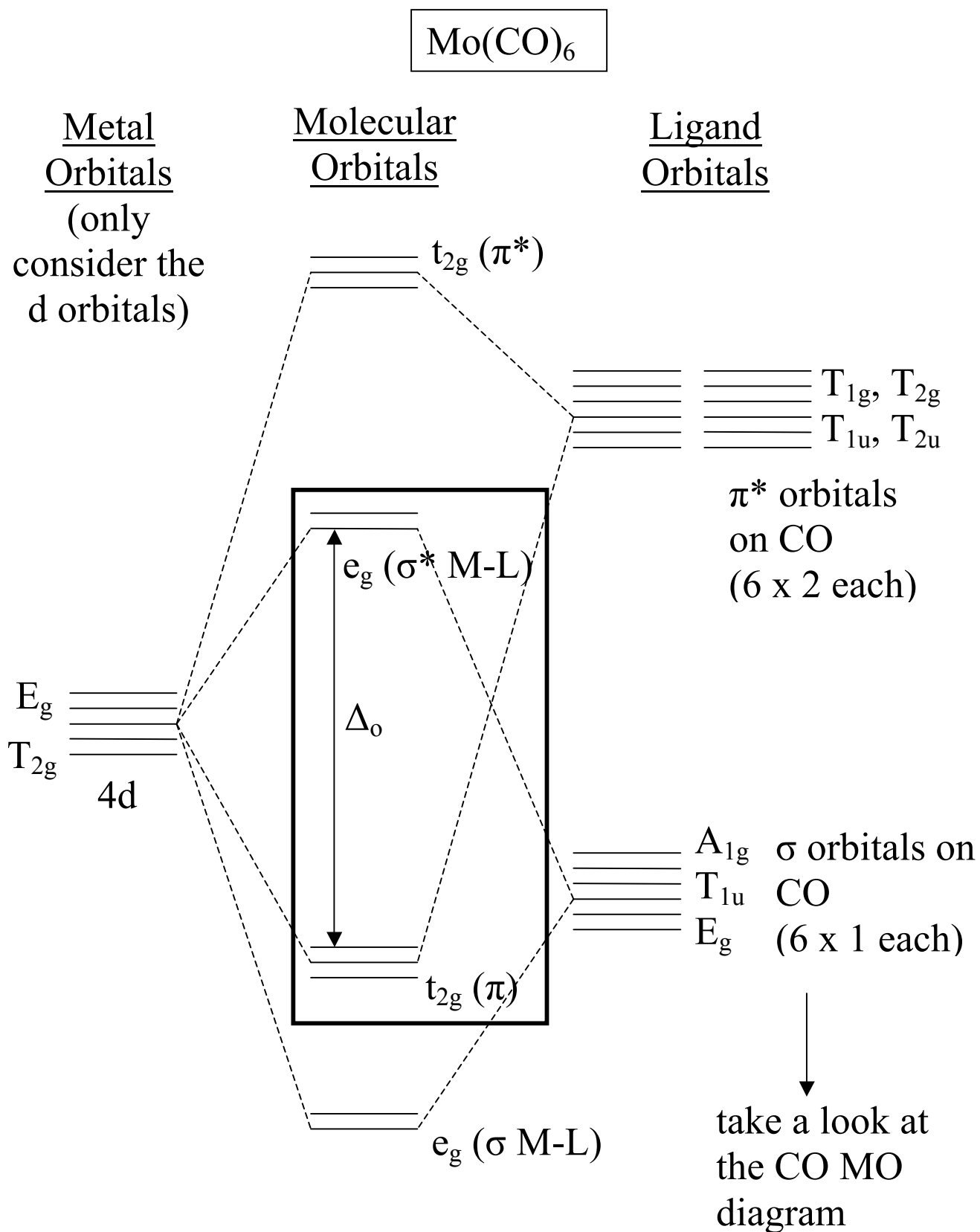
Note:
   There are two more sets based on M d_{yz} and M d_{xy}.

O_h M.O. Diagram π – Donor $[CoCl_6]^{5-}$
## (Don't need to sketch the whole diagram)

Metal
Orbitals

Molecular
Orbitals

Ligand
Orbitals

focus on this
part only

both sets of d
orbitals are
driven ↑ in
energy due to
lower lying
ligand orbitals

T_{1u} —— 4p

A_{1g} —— 4s

E_g
T_{2g} —— 3d

$e_g (\sigma^*)$

Δ_o

$t_{2g} (\pi^*)$

T_{1g}, T_{2g}

T_{1u}, T_{2u}
π-orbitals
p_x, p_y

$t_{2g} (\pi)$

A_{1g}

T_{1u} σ-orbital

E_g p_z

$e_g (\sigma)$

O_h M.O. Diagram π – acceptor
CO, NO^+, CNR, CN^-

$\boxed{Mo(CO)_6}$

Metal
Orbitals
(only
consider the
d orbitals)

Molecular
Orbitals

Ligand
Orbitals

$t_{2g}(\pi^*)$

T_{1g}, T_{2g}
T_{1u}, T_{2u}

π^* orbitals
on CO
(6 x 2 each)

$e_g (\sigma^* M\text{-}L)$

Δ_o

E_g

T_{2g}

4d

$t_{2g}(\pi)$

A_{1g} σ orbitals on
T_{1u} CO
E_g (6 x 1 each)

$e_g (\sigma M\text{-}L)$

take a look at
the CO MO
diagram

Bottom Line and this **ALL I WANT YOU TO HAVE TO BE RESPONSIBLE FOR KNOWING (you don't have to know how to derive the previous results):** M.O. Theory predicts different energy separations for the d orbitals (which are where the outer electrons reside on the metal) **depending on the type of ligand**

①

e_g

② Δ_o

t_{2g}

Octahedral, ML_6, symmetry (geometry) dictates the two sets of orbitals
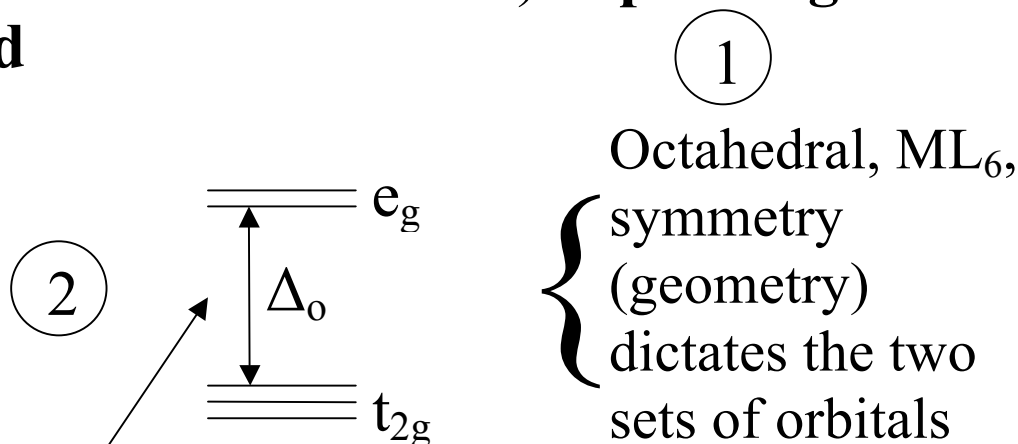
<u>extent</u> and <u>type</u> of M-L bonding dictates the separation!

To summarize O_h M.O. Splittings

$e_g (\sigma^*)$

Δ_o

$t_{2g} (\pi)$

M-L bonding

π-acceptor

<u>largest separation</u>
between sets of d-orbitals

antibonding

$e_g (\sigma^*)$

Δ_o

t_{2g} (n.b.)
non-bonding

σ-donor

<u>intermediate</u>
separation

$e_g (\sigma^*)$

Δ_o

$t_{2g} (\pi^*)$
both are
antibonding

π-donor

<u>smallest</u>
separation
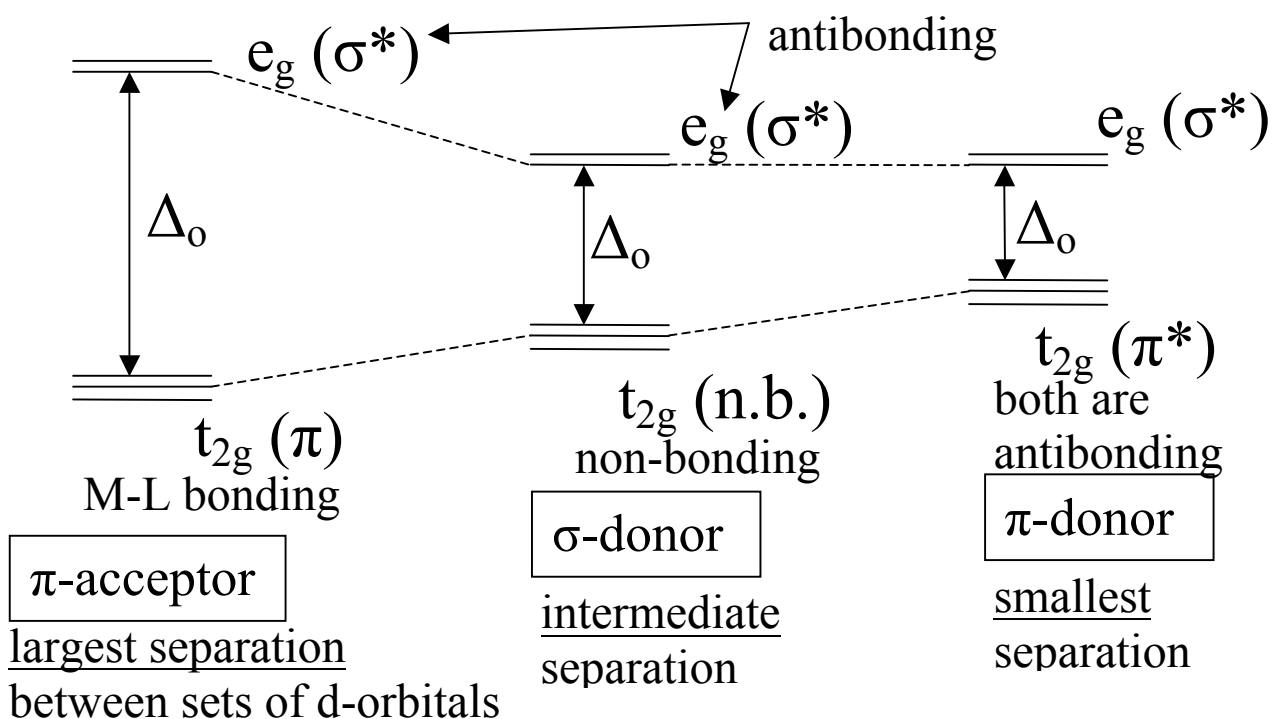
These trends reflect the energies of the orbitals from the ligands and their symmetries. Also, the <u>strength</u> of their interaction is going to affect the Δ_o separation <u>strong – field</u> (bigger splitting) versus <u>weak – field</u> ligands (smaller splitting) and the metal dependence.

<u>Metal dependence</u>

<u>Lower field (smaller splittings)</u>
$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$
$< Mn^{4+} < Mo^{3+} < Rh^{3+} < Pd^{4+} < Ir^{3+} < Re^{4+} < Pt^{4+}$
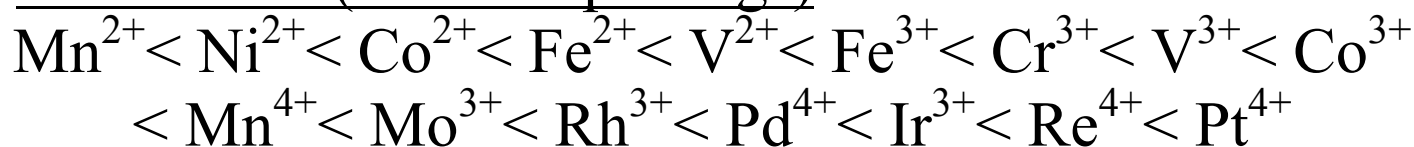
<u>Stronger Field</u>
(larger splittings)

<u>Ligand dependence</u>
<u>Spectrochemical Series</u>

<u>π – acceptors</u>
$NO^+ > CO, PF_3 > CN^- > NO_2 > NH_3 > H_2O > OH^- > F^-$
$> S^{2-} > Cl^- > Br^- > I^-$
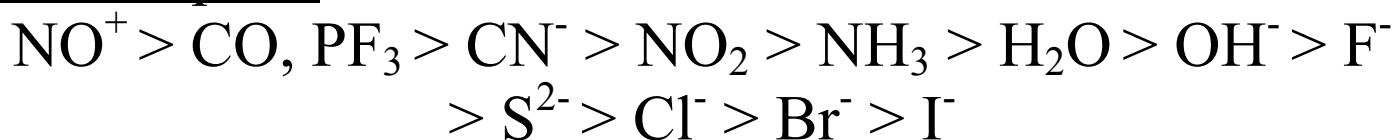
<u>π – donors</u> (weak)

<u>More simple theories then M.O. theory:</u>

Crystal Field Theory and Ligand Field Theory

(CFT and LFT)

CFT assumes that bonds between the metal atom and the ligands are totally ionic – in other words, point charges

LFT is a modification of CFT that allows for the effects of covalent character in the bonds, but the two theories are used in essentially the same manner.

CFT/LFT theories are especially well-adapted to explaining the spectroscopic properties of transition metal complexes and accounting for magnetic properties.
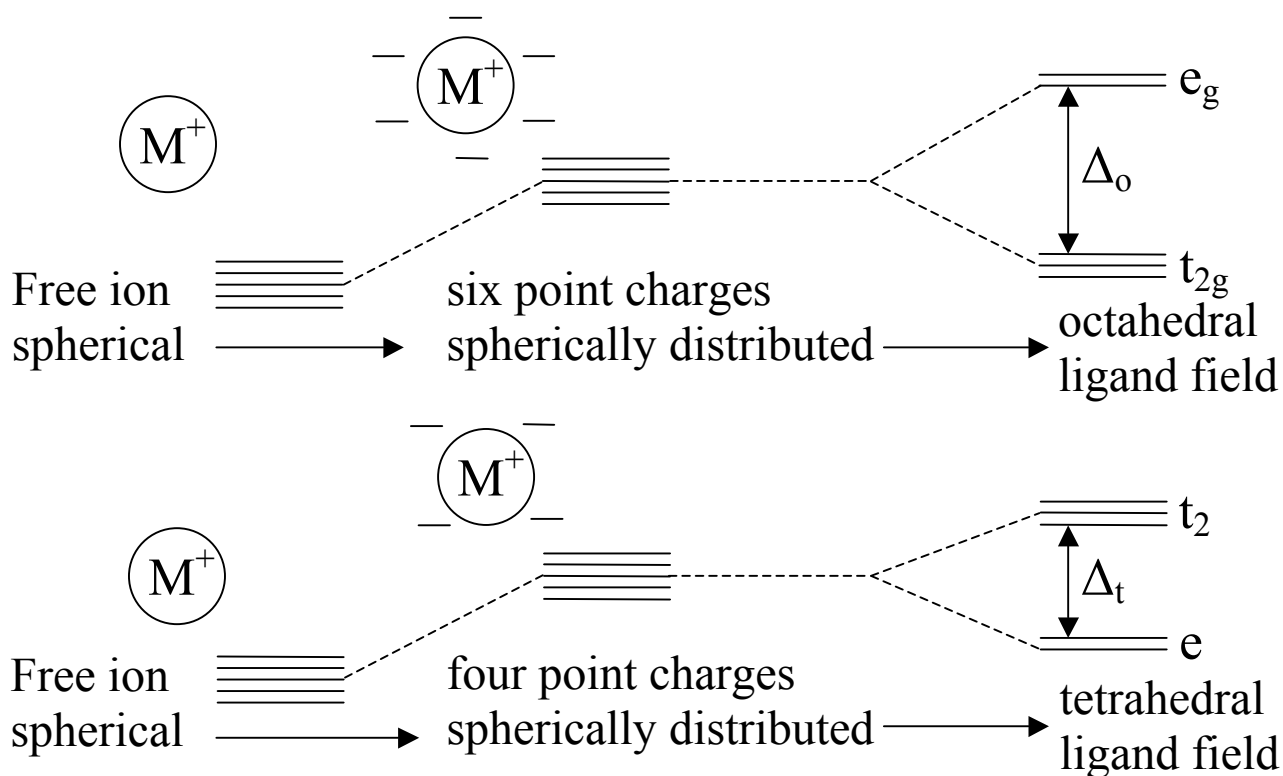
Group theory tells us that there are two different groups of orbitals in

O_h → T_{2g}, E_g ← symmetry labels
(octahedral)

d_{xy}, d_{yz}, d_{xz} $d_{x^2-y^2}$, d_{z^2}

T_d → T_2, E ← symmetry labels
(tetrahedral)   (same as above without g)
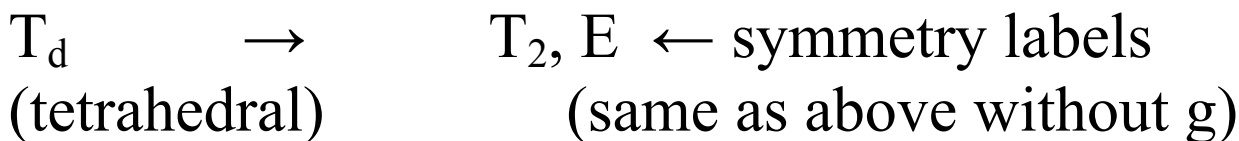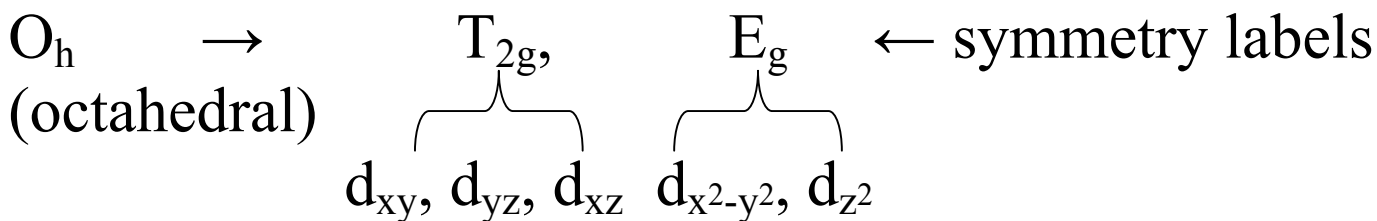
Just as in O_h, T_d has a different amount of d orbital splittings with different types of ligands- the trend is the same as in O_h

$$\sigma \text{ donors, } \pi - \text{ donors, } \pi - \text{ acceptors}$$
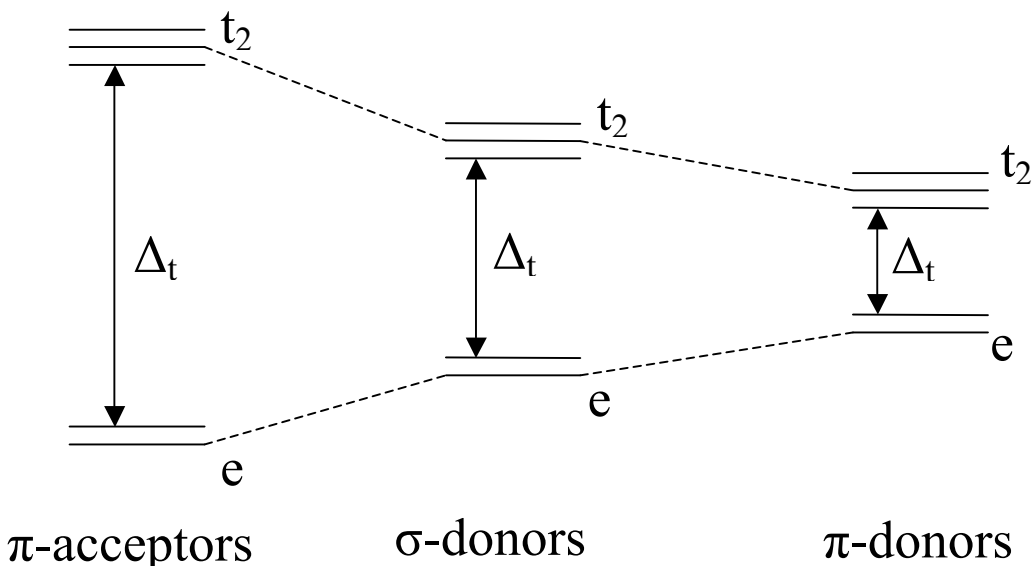
What is the relationship between Δ_o (10 Dq) and Δ_t?

another way to write the energy separation

$\Delta_t = 4/9 \; \Delta_o$ for similar metal cations/ligands

But how was the relative ordering decided without the arguments of Molecular Orbital Theory?

With the Cartesian coordinate system selected for an O_h symmetry molecule, the $\ominus$ charges are directed along the x, y and z axes where the $d_{x^2-y^2}$ and the d_{z^2} orbital point.

Since electrons in these orbitals would be expected to <u>repel</u> the negative charges of the ligands, these orbitals are <u>raised</u> in energy from a spherically distributed set of charges. The other orbitals point in <u>between</u> the negative charges of the ligands.

lower case letters for orbital

d_{z^2}, $d_{x^2-y^2}$ (e_{2g})
(destabilized)

10Dq or Δ_o

spherical field
of 6 charges

d_{xy}, d_{xz}, d_{yz} (t_{2g})
O_h (stabilized)
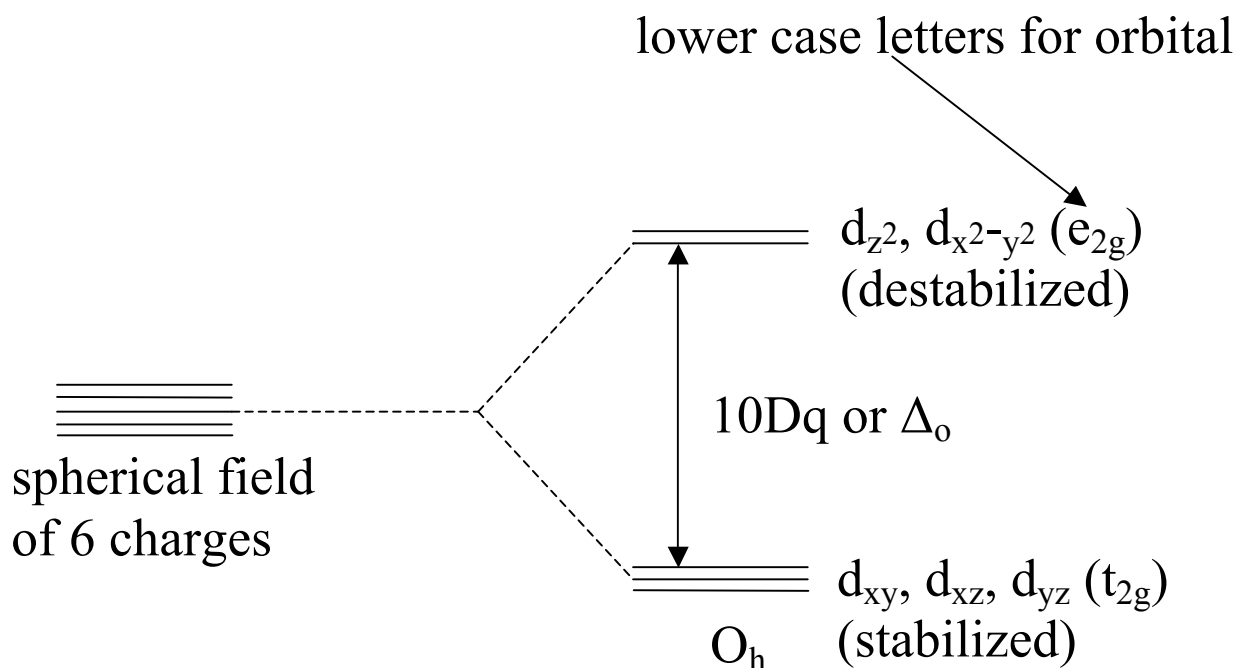
In T_d symmetry the coordinate system does not directly point along any of the orbitals, but if one considers the drawing below:
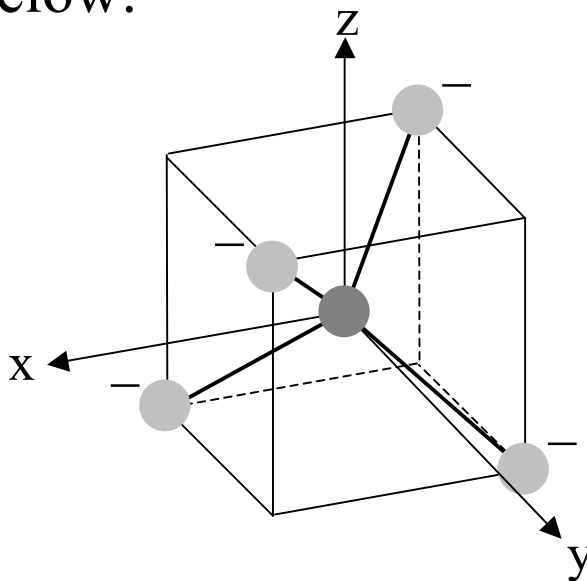

It should be possible to convince oneself that the d_{xy} orbital will have more contact with the negative charges than the $d_{x^2-y^2}$ orbital (no charges point at the $d_{x^2-y^2}$ orbital but the d_{xy} orbital is between the axes). Likewise d_{z^2} (along z) does not contact the negative charges.

$\left.\begin{array}{l} d_{x^2-y^2} \\ d_{z^2} \end{array}\right\}$ e set (stabilized)

$\left.\begin{array}{l} d_{xy} \\ d_{yz} \\ d_{xz} \end{array}\right\}$ t_2 set (destabilized)

What happens to the octahedral orbitals (t_{2g} and e_g sets) when we distort the geometry?

increasing distortion

pull two ligands away along z
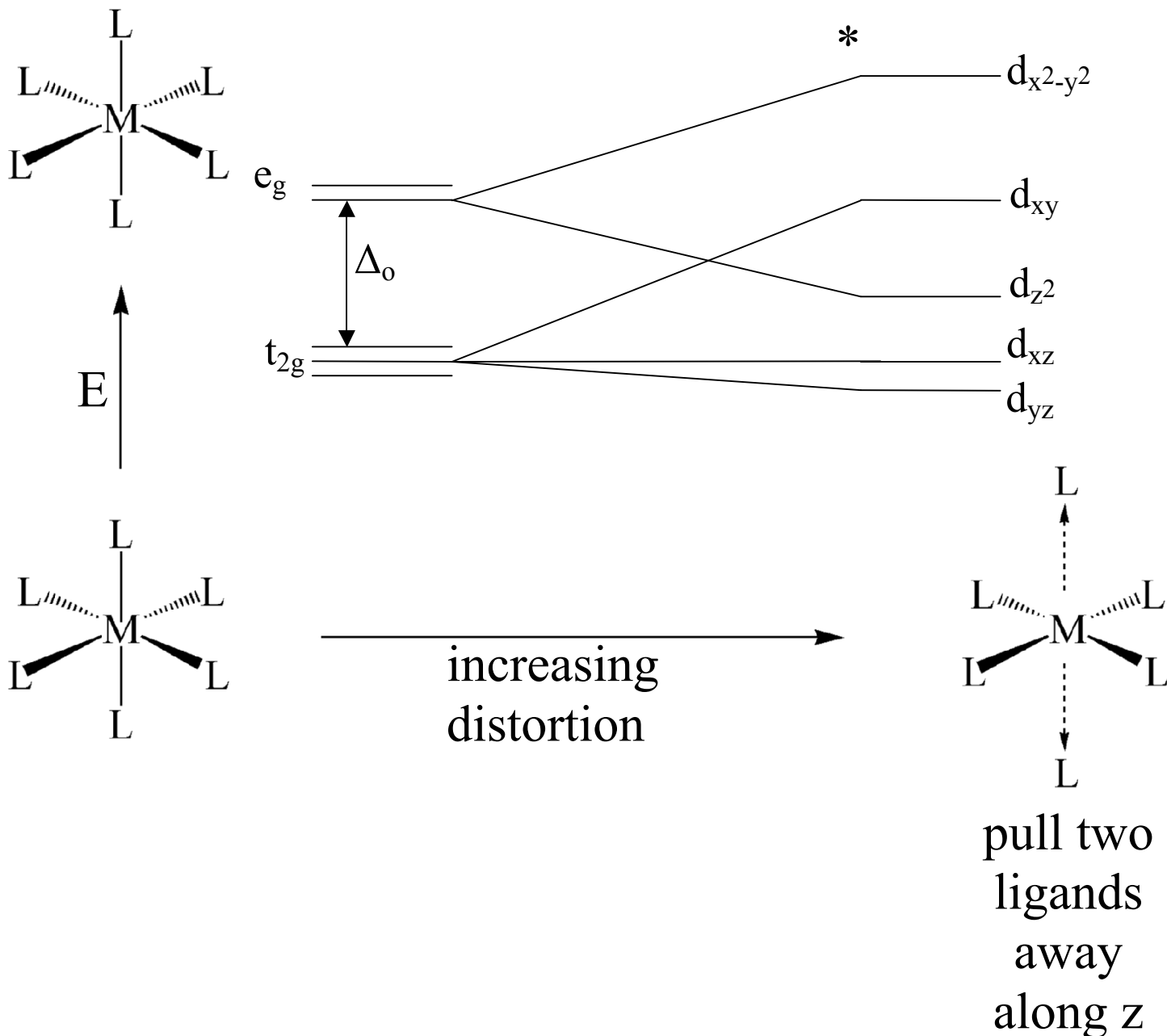
Why? Because z isn't as close to electrons on ligands which would be repulsive, so orbitals with a z component will drop in energy and the others will have to pick up the slack so they bond more strongly (go up)

d – orbital splitting diagrams

In the limit of going from ML_6 to ML_4:

(Octahedral to square planar)

$d_{x^2-y^2}$

e_g

Δ_o

d_{xy}

d_{z^2}

t_{2g}

d_{xz}
d_{yz} (degenerate)

ML_6 ML_4
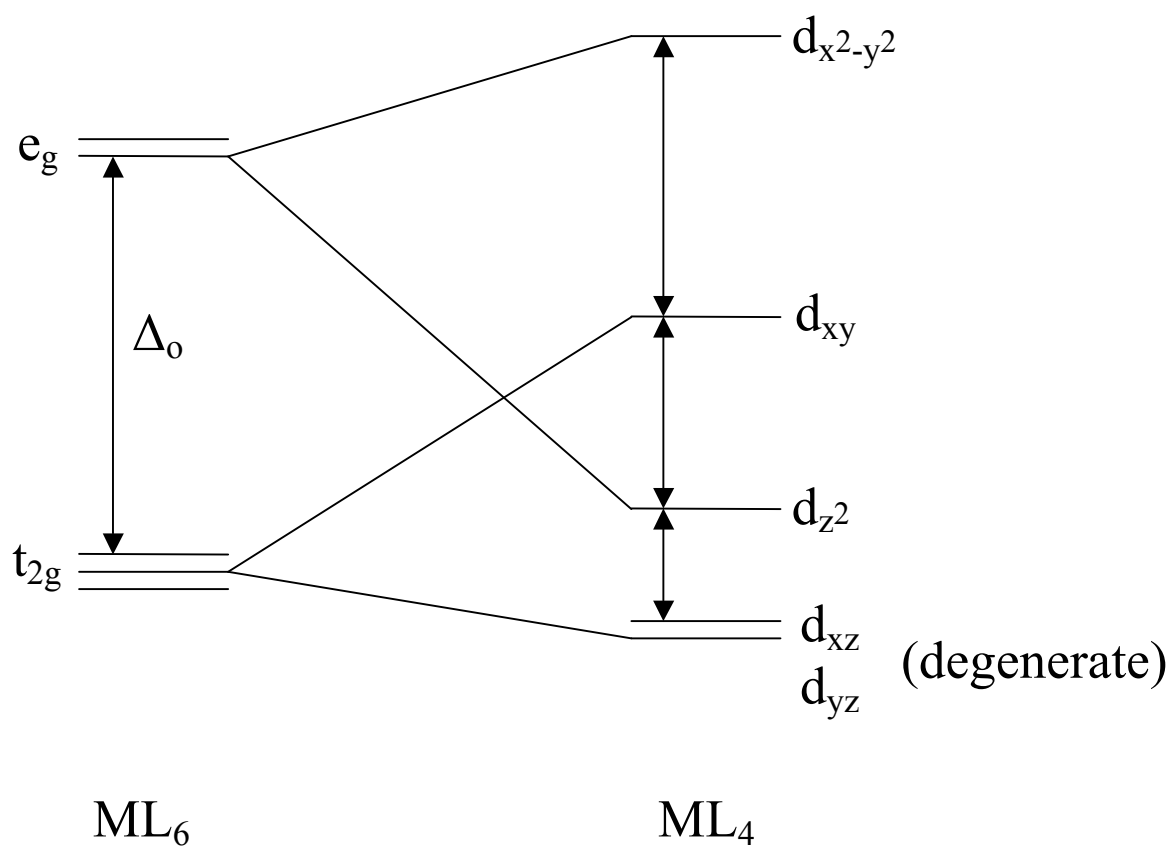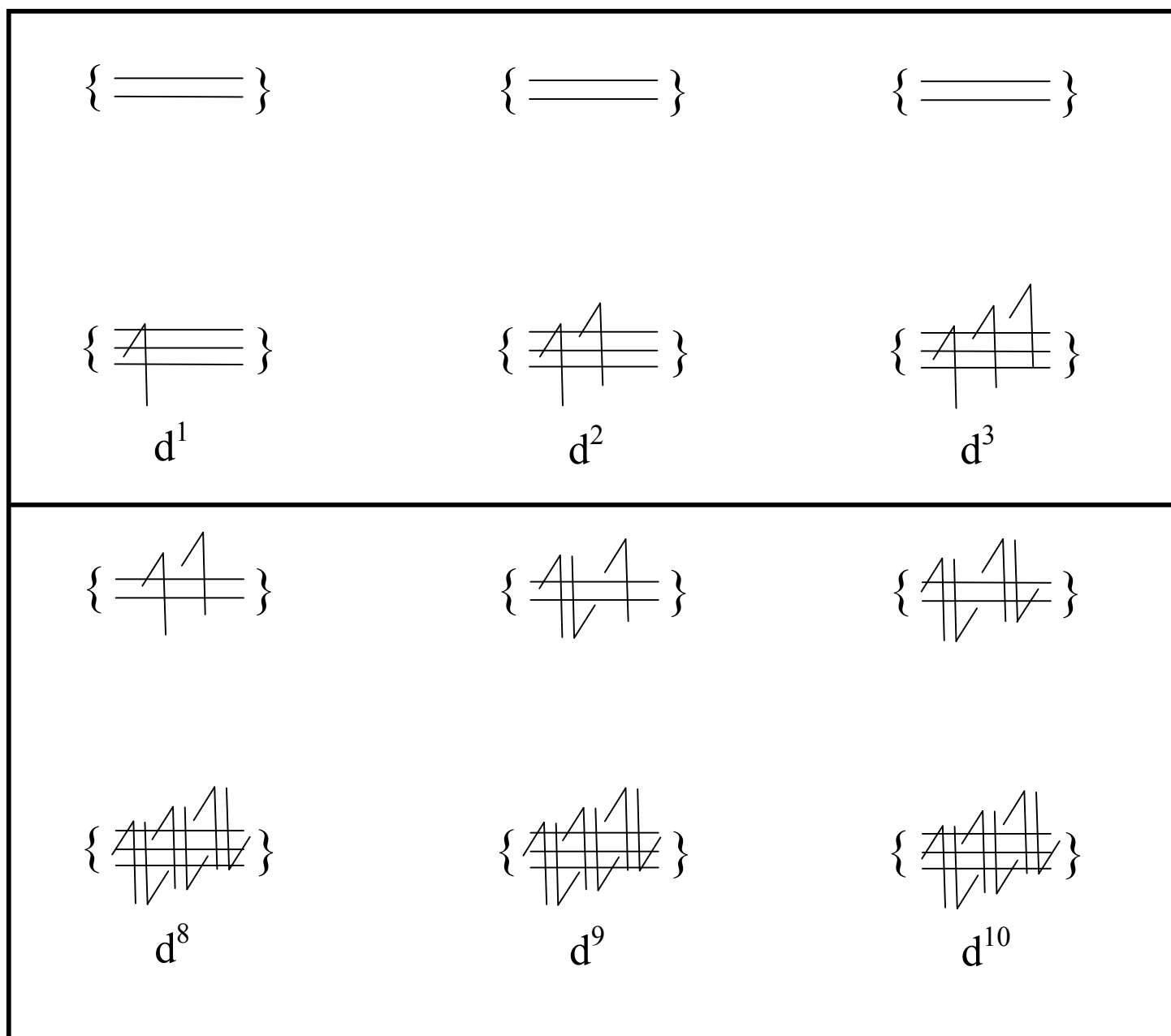
adapted from Fig 23-13 on page 514.
Sketches showing the unique ground-state electron configurations for *d* orbitals in octahedral fields with the *d* configurations d^1, d^2, d^3, d^8, d^9, and d^{10}.

High-spin state · Low-spin state · High-spin state · Low-spin state

d^4

d^5

$t_{2g}^3 e_g^1$
$E = -3/5\Delta_o$

t_{2g}^4
$E = -8/5\Delta_o + P_E$

$t_{2g}^3 e_g^2$
$E = 0$

t_{2g}^5
$E = -2\Delta_o + 2P_E$

High-spin state · Low-spin state · High-spin state · Low-spin state

d^6

d^7

$t_{2g}^4 e_g^2$
$E = -2/5\Delta_o + P_E$

t_{2g}^6
$E = -12/5\Delta_o + 3P_E$

$t_{2g}^5 e_g^2$
$E = -4/5\Delta_o + 2P$

$t_{2g}^6 e_g^1$
$E = -9/5\Delta_o + 3P$

adapted from figure 23-14 on page 515.

Diagrams showing the two possibilities (high spin and low spin) for ground-state electron configurations of d^4, d^5, d^6 and d^7 ions in octahedral fields. Also shown is the notation for writing out the configurations and expressions for their energies, derived as explained in the text.
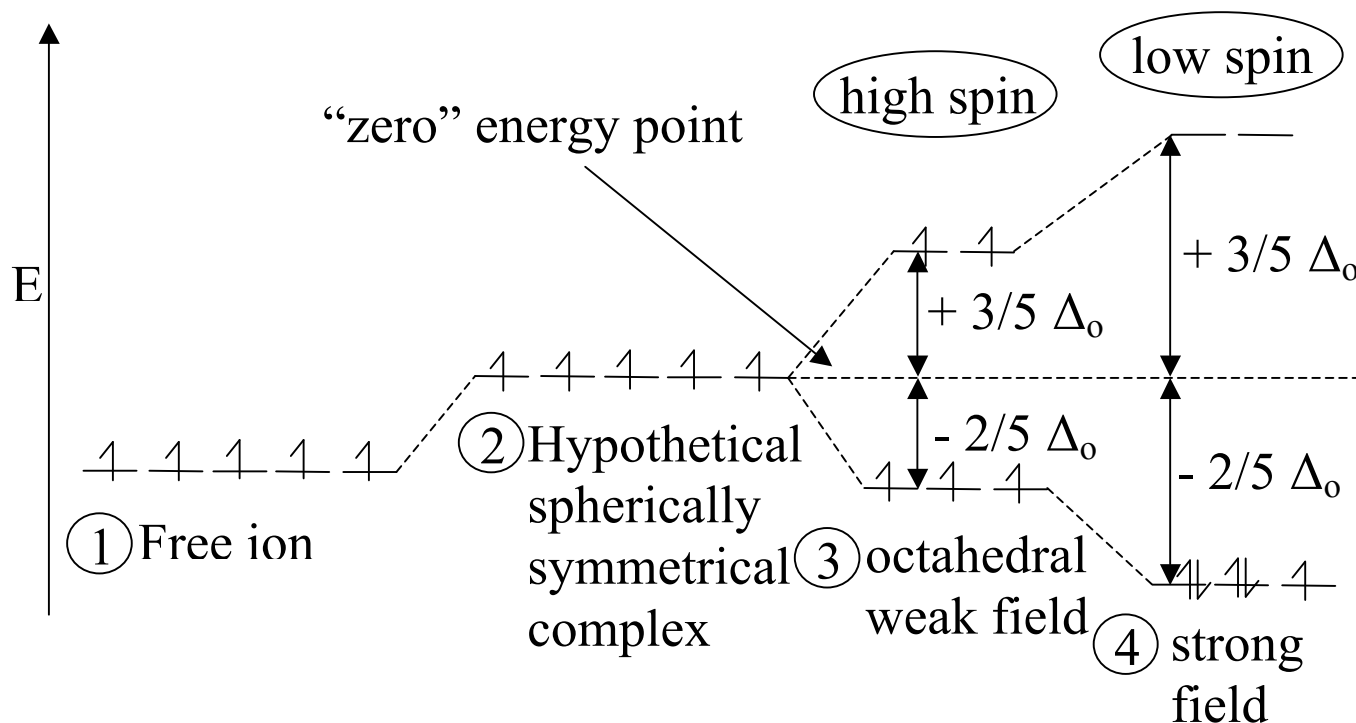
Use Fe(III) as an example:

This shows the energies of the d orbitals in various fields

10 Dq changes in weak versus strong fields

The center of the energy levels ("Bary center") remains the same as you split orbitals by imposing symmetry
$10Dq = \Delta_o = \Delta E$

High – spin Fe(III) example $[Fe(H_2O)_6]^{3+}$
Low – spin Fe(III) example $[Fe(CN)_6]^{3-}$

What is the difference in the energies of the electrons in $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ → called **Crystal Field Splitting Energy (CFSE)**

$$\boxed{t_{2g}{}^3\ e_g{}^2}$$ versus $$\boxed{t_{2g}{}^5\ e_g{}^0}$$

$3x(-2/5\Delta_o)$ $5x(-2/5\Delta_o)$
$\underline{+\ 2x(3/5\Delta_o)}$ $\underline{+\ 0x(3/5\Delta_o)}$
     0 $-2\Delta + 2\ P.E_.$

This is why the cyanide complex $[Fe(CN)_6]^{3-}$ is so much more stable than the water complex $[Fe(H_2O)_6]^{3+}$

CN^- has a much stronger effect than H_2O to split the d orbitals (bigger separation between lower and higher set) – that is why one complex $[Fe(H_2O)_6]^{3+}$ will fill all the oribitals with one electron before pairing (high spin) and the other pairs up because of the overwhelming favorable CFSE. $[Fe(CN)_6]^{3-}$ is the greatest achievement of CFT!

Generalize this concept:

in O_h t_{2g} electrons are $-2/5\Delta_o$ each

                e_g electrons are $+3/5\Delta_o$ each

$\therefore$ you can calculate CFSE (LFSE) for any d^n configuration.