

## 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 Complexes: Two Considerations

### A. Geometry

$ML_6$        $O_h$       (octahedral)

$ML_4$        $T_d$  vs  $D_{4h}$   
(tetrahedral vs. square planar)

### B. Ligand Type      $\pi$ – acceptors

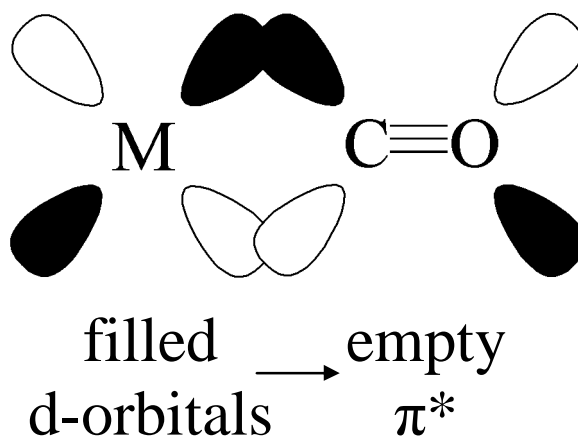
$\pi$  – donors

$\sigma$  – donors

many ligands are a combination of donor types, but the “pure” donor diagrams can be considered

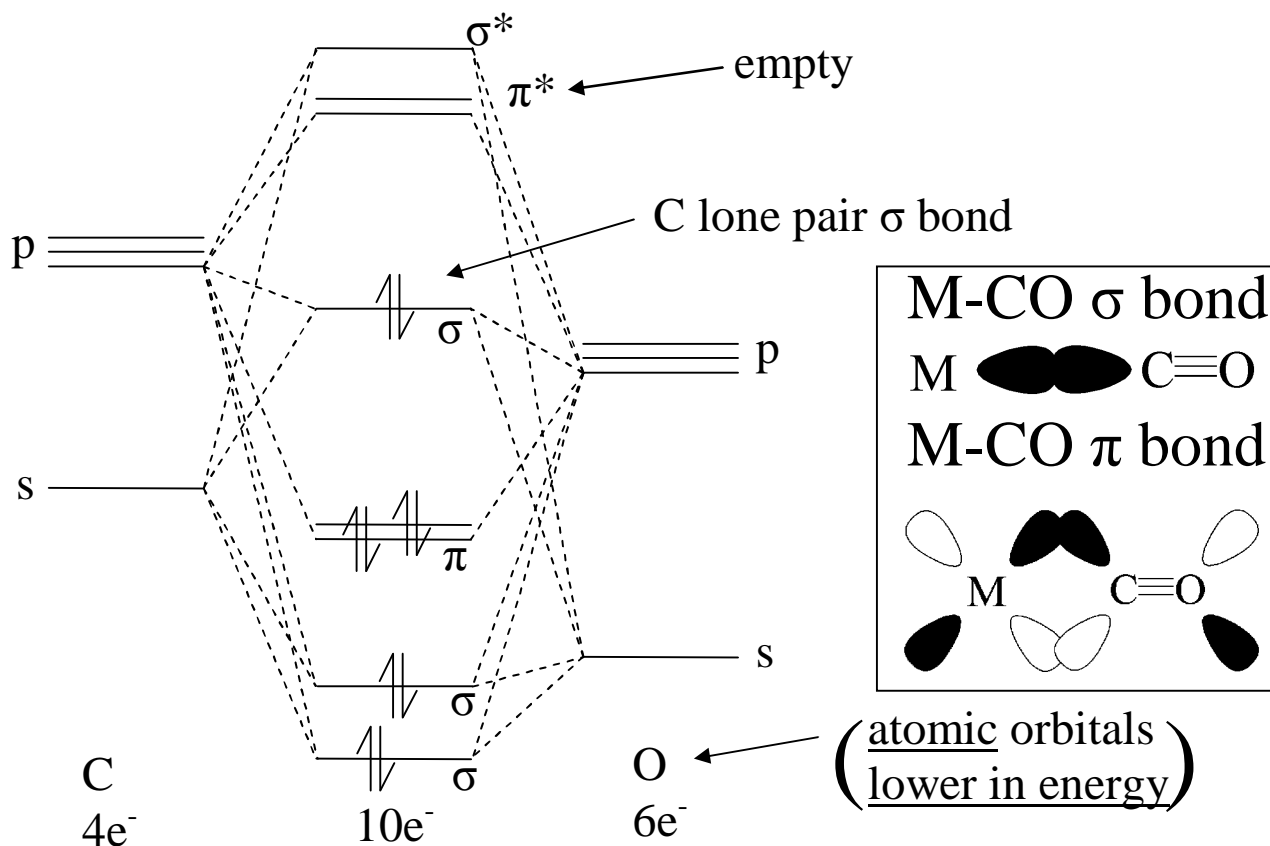
#### $\pi$ – acceptors

$CO$ ,  $NO^+$ ,  $CNR$ ,  $CN^-$



$\pi$  – donorshalides ( $X^- = \text{Cl, Br, I}$ ) $\text{NH}_2^-$  (amide) $\text{NR}_2^-$  $\text{O}_2^-$  $\text{OR}^-, \text{SR}^-$  $\sigma$  – donors $\text{H}^-, \text{NH}_3$ 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.





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  $4 \times 6 = 24$  orbitals

}

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

→ symmetry adapted linear combinations (SALC'S)

## Electronic Structure of Transition Metal Complexes

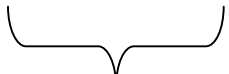
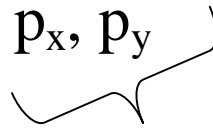
Q. What are we trying to accomplish?

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

ML <sub>n</sub>	n = 6	Octahedral	}	basic
	n = 4	Tetrahedral		geometry

The d orbitals on M change energy according to the types of orbitals on L ( $\sigma$ ,  $\pi$ ,  $\pi^*$ )

## $\sigma$ – Donor Only Case

Metal	d (5)	s (1)	p (3)	Energy-wise $d < s < p$ highest occupied are d as s and p are empty for $M^{n+}$
Ligands	$s, p_z,$ 		$p_x, p_y$ 	
	along M-L axis so used in $\sigma$ - bonding			these form $\pi$ - bonds

$\therefore$  on the ligands, if only  $\sigma$  – bonding is possible for an  $ML_6$  compound:

Metal

d, s, p = 9 orbitals

Ligand

$s + p_z \rightarrow sp$

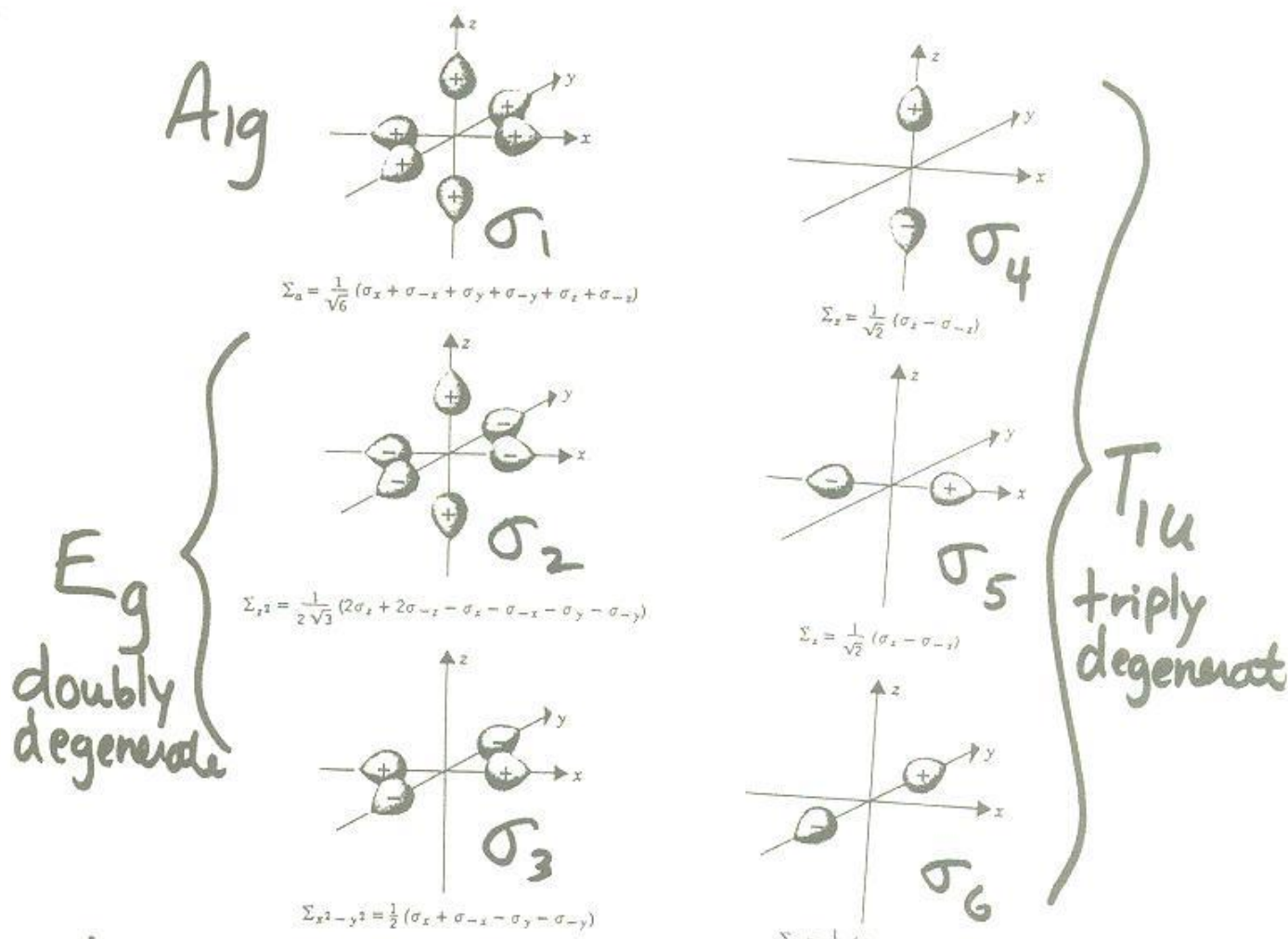


6 x  orbitals

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

## Six SALC

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



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!



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)  $d_{x^2-y^2}, d_{z^2}$   
 $d \searrow T_{2g}$  (three orbitals so triply degenerate)  
 $d_{xy}, d_{xz}, d_{yz}$

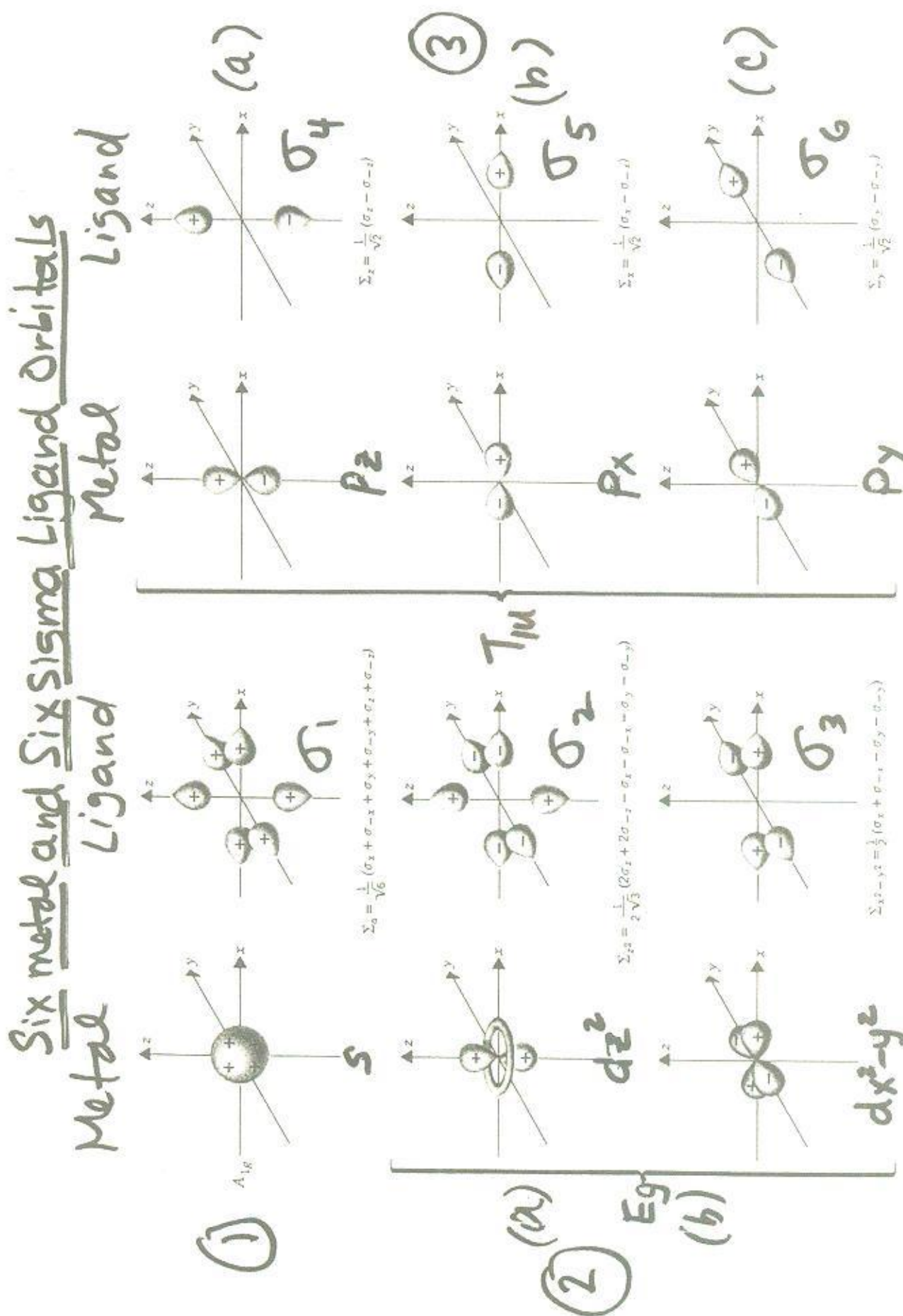
since  $d < s < p$  in energy, the M.O. diagram arranges them

=====  $T_{1u}$

—————  $A_{1g}$

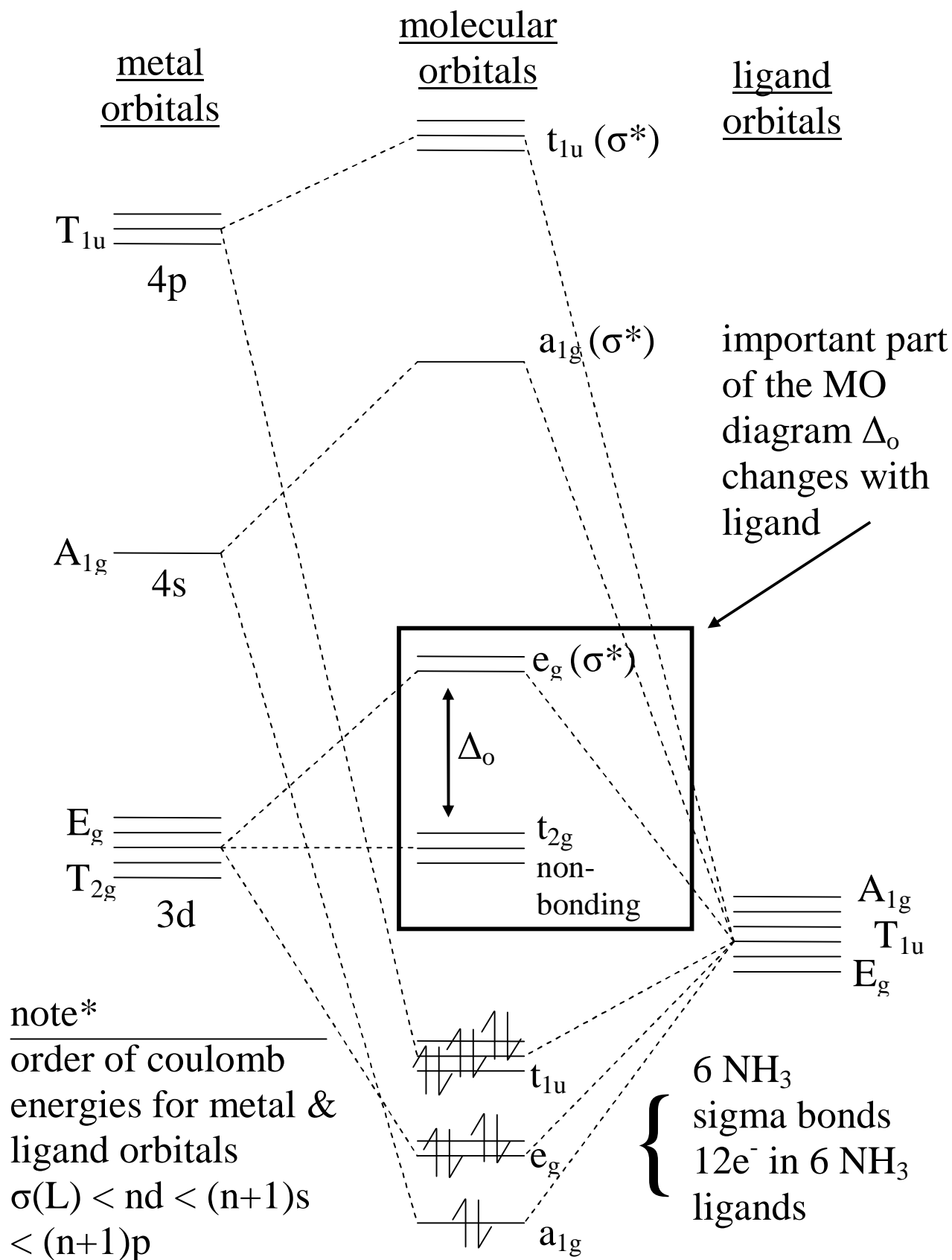
=====  $E_g$

=====  $T_{2g}$



**Figure 23-8** The six metal orbitals with  $\sigma$  symmetry and the ligand group orbitals ( $\Sigma$ ) that overlap properly with these metal orbitals to form  $\sigma$ -type MO's in an  $ML_6$  complex. Each ligand group orbital ( $\Sigma$ , 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.

# O<sub>h</sub> M.O. Diagram     σ-Donor [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>

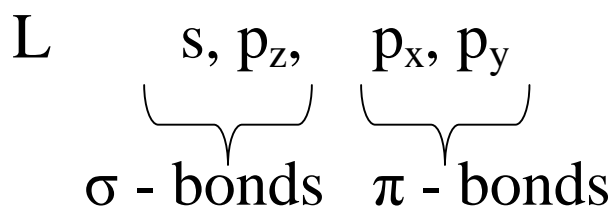


$\pi$  – Donor Case

you have  $\sigma$  and  $\pi$  bonding

( there are lone pairs that can make both types of bonds as opposed to  $:\text{NH}_3$  which only has a lone pair for  $\sigma$  – bonding )

(sp hybrid)



for  $\text{ML}_6$ :

M: (same as before)



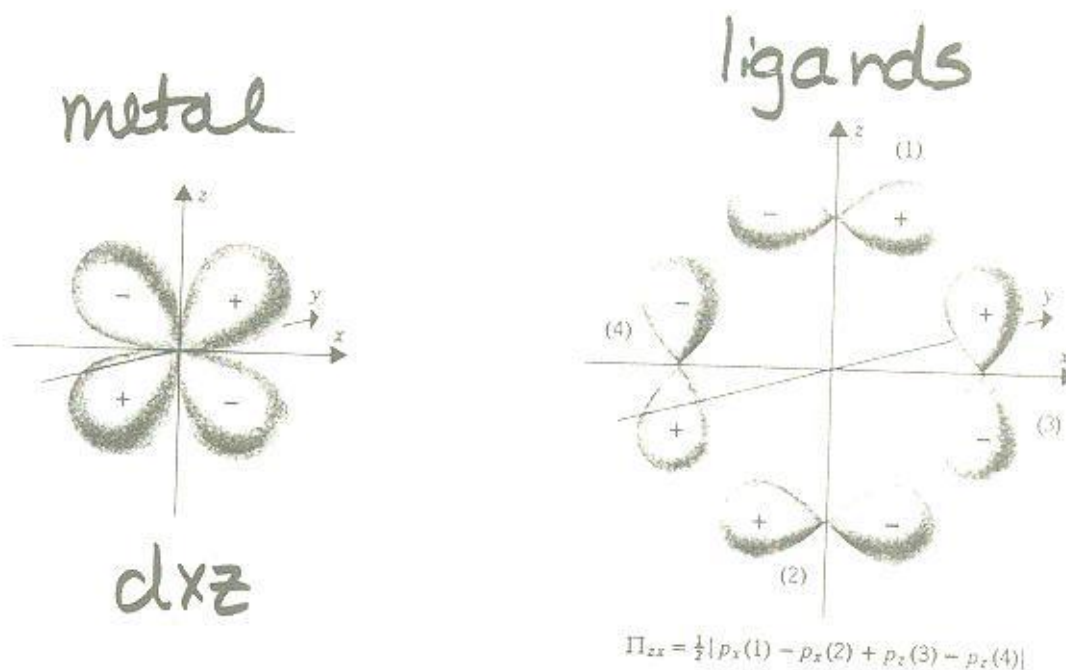
L: 6  $\sigma$  orbitals ( $\text{A}_{1g}, \text{T}_{1u}, \text{E}_g$ )

6 x 2 ( $\text{p}_x, \text{p}_y$ ) = 12  $\pi$  orbitals

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

What are ligands that use  $\pi$  – bonds?

( $\pi$  – donors like halides for example)

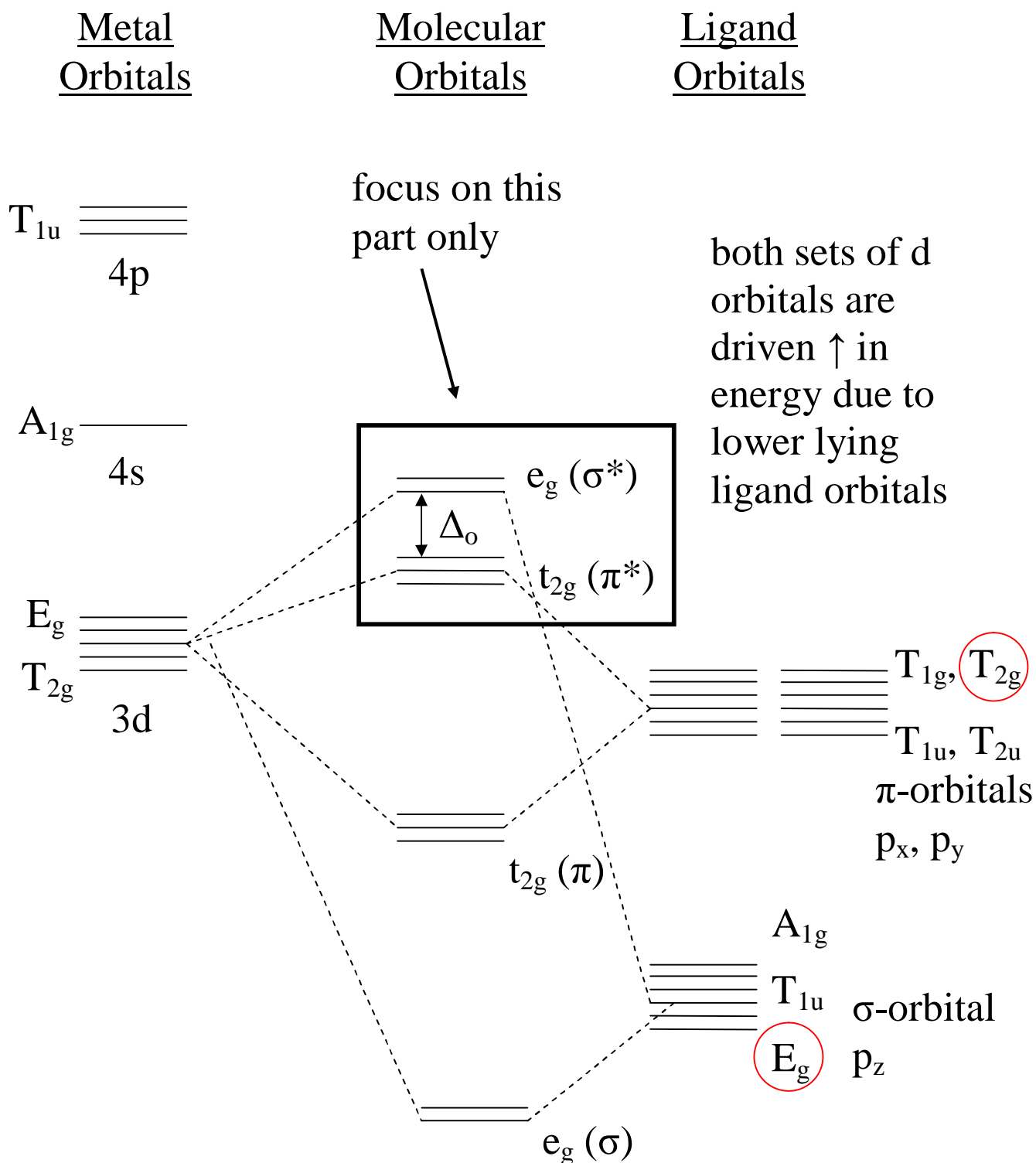


Group orbital made up of combinations of  $p_x$  and  $p_z$  orbitals on four of the atoms

Note:

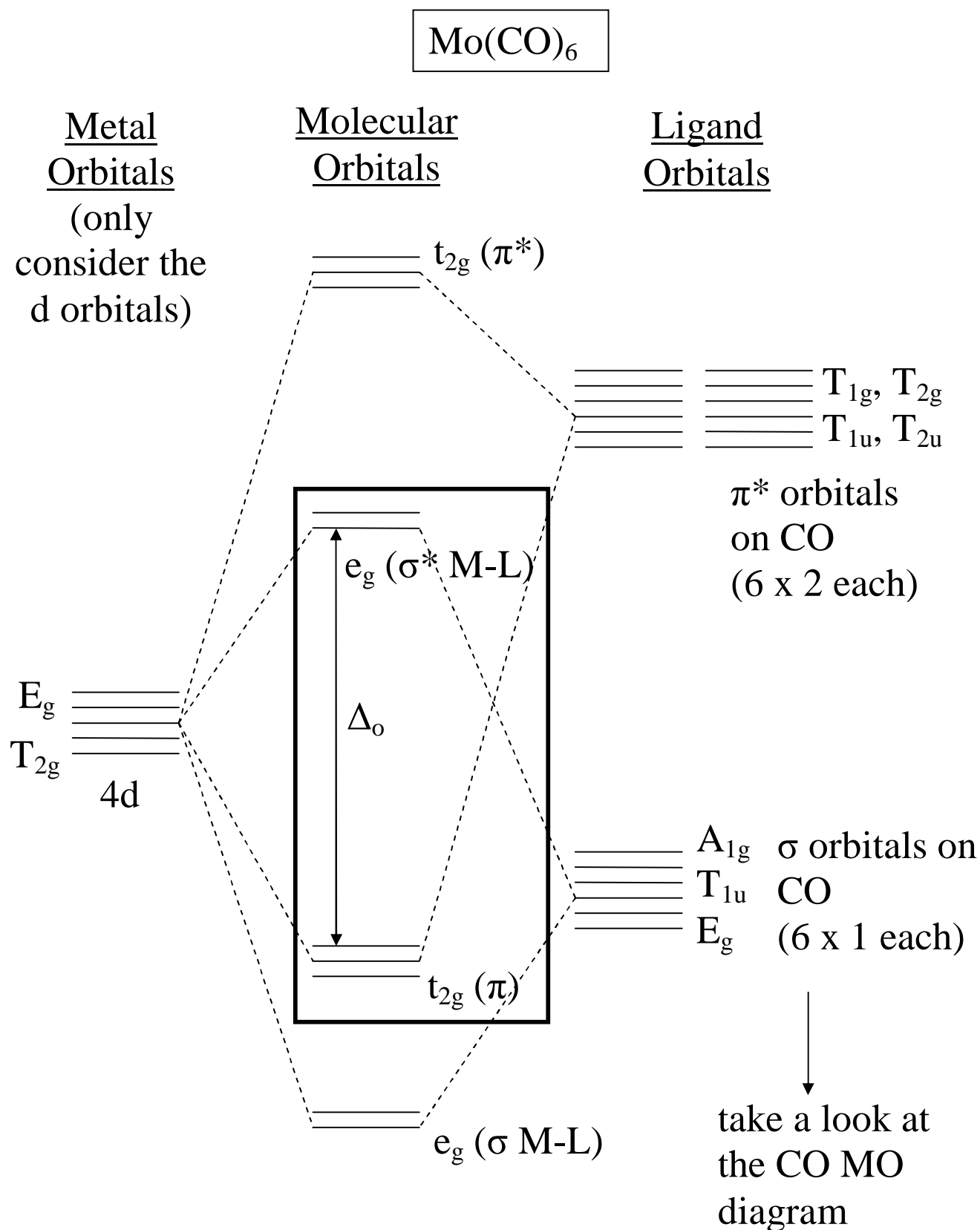
There are two more sets based on  $M d_{yz}$  and  $M d_{xy}$ .

$O_h$  M.O. Diagram  $\pi$  – Donor  $[\text{CoCl}_6]^{5-}$   
 (Don't need to sketch the whole diagram)

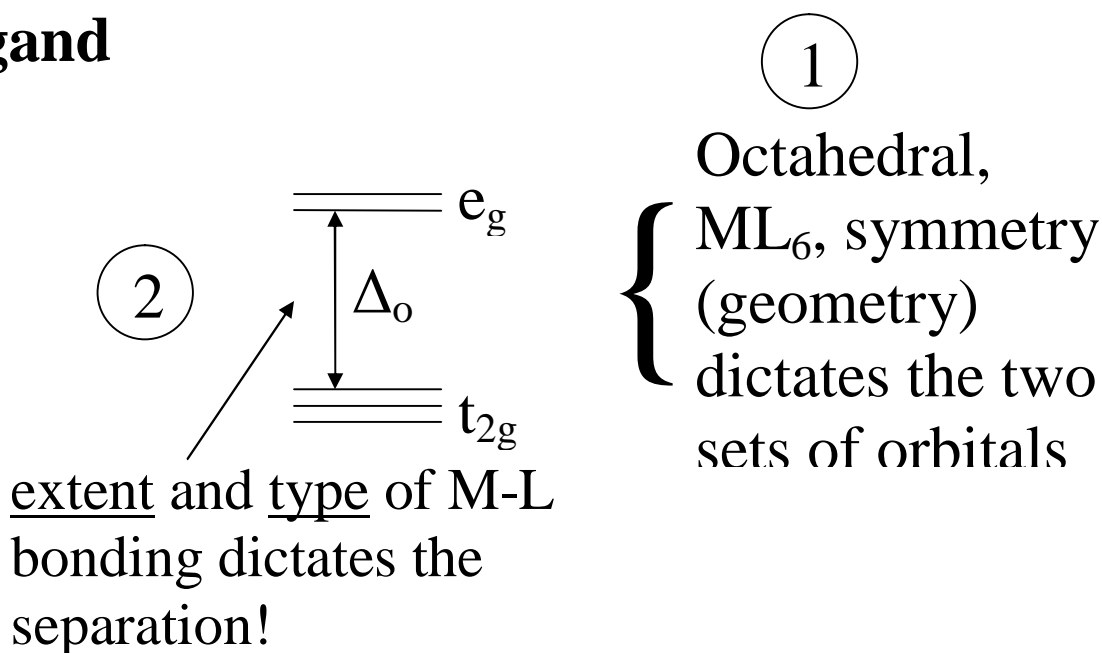


# O<sub>h</sub> M.O. Diagram π – acceptor

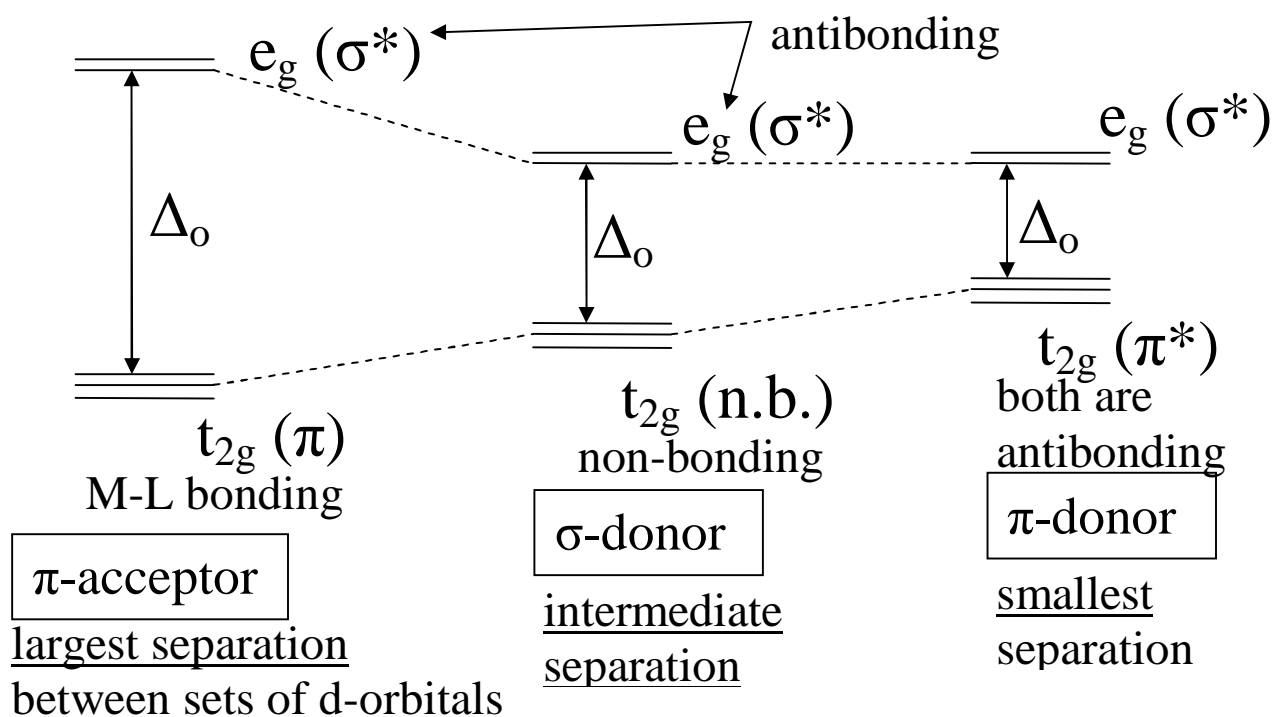
CO, NO<sup>+</sup>, CNR, CN<sup>-</sup>



**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**



To summarize O<sub>h</sub> M.O. Splittings

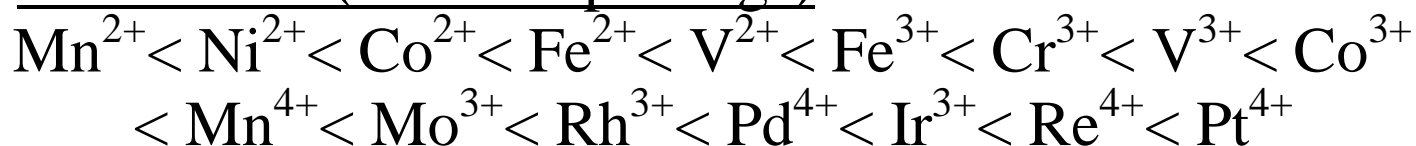




These trends reflect the energies of the orbitals from the ligands and their symmetries. Also, the strength of their interaction is going to affect the  $\Delta_o$  separation strong – field (bigger splitting) versus weak – field ligands (smaller splitting) and the metal dependence.

### Metal dependence

#### Lower field (smaller splittings)

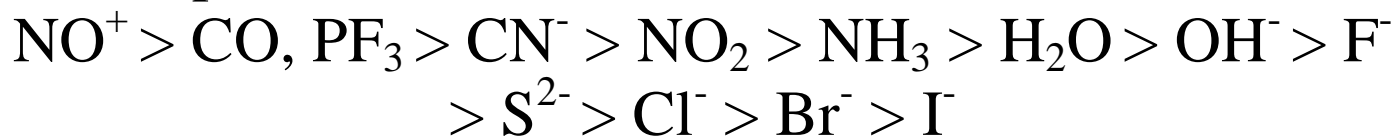


Stronger Field  
(larger splittings)

### Ligand dependence

#### Spectrochemical Series

#### $\pi$ – acceptors



$\pi$  – donors (weak)

More simple theories than M.O. theory:

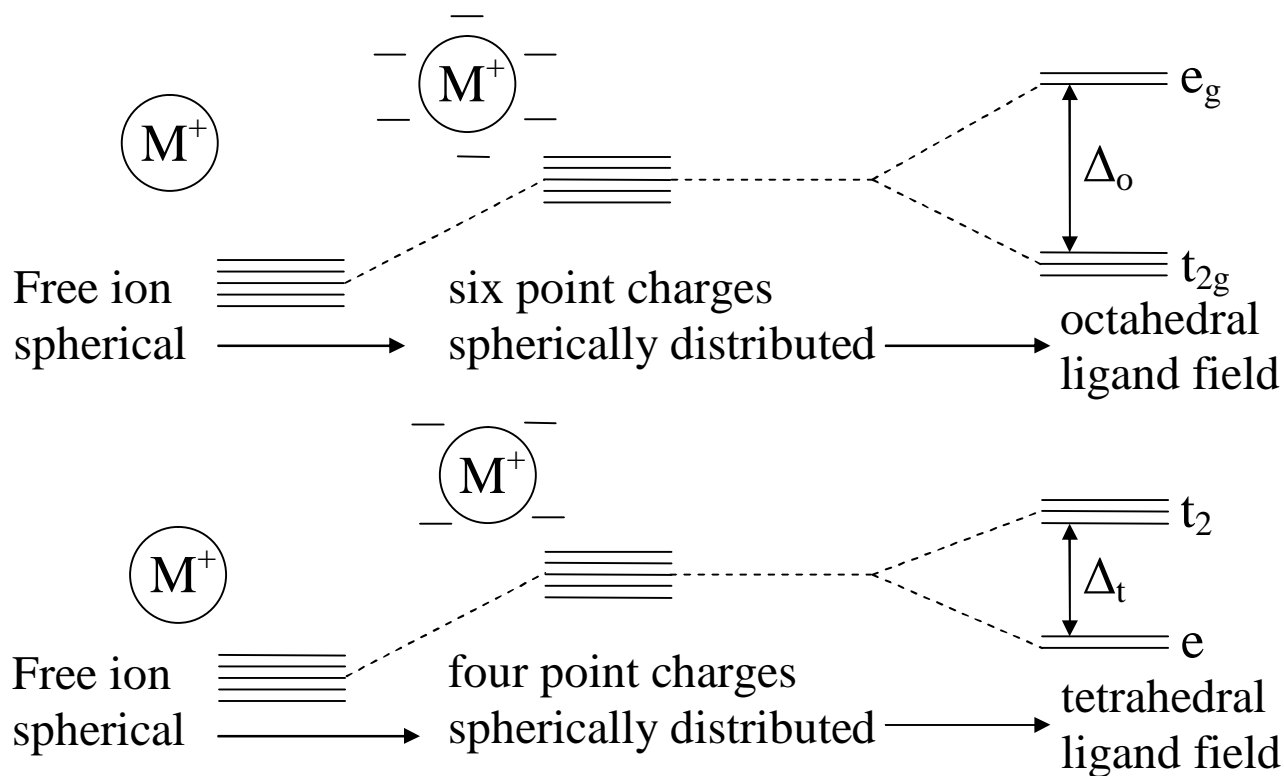
Crystal Field Theory and Ligand Field Theory

(CFT and LFT)

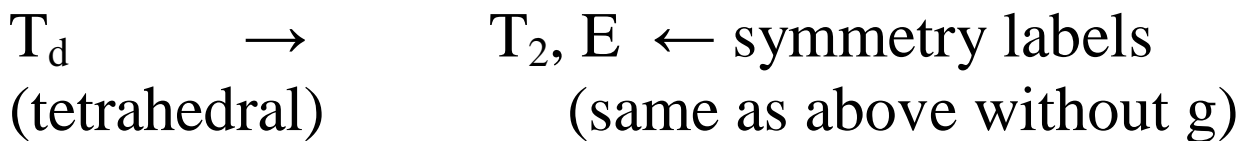
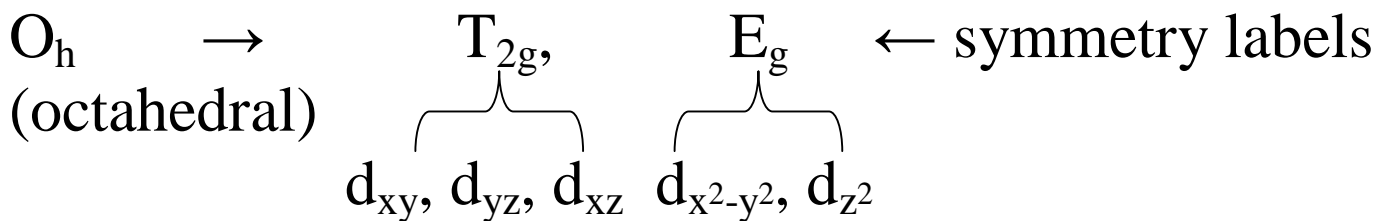
CFT assumes that bonds between the metal atom and the ligands are totally ionic – in other words, point charges

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.

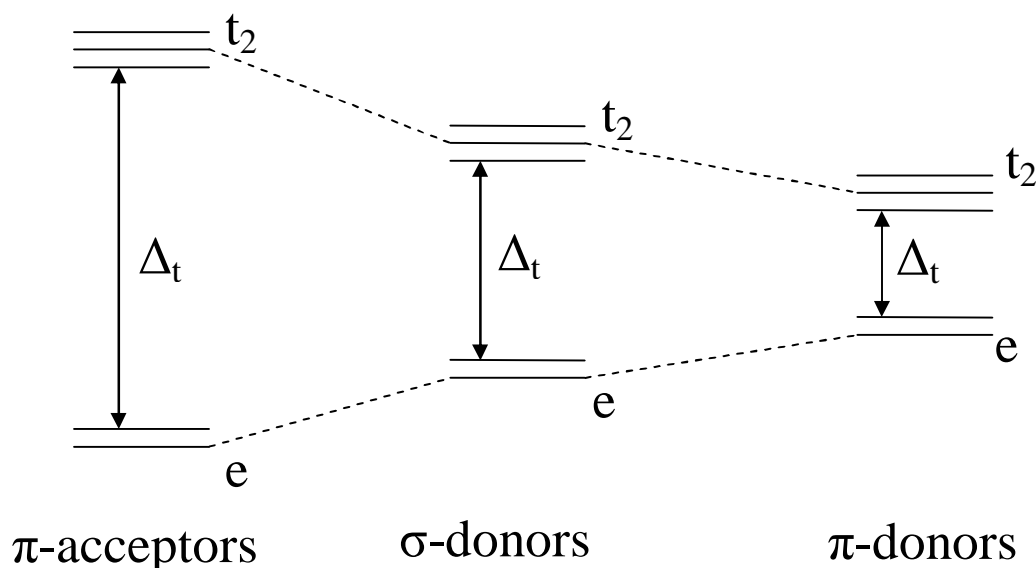


Group theory tells us that there are two different groups of orbitals in



Just as in  $O_h$ ,  $T_d$  has different amount of d orbital splittings with different types of ligands- the trend is the same as in  $O_h$

$\sigma$  donors,  $\pi$  – donors,  $\pi$  – acceptors



What is the relationship between  $\Delta_o$  ( $10 Dq$ ) and  $\Delta_t$ ?

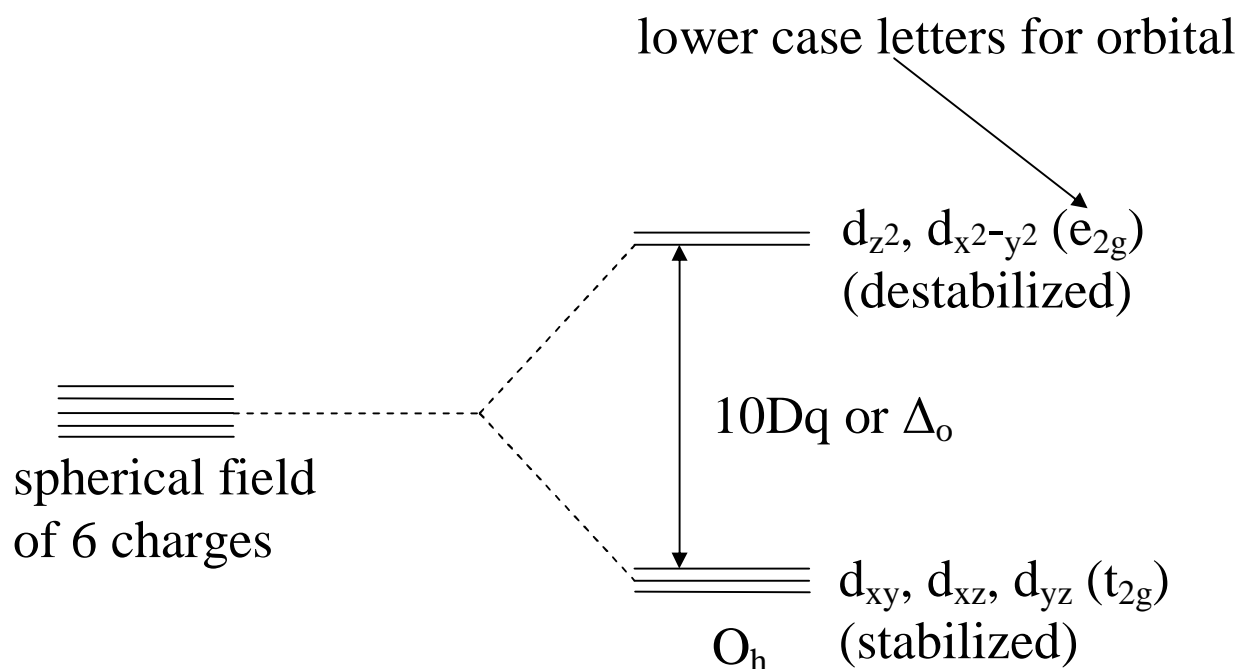
another way to write the energy separation

$$\Delta_t = 4/9 \Delta_o \quad \text{for similar metal cations/ligands}$$

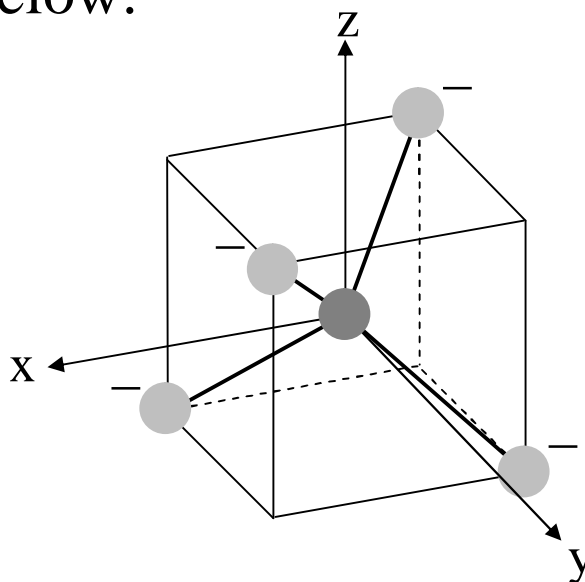
But how was the relative ordering decided without the arguments of Molecular Orbital Theory?

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 repel the negative charges of the ligands, these orbitals are raised in energy from a spherically distributed set of charges. The other orbitals point in between the negative charges of the ligands.



In  $T_d$  symmetry the coordinate system does not directly point along any of the orbitals, but if one considers the drawing below:

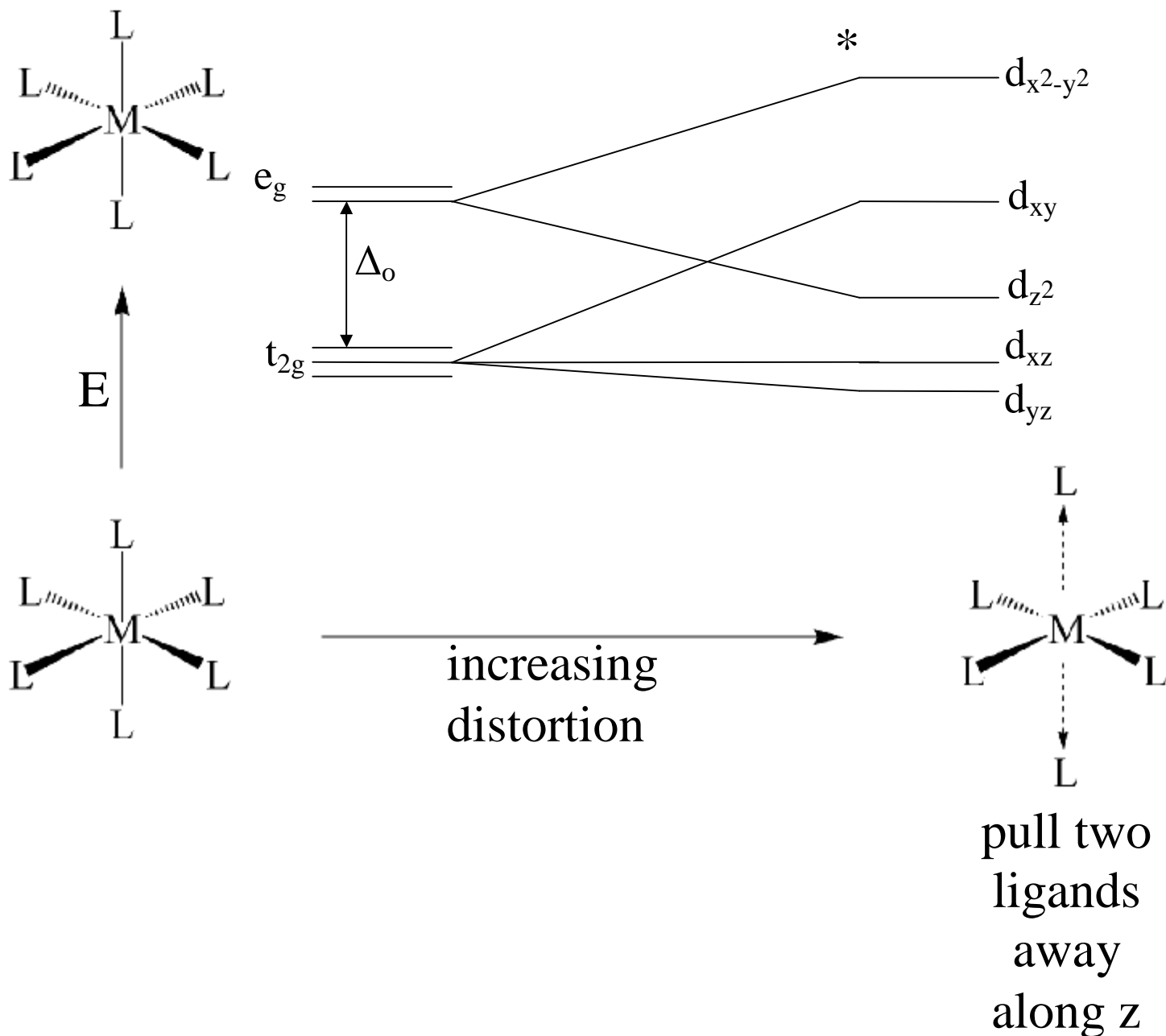


It should be possible to convince oneself that the  $d_{xy}$  orbital will have more contact with the negative charges than the  $d_{x^2-y^2}$  orbital (no charges point at the  $d_{x^2-y^2}$  orbital but the  $d_{xy}$  orbital is between the axes). Likewise  $d_{z^2}$  (along z) does not contact the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

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

$$\left. \begin{array}{l} d_{xy} \\ d_{yz} \end{array} \right\} \text{t}_2 \text{ set} \\ \text{(destabilized)}$$

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

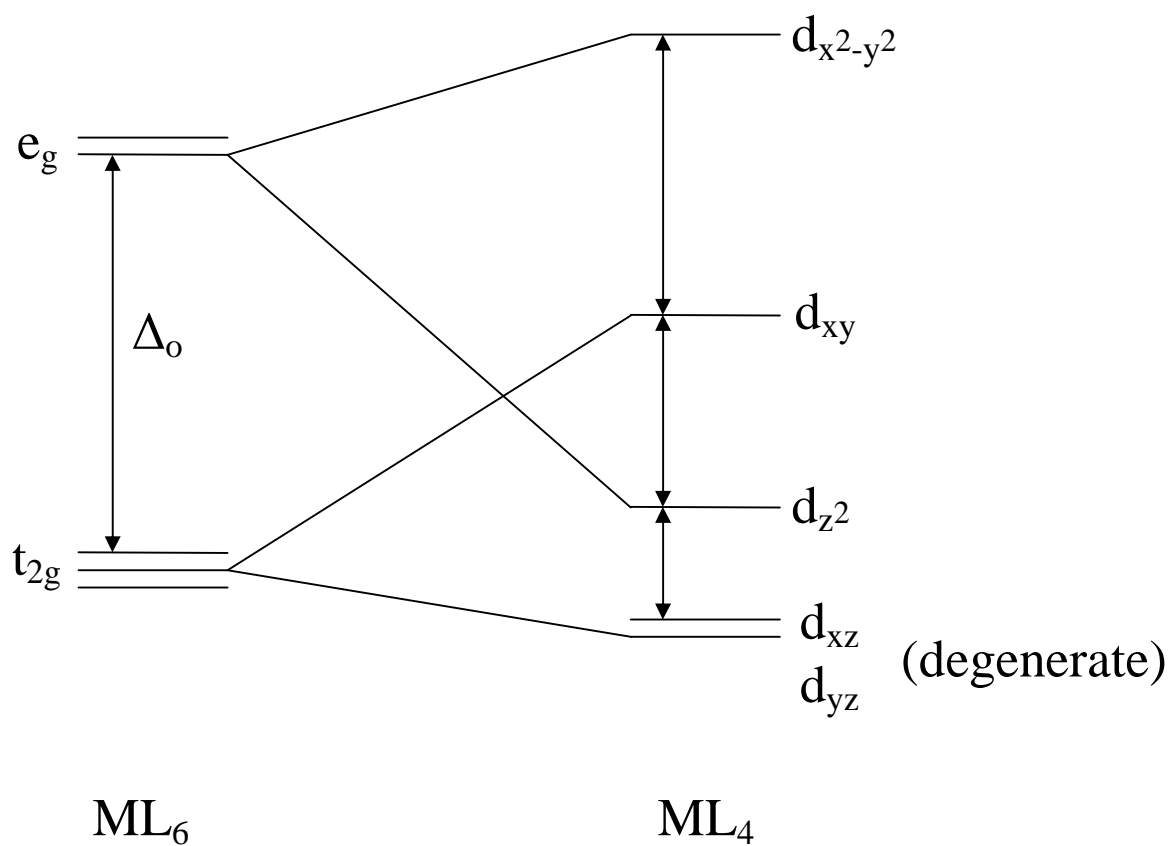


Why? Because z isn't as close to electrons on ligands which would be repulsive, so orbitals with a z component will drop in energy and the others will have to pick up the slack so they bond more strongly (go up)

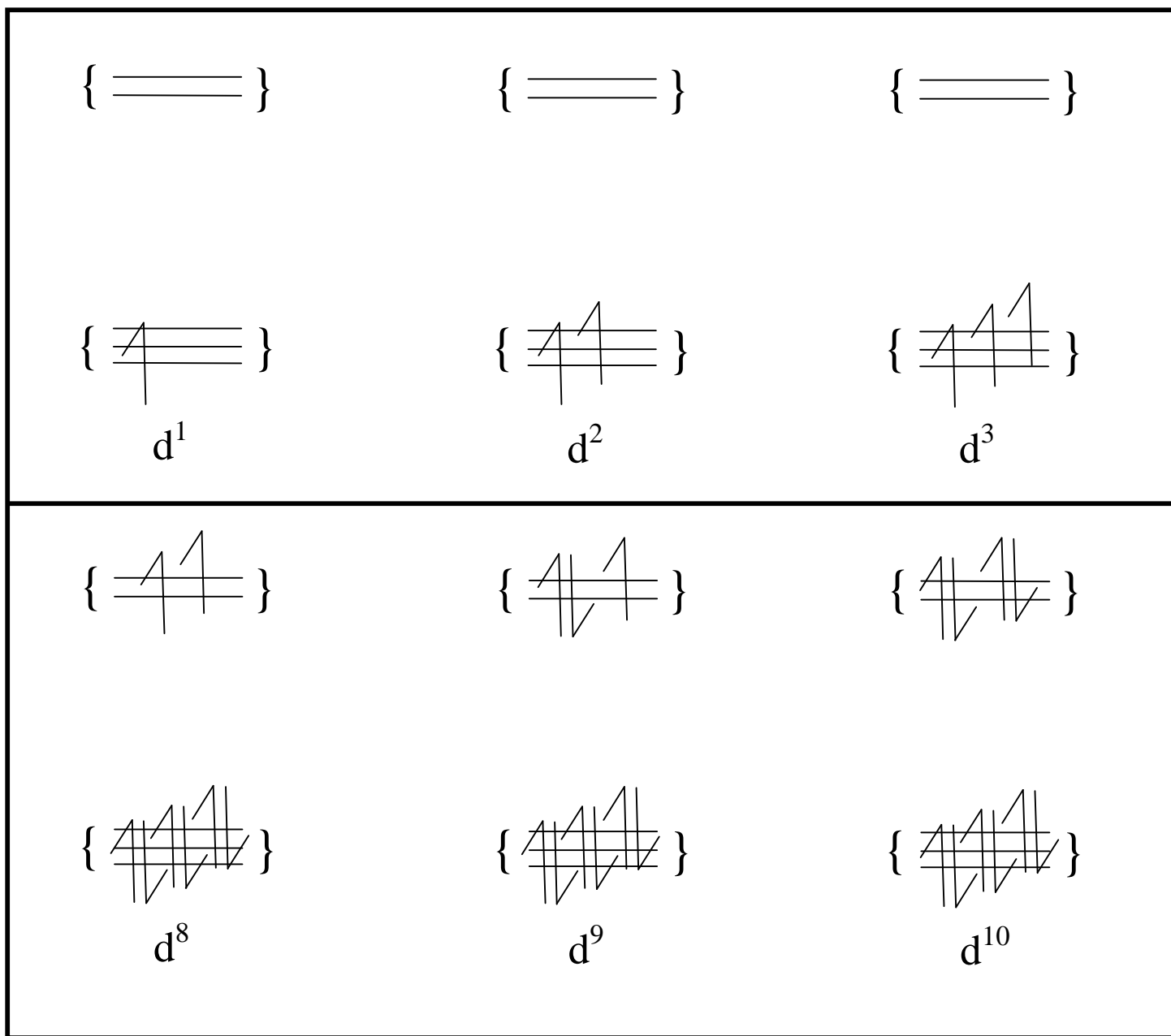
## d – orbital splitting diagrams

**In the limit of going from  $ML_6$  to  $ML_4$ :**

**(Octahedral to square planar)**







**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
$d^6$			$d^7$		
	$t_{2g}^4 e_g^2$ $E = -2/5\Delta_o + P_E$	$t_{2g}^6$ $E = -12/5\Delta_o + 3P_E$		$t_{2g}^5 e_g^2$ $E = -4/5\Delta_o + 2P_E$	$t_{2g}^6 e_g^1$ $E = -9/5\Delta_o + 3P_E$

**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.

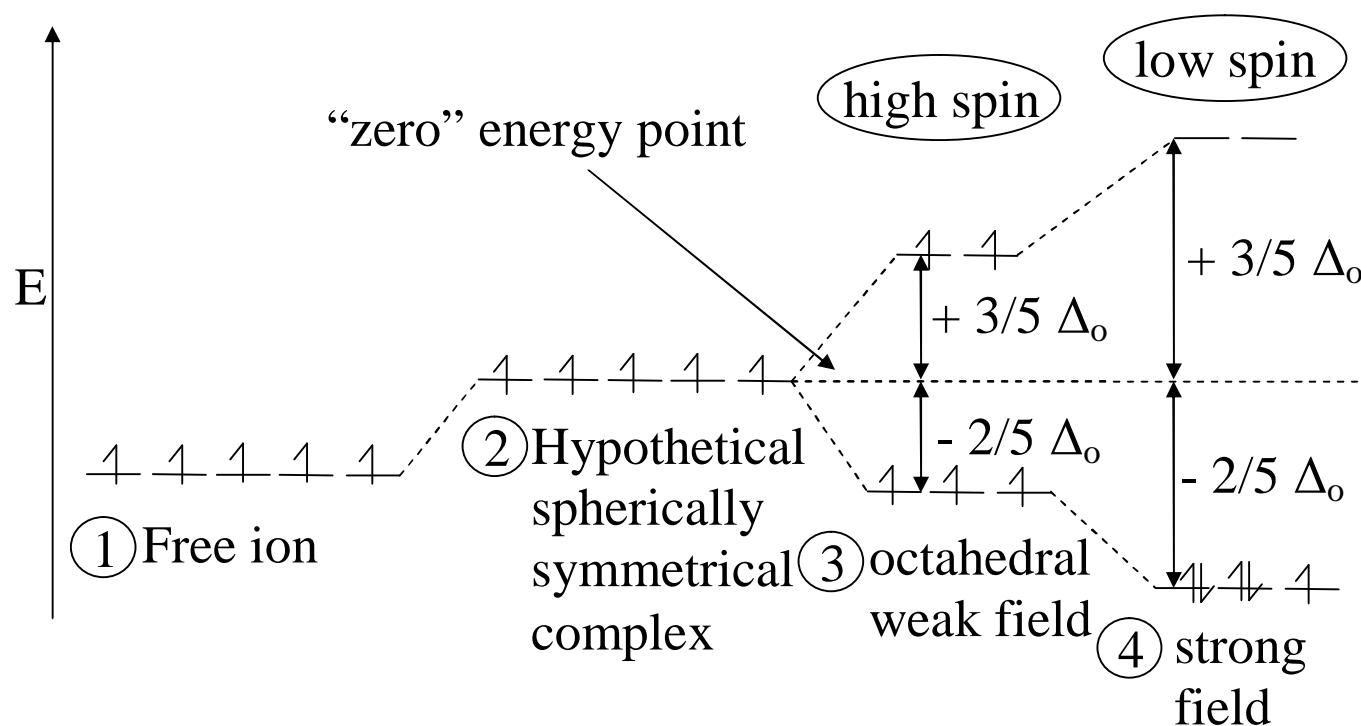
## Use Fe(III) as an example:

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

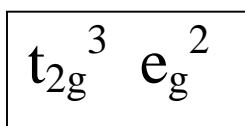
$$10Dq = \Delta_o = \Delta E$$



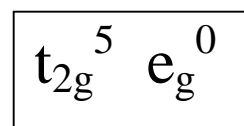
High – spin Fe(III) example  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

Low – spin Fe(III) example  $[\text{Fe}(\text{CN})_6]^{3-}$

What is the difference in the energies of the electrons in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  → called **Crystal Field Splitting Energy (CFSE)**



versus



$$\frac{3x(-2/5\Delta_o) + 2x(3/5\Delta_o)}{0}$$

$$\frac{5x(-2/5\Delta_o) + 0x(3/5\Delta_o)}{-2\Delta_o}$$

This is why the cyanide complex  $[\text{Fe}(\text{CN})_6]^{3-}$  is so much more stable than the water complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

$\text{CN}^-$  has a much stronger effect than  $\text{H}_2\text{O}$  to split the d orbitals (bigger separation between lower and higher

set) – that is why one complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  will fill all the orbitals with one electron before pairing (high spin) and the other pairs up because of the overwhelming favorable CFSE.  $[\text{Fe}(\text{CN})_6]^{3-}$  is the greatest achievement of CFT!

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Generalize this concept:

in  $\text{O}_h$        $t_{2g}$  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.