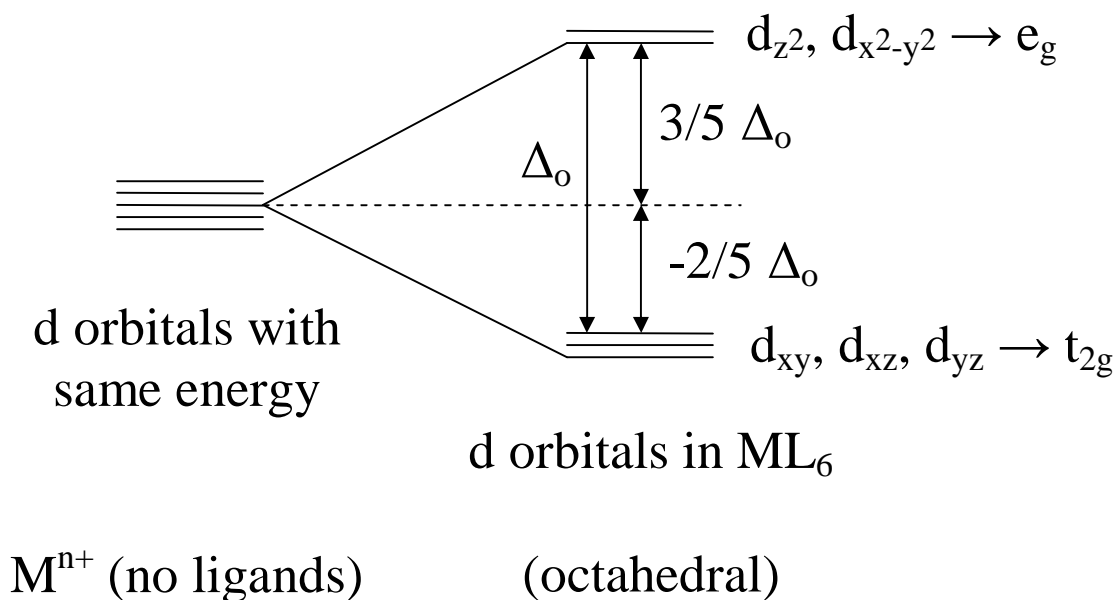


Bonding in Octahedral and Tetrahedral Metal Complexes

Molecular Orbital Theory and Crystal Field/Ligand Field Theory

→ Predict how the d orbitals are affected by the Metal-Ligand Bonding

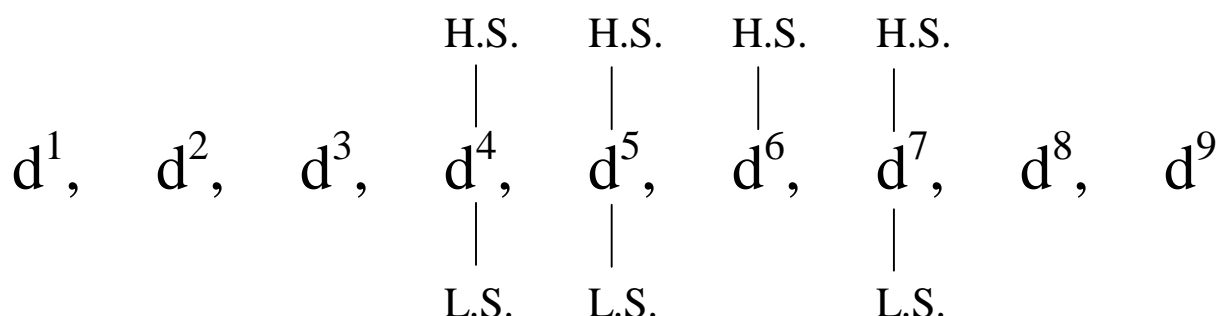


the d_{z^2} and $d_{x^2-y^2}$ orbitals point exactly at the negative charges of the ligand electrons, so electrons in these orbitals are repelled

Figure 1 illustrates the construction of the 10th degree of the diatonic scale. The diagram shows a sequence of musical staves, each representing a degree of the scale. The degrees are labeled d^1 through d^{10} . The construction involves adding notes and accidentals to the previous degree, with specific intervals (Half Step, H.S., and Lower Step, L.S.) indicated by brackets and labels. The notation uses various accidentals (sharps, flats, naturals) and ledger lines to represent the intervals between notes.

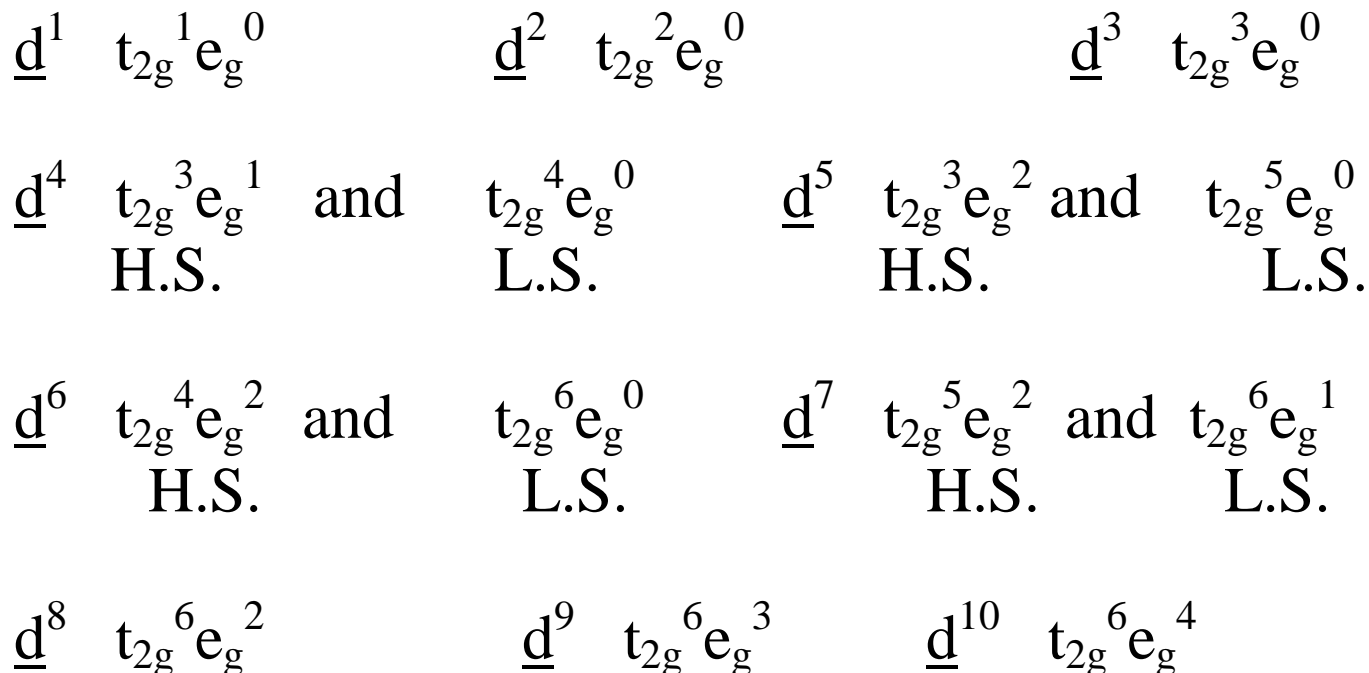
d^1 one unpaired e^- ; d^2 two unpaired e^- ; d^3 three unpaired e^- ; d^4 H.S.(4) L.S.(2); d^5 H.S.(5) L.S.(1); d^6 H.S.(4) L.S.(0); d^7 H.S.(3) L.S.(1); d^8 (2); d^9 (1); d^{10} (0)

So paramagnetic electronic configurations are:
(those with unpaired electrons)



that is, most of them!

Write the electronic configurations with the correct t_{2g} , e_g filling



Consider the series below:

<u>Complex</u>	<u>Δ_o (in cm^{-1})</u>	
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	9,000	Co(II) ←
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	18,000	Co(III) ←
$[\text{Co}(\text{NH}_3)_6]^{2+}$	12,000	Co(II) ←
$[\text{Co}(\text{NH}_3)_6]^{3+}$	22,000	Co(III) ←
<hr/>		
$[\text{Co}^{\text{III}}\text{F}_6]^{3-}$	13,000	<u>weak field</u> Co(III)
$[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$	32,000	<u>strong field</u> Co(III)

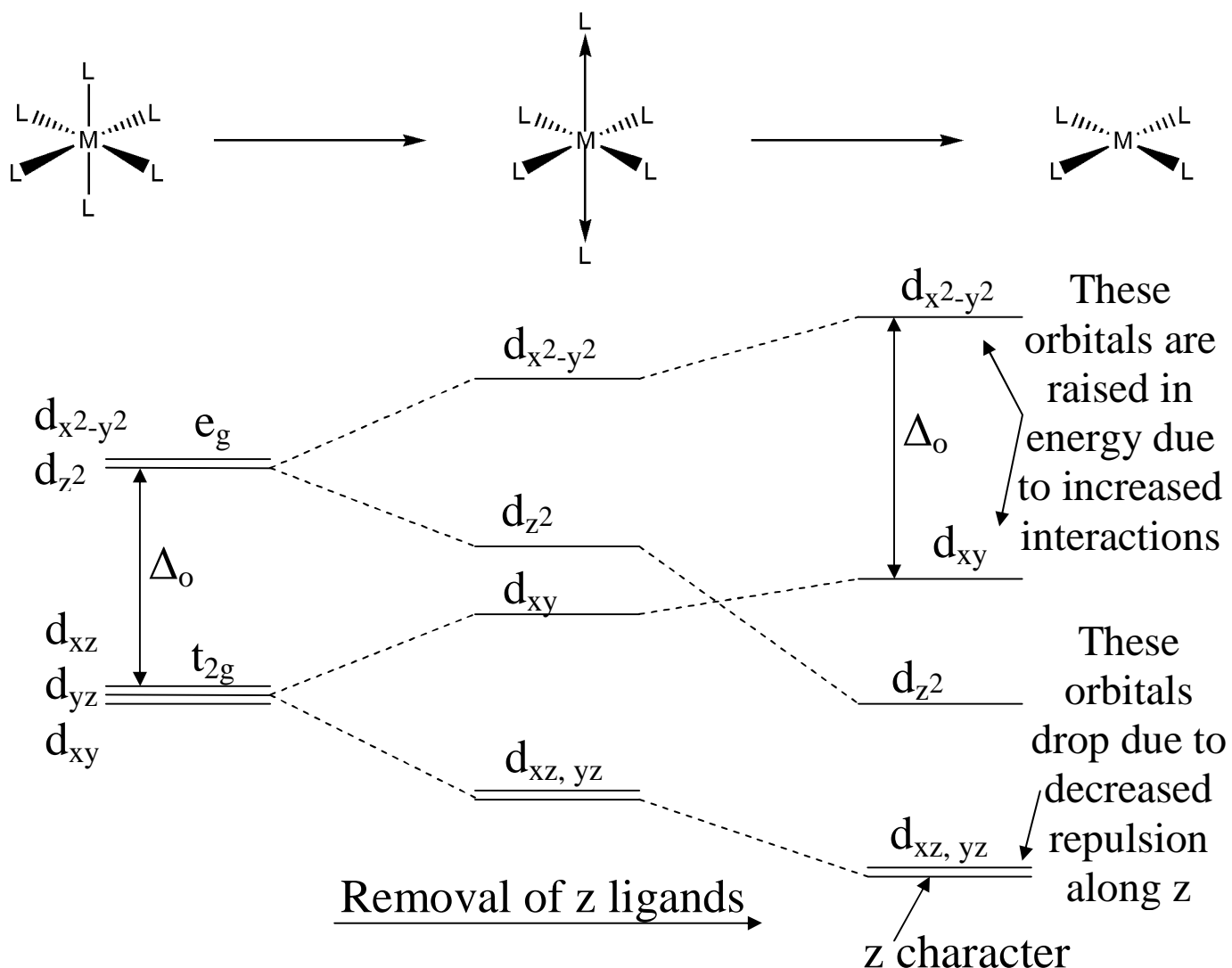
Compare the same oxidation states and then look at the ligand type.

For Co(III)

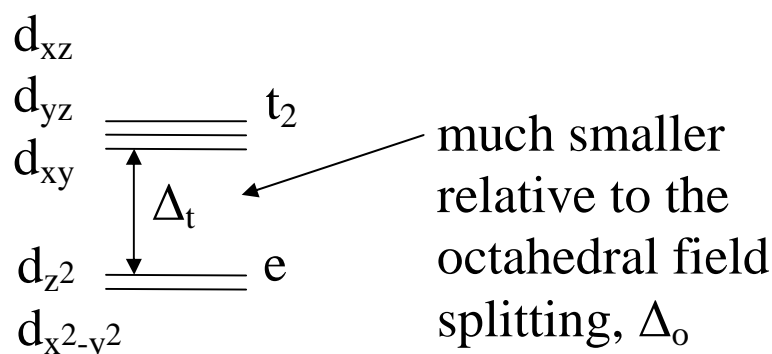
$\text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$ in terms of donor strength

Bonding in Square Planar Complexes

All you have to do is begin with the octahedral d-orbital splitting and consider how the repulsions between metal electrons and ligand electrons change when you pull two trans ligands away

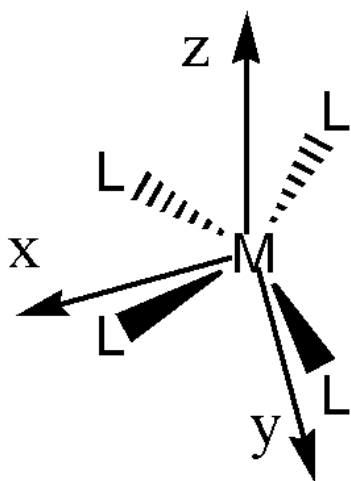


Bonding in Tetrahedral Complexes



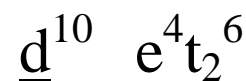
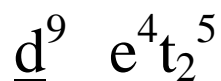
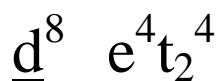
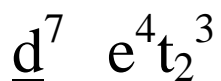
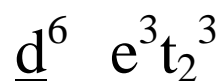
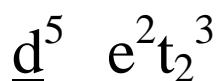
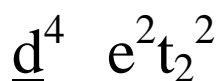
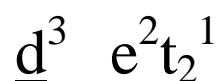
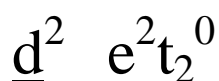
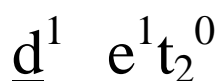
Q. Why?

A. Interactions are weaker in tetrahedral geometries (ligands do not point to orbitals on the metal)

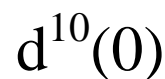
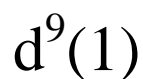
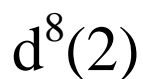
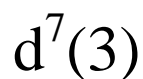
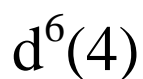
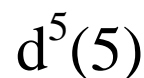
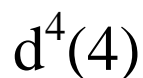
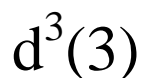
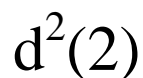
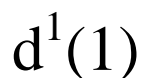


None of the ligands in a tetrahedron point directly at the x, y, z coordinates (and therefore they do not directly contact the d_{z^2} or $d_{x^2-y^2}$ orbitals. They have more contact with the orbitals between the axes i.e. d_{xy} , d_{xz} , d_{yz} , so these are destabilized.

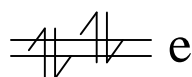
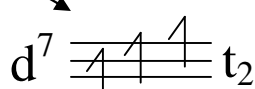
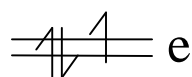
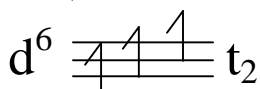
in tetrahedral geometry, one can have $d^1 - d^{10}$ configurations but since $\Delta_t = 4/9 \Delta_o$, there are no L.S. possibilities (Pairing Energy of two electrons $> 4/9\Delta_o$)



all have unpaired electrons except for d^{10} ! How many unpaired electrons does each have?



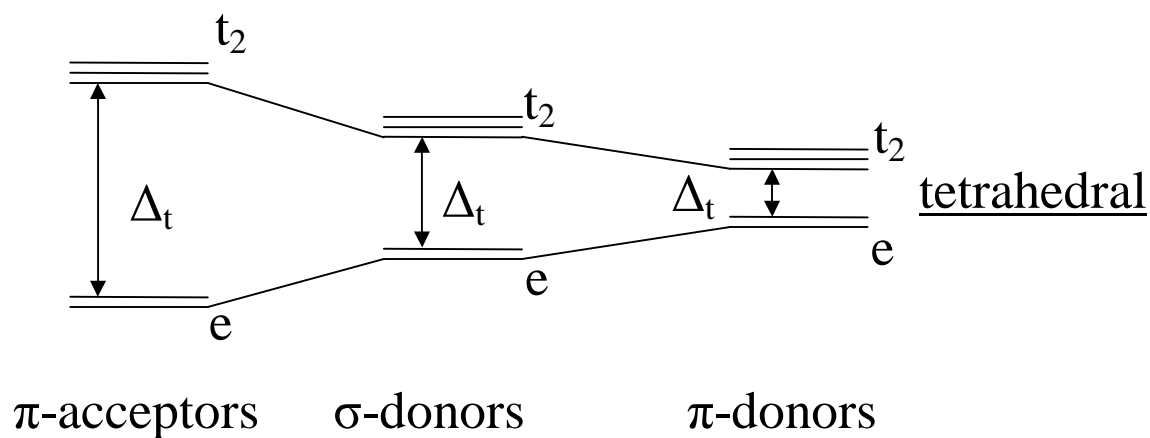
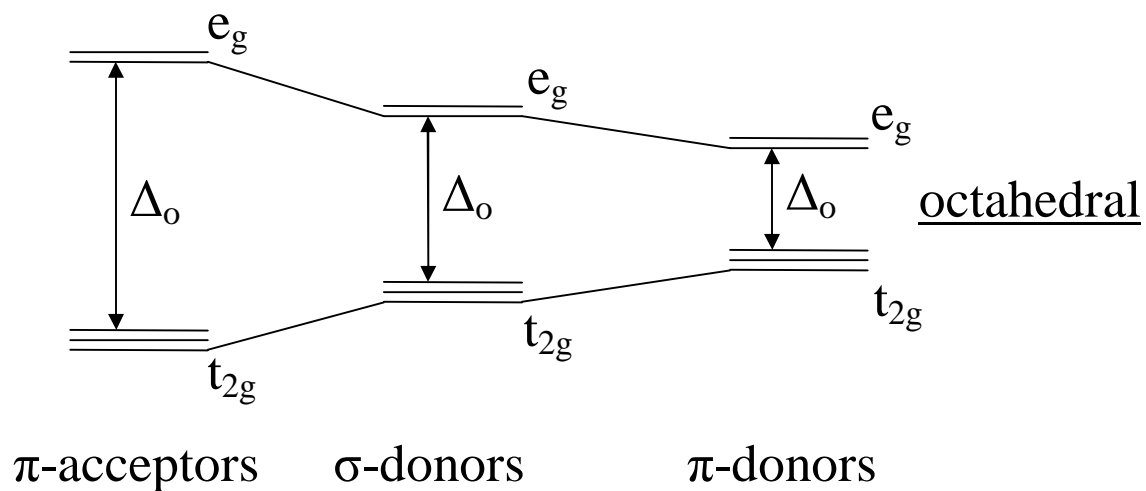
e.g.



etc.,

Ligands dictate how big Δ_o and Δ_t are

- For the same metal and ligands, $\Delta_t = 4/9\Delta_o$

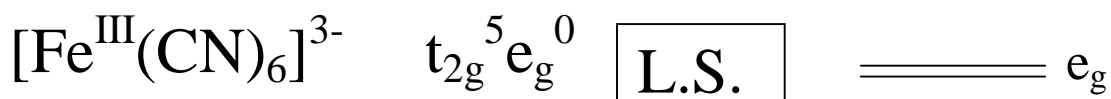


Ligand Field Stabilization Energy (LFSE)

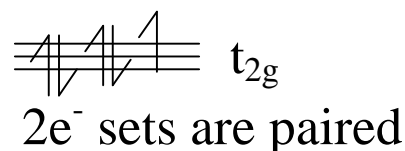
LFSE in Octahedral Complexes

each t_{2g} electron is assigned the energy $-2/5\Delta_o$
 each e_g electron is assigned the energy $+3/5\Delta_o$
 (P_E pairing energy)

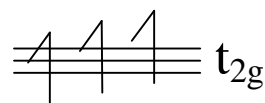
Calculate LFSE for L.S. vs H.S. Fe^{III}



$$\begin{aligned} \text{LFSE} &= 5(-2/5\Delta_o) + 2P_E \\ &= -10/5\Delta_o + 2P_E \\ &= -2\Delta_o + 2P_E \end{aligned}$$



$$\text{LFSE} = 3(-2/5\Delta_o) + 2(+3/5\Delta_o) = 0$$



$\therefore [Fe(CN)_6]^{3-}$ is much more stable!!

Example: d^4 high-spin $t_{2g}^3 e_g^1$

$$= 3 \times (-2/5\Delta_o) + 1(3/5\Delta_o)$$

H.S.

$$= -6/5\Delta_o + 3/5\Delta_o$$

$$= -3/5\Delta_o \text{ stabilization}$$

d^4 low-spin $t_{2g}^4 e_g^0$

$$\text{L.S.} \quad 4 \times (-2/5\Delta_o) + P_E = -8/5\Delta_o + P_E$$

In the H.S. case, obviously the pairing energy $P_E > \Delta_o$

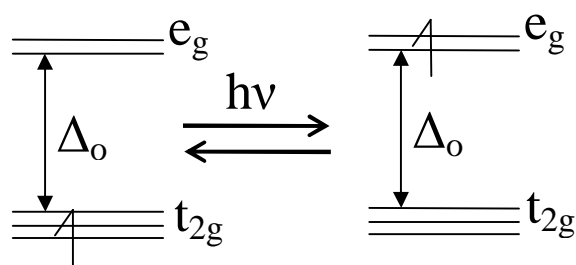
In the L.S. case, the opposite is true $\Delta_o > P_E$

Electronic Spectroscopy

1. Promoting an electron from the ground state (g.s.) to an excited state (e.s.) takes energy.
2. The energy of the transition depends on Δ_o , Δ_t primarily for octahedral and tetrahedral complexes respectively
3. The number of transitions that we observe depends on the number of available excited states that match with the ground state in terms of selection rules.

Two main selection rules

- (a) orbital selection or Laporte selection rule
- (b) spin selection rule



Simplistically, you may want to view the promotion of an electron from the t_{2g} to the e_g level as the basis for the $h\nu$ absorption peak. In the case of $t_{2g}^1 e_g^0$ compounds $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, this is “sort of ” correct. In other words the energy, $h\nu$, will be very similar to Δ_o .

Realistically, transitions occur between “states” and not “orbitals” $t_{2g}^1 e_g^0$ can be defined by a state symbol, called a term symbol.