

Topic II

Chemistry of Transition Metals

Part 1. General Considerations

Some general properties of TM elements

- 1. Metals**
- 2. Almost all: HARD, STRONG, High m.p., b.p.**
- 3. Conduct heat & electricity (Cu and Al wire)**
- 4. Form Alloys**
- 5. Show variable oxidation states**
- 6. At least one of the ions & compounds colored.**
- 7. Form paramagnetic species because of partially filled shells**
- 8. Form coordination compounds (complexes) and organometallic compounds.**

Variable oxidation states

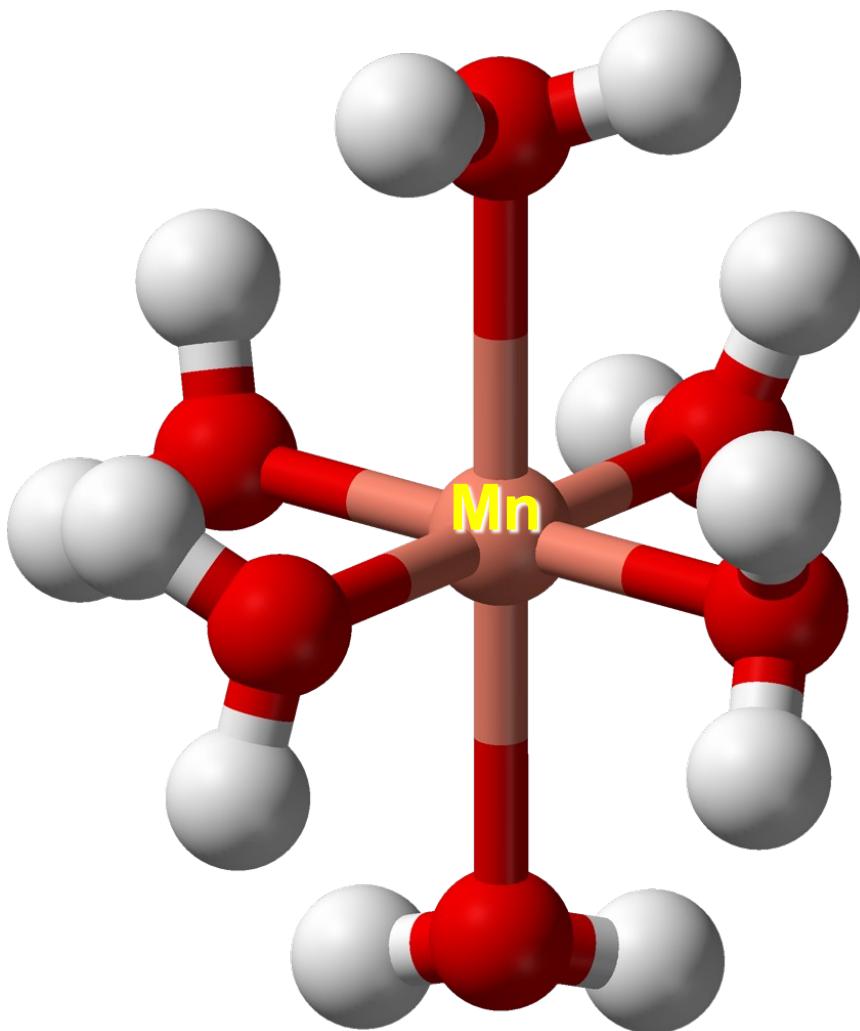
Sc		+3					
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

1. Increase in the number of oxidation states from Sc to Mn. All are possible only in case of Mn.
2. Decrease in the number of oxidation states from Mn to Zn, due to the pairing of d-e's after Mn.
3. Stability of higher oxidation states decreases along Sc to Zn. Mn(VII) and Fe(VI) are powerful oxidizers.
4. Down the group, the stability of high oxidation states increases (easier availability of both d and s electrons for ionization).

How to stabilize higher and lower oxidation states?

- Low oxidation state using π -acceptor ligands such as CN⁻
example: [Cr(CO)₆]
- Intermediate oxidation state complexes often have ligands such as chloride, ammonia or water
example: [Cr(Cl)₃(H₂O)₃]
- High oxidation state complexes usually have oxide or fluoride ligands.
example: K₂[Cr₂O₇]

An example of a metal complex



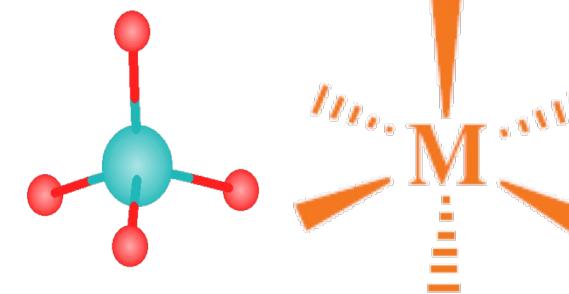
Metal ion: Central & is a Lewis acid

Ligand: Is bound to the metal ion & is a Lewis base

Coordination number: The number of ligands surrounded by a metal ion.

Coordination Number & Geometry

- TM ions generally form complexes with well defined number of ligands.
- Common coordination geometry



Factors controlling geometry

Metal & Ligand

Low Coord. Number

- Soft ligand with
- Low M oxidation state
- Counter ion with low basicity
- Steric ligand

Size

type

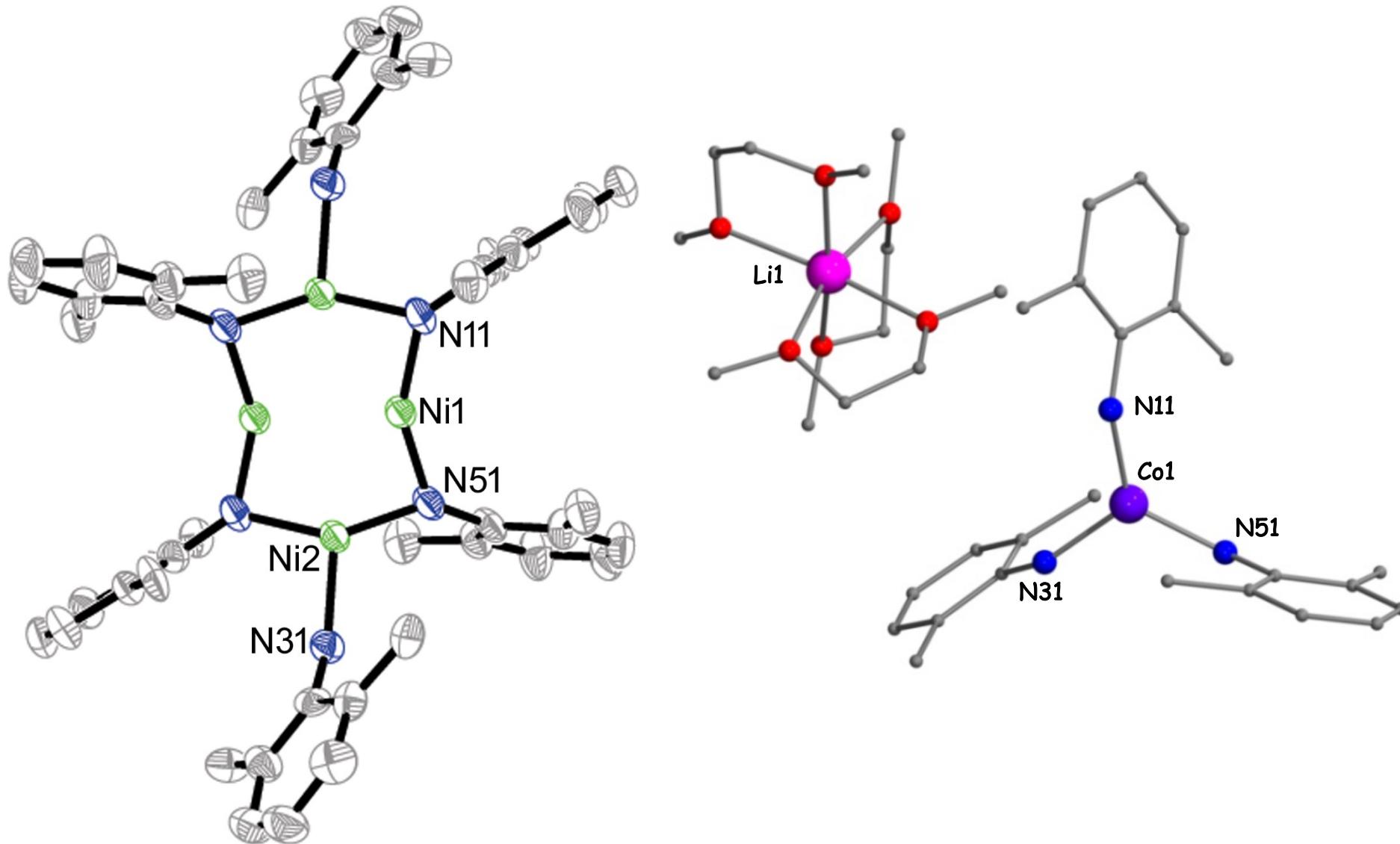
Charge

Electronic factors

High Coord. Number

- hard ligand with
- high M oxidation state
- Large non acidic cation
- small steric

Influence of sterically bulky ligand on geometry



Open questions in coordination chemistry

- (i) Why the complexes are colored?**
- (ii) Why same stoichiometric species ($\text{CoCl}_3 \cdot 4\text{NH}_3$) yield different colour?**
- (iii) Why some compounds are high-spin while others are low-spin?**
- (iv) Some coordination compounds the metal-ligand bond lengths are different?**
- (v) Can the structure of spinel's be rationalized?**

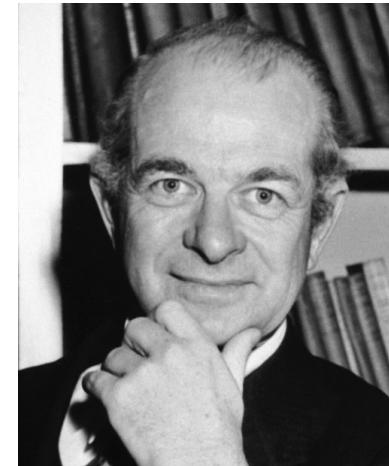
Theoretical foundations of coordination complexes

- (i) Werner's coordination theory
- (ii) Valence bond theory (VBT; Linus Pauling)
- (iii) (self-reading Ref: Concise Inorganic Chemistry by J. D. Lee)

(iii) Crystal field theory
(Hans Bethe and J. H. Van Vleck)

(iv) Ligand field theory
(Molecular orbital approach; J. H. Van Vleck,
John Stanley Griffith and Leslie Orgel)

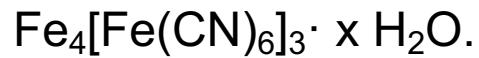
Ref: Inorganic Chemistry by Shriver & Atkins')



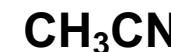
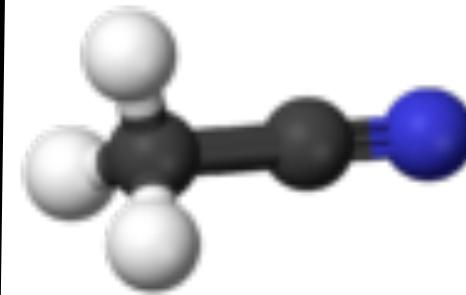
How strong is the co-ordinate bond?



Prussian blue



Prussian blue is used for certain heavy metal poisons.



Modest toxicity.
Can be metabolised to produce HCN, which is very toxic



KCN is a poison by itself....

Limitation of VBT

❖ **VBT could not explain**

- The origin of color in transition metal complexes
- Thermodynamic stability

Crystal Field Theory (CFT)

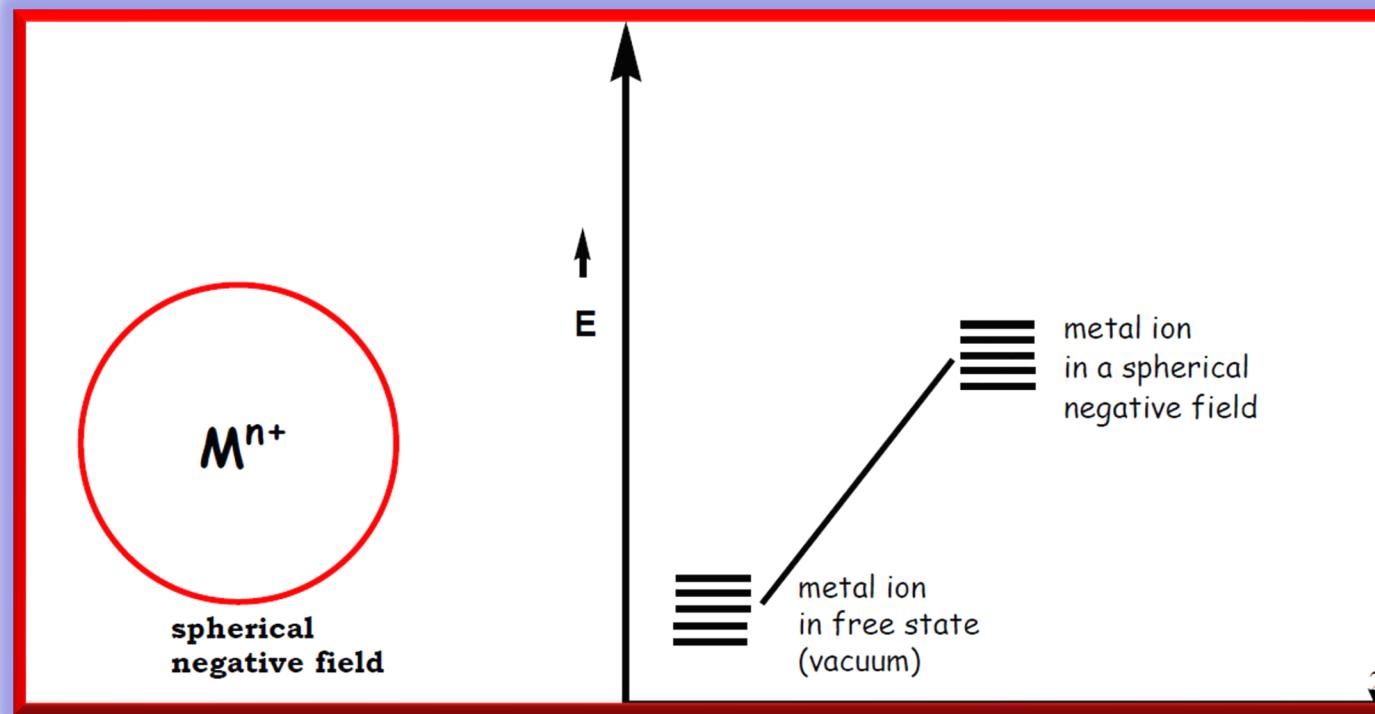
❖ **CFT could explain**

- The stability and origin of colour
- Optical spectrum (UV-Vis) of 3d complex
- Magnetic properties of metal complex
- Predict the structure of spinel or inverse spinel

CFT - Assumptions

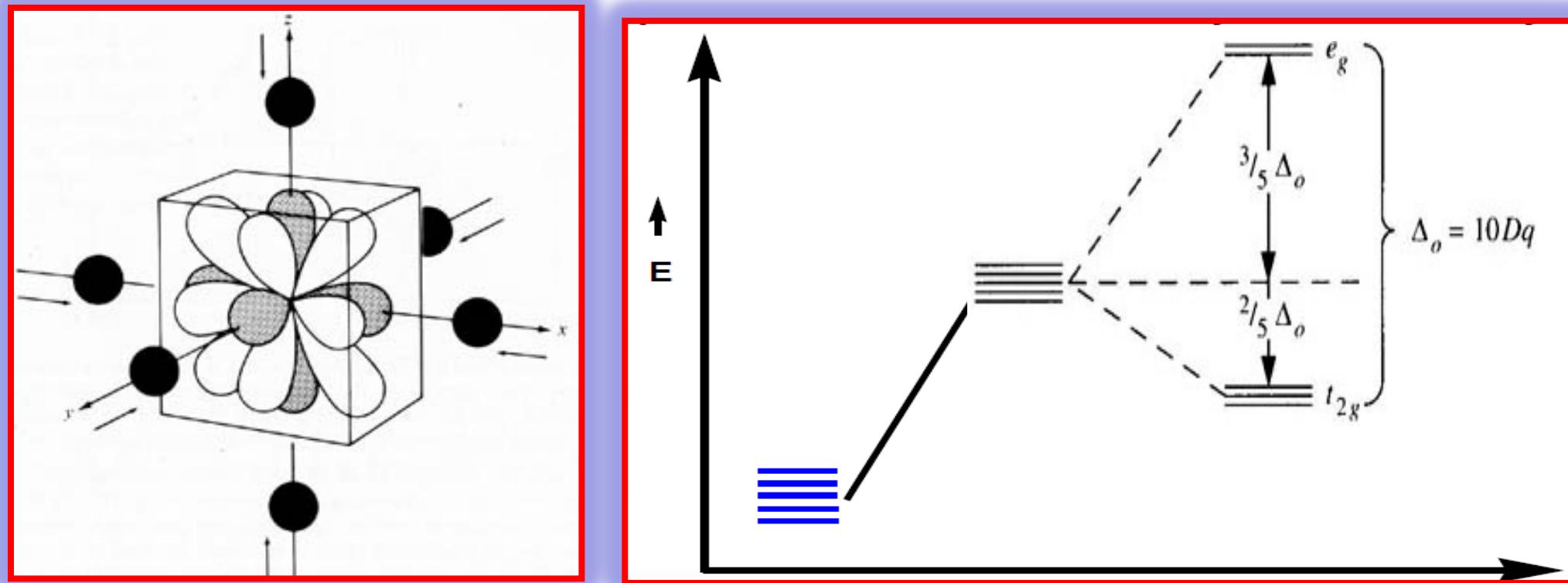
- (i) Interactions between the metal ion and ligands are purely electrostatic (ionic in nature).
- (ii) Ligands are considered as point charge
 - (a) For anionic ligand - ion- ion
 - (b) For neutral ligand - ion-dipole
- (iii) Electrons on the metals are under repulsive force from the ligands.
- (iv) Electrons on the metal occupy those d-orbitals which face least repulsion from the ligands.

Influence of symmetric ligand field on the d-orbitals

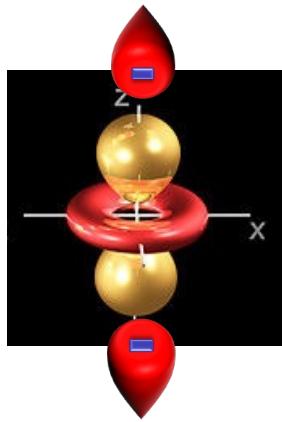
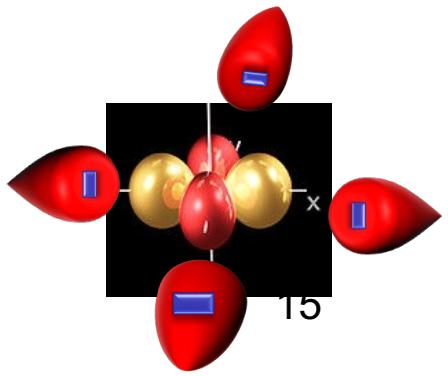


- The $5 \times d$ orbitals in an isolated gaseous metal are degenerate
- If a spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and electrons present in the d orbitals.

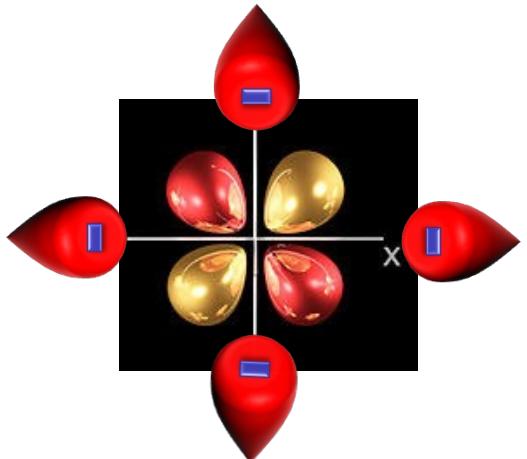
Octahedral Field



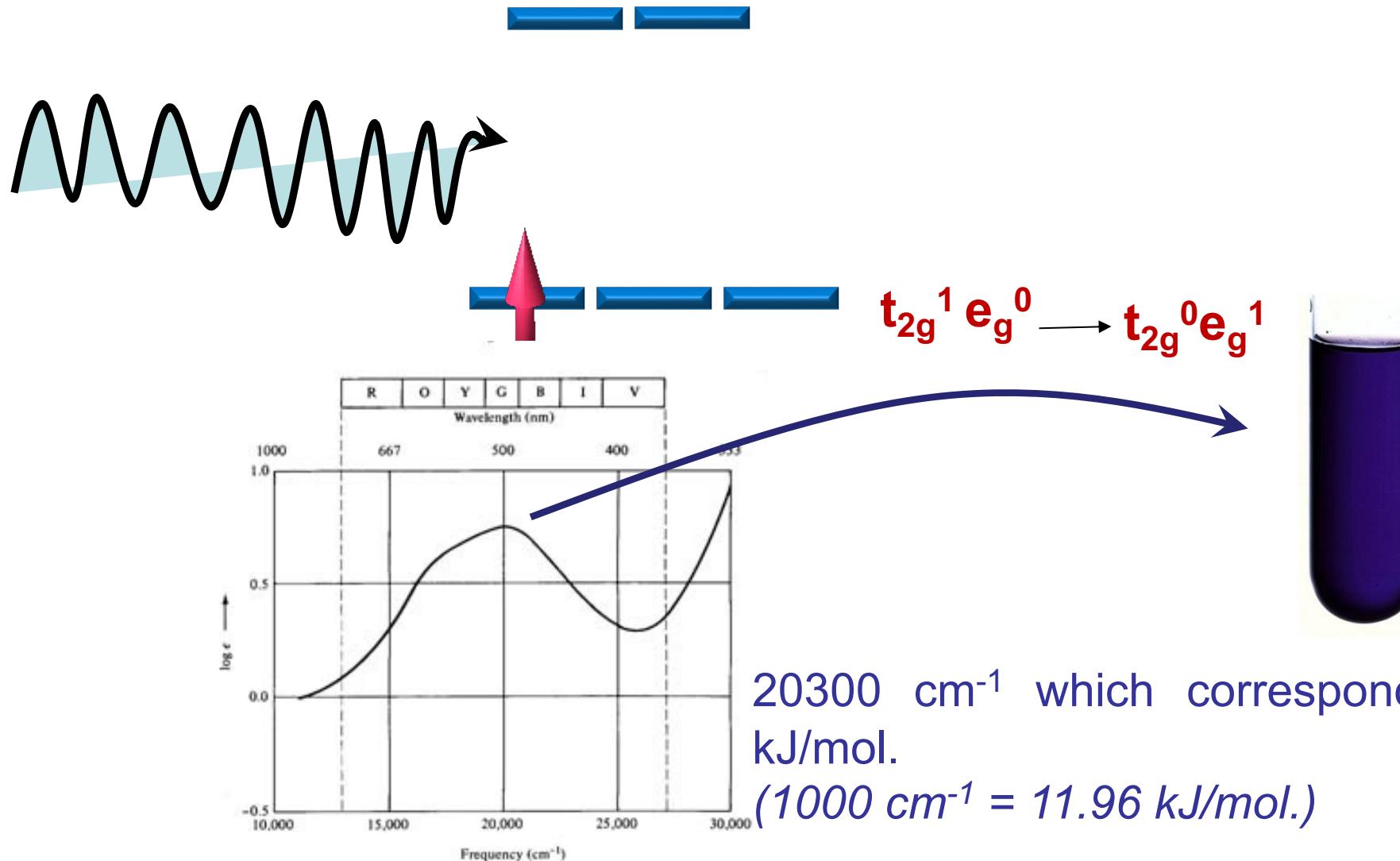
- ✓ Not all d- orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.
- ✓ The orbitals which lie along these axes (i.e. x^2-y^2 , z^2) will be destabilized more than the orbitals which lie in-between the axes (i.e. xy , xz , yz).



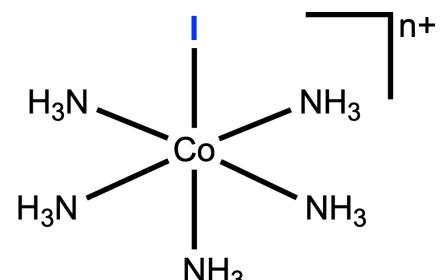
d_z^2 $d_{x^2-y^2}$ d_{xy} d_{xz} d_{yz}



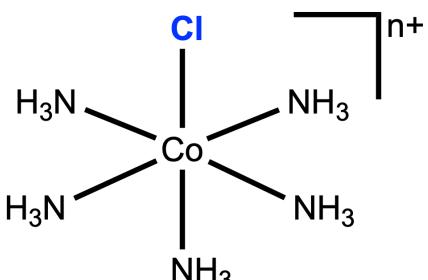
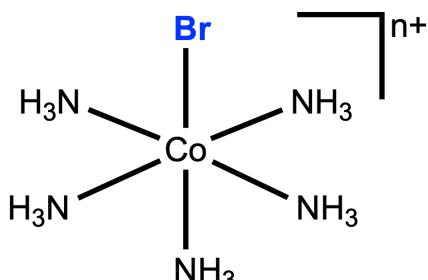
Rationale for the observation of UV-Vis spectrum



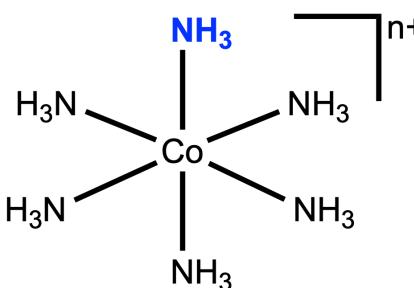
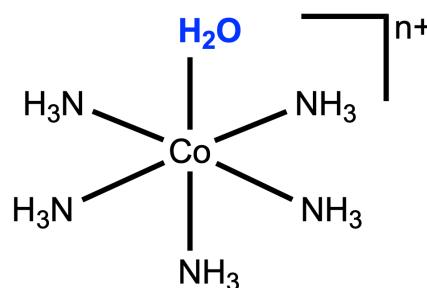
Why color of the complexes change when changing a ligand?



Purple

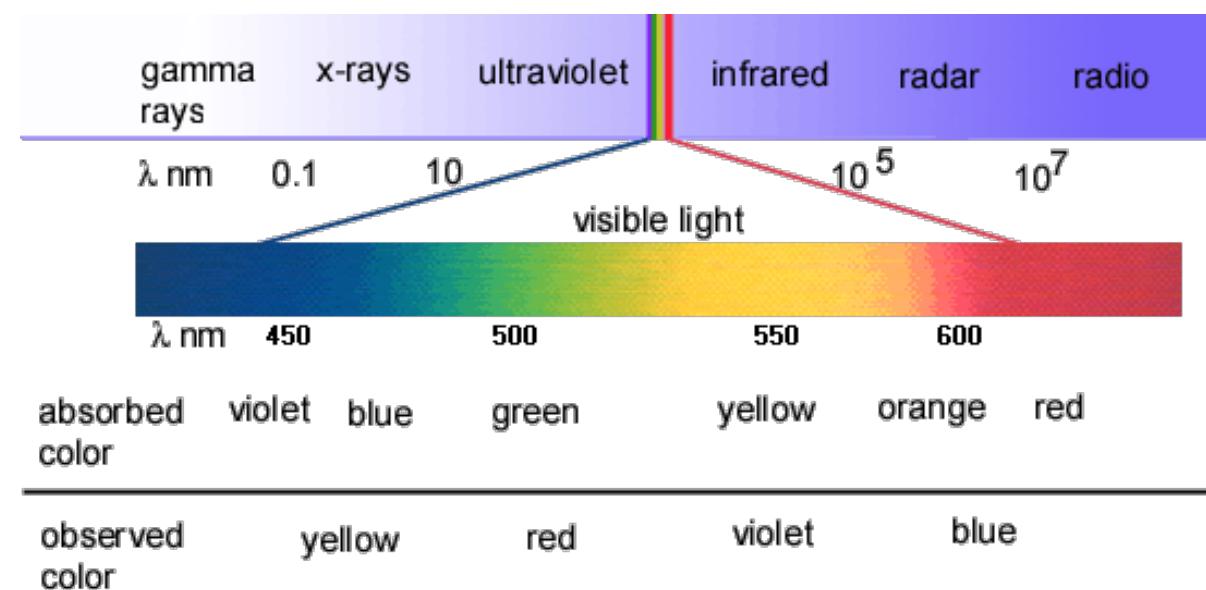


Pink



Yellow

Δ_o follows the order of
 $\text{I} < \text{Br} < \text{Cl} < \text{H}_2\text{O} < \text{NH}_3$

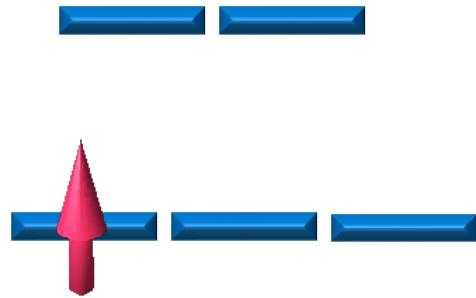


Spectrochemical series

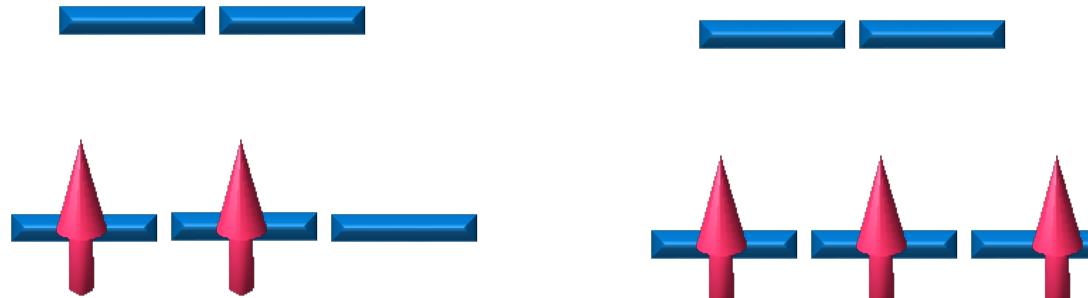
$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-$, $\text{F}^- < \text{urea}$, $\text{OH}^- < \text{ox}$, $\text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}$, $\text{NH}_3 < \text{en} < \text{bpy}$, $\text{phen} < \text{NO}_2^- < \text{CH}_3^-$, $\text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$.

What happens for more than 1 electron in d orbitals? / Magnetic property of paramagnetic systems

For d^1 - d^3 system



Electron-electron repulsion; Hund's rule

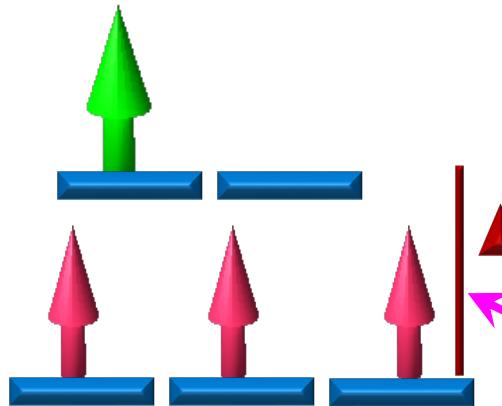


Due to the e^-e^- repulsion, calculating Δ_o is not straight forward for system with more than one unpaired electrons.

High spin and Low spin complexes

For d⁴-d⁷ systems

d⁴: High spin



So which one?

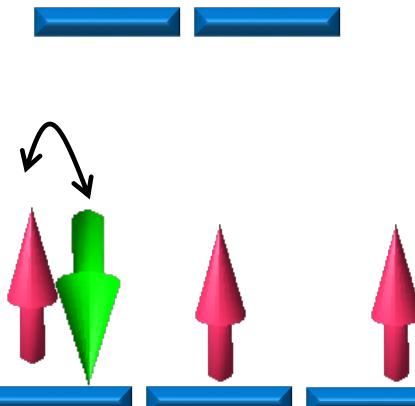
Decided by

- (i) Δ_0
- (ii) Pairing E.

$$\Delta_0 < P$$

$$\Delta_0 > P$$

d⁴: Low spin



Δ_0 vs. Pairing Energy (repulsive energy)

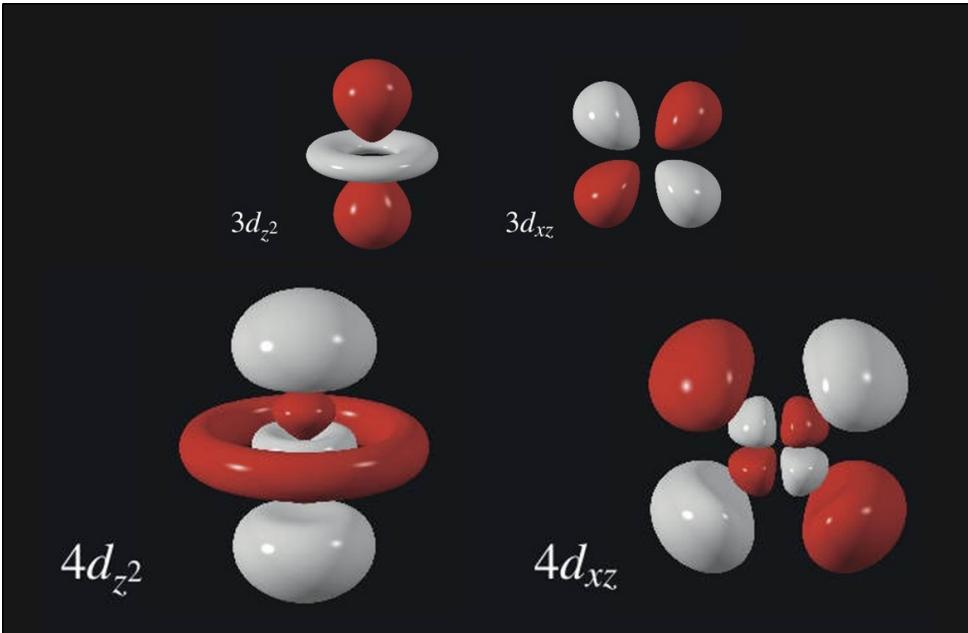
Complex	Config.	Δ_0 , cm ⁻¹	P, cm ⁻¹	spin-state
[Fe(OH ₂) ₆] ²⁺	d ⁶	10,400	17,600	high-spin
[Fe(CN) ₆] ⁴⁻	d ⁶	32,850	17,600	low-spin
[CoF ₆] ³⁻	d ⁷	13,000	21,000	high-spin
[Co(NH ₃) ₆] ³⁻	d ⁷	23,000	21,000	low-spin

Factors affecting Δ_o

(i) The charge on the metal ion



(ii) Nature of orbital (3d, 4d, or 5d)



[Co(NH ₃) ₆] ³⁺	24800 cm ⁻¹	297 kJ/mol
[Rh(NH ₃) ₆] ³⁺	34000	407
[Ir(NH ₃) ₆] ³⁺	41000	490

3d < 4d < 5d

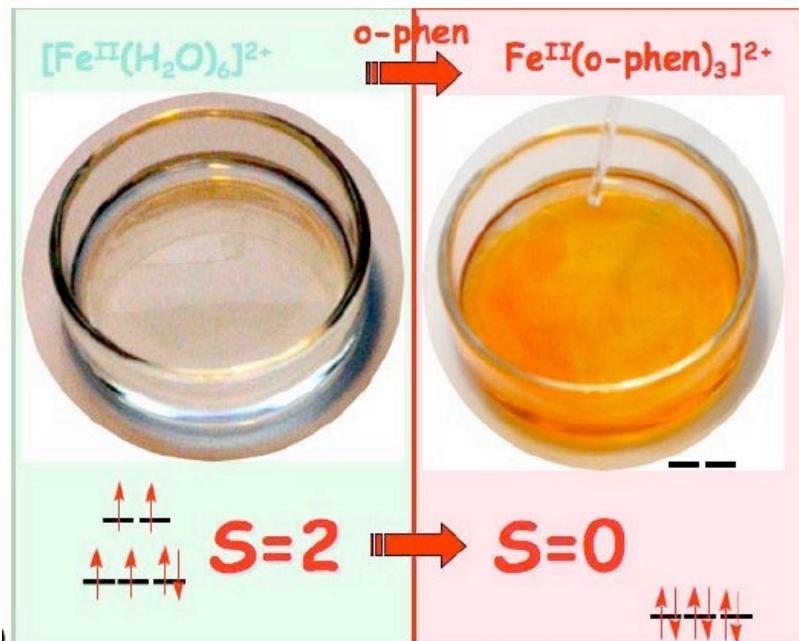
Factors affecting Δ_o

(iii) Nature of ligand

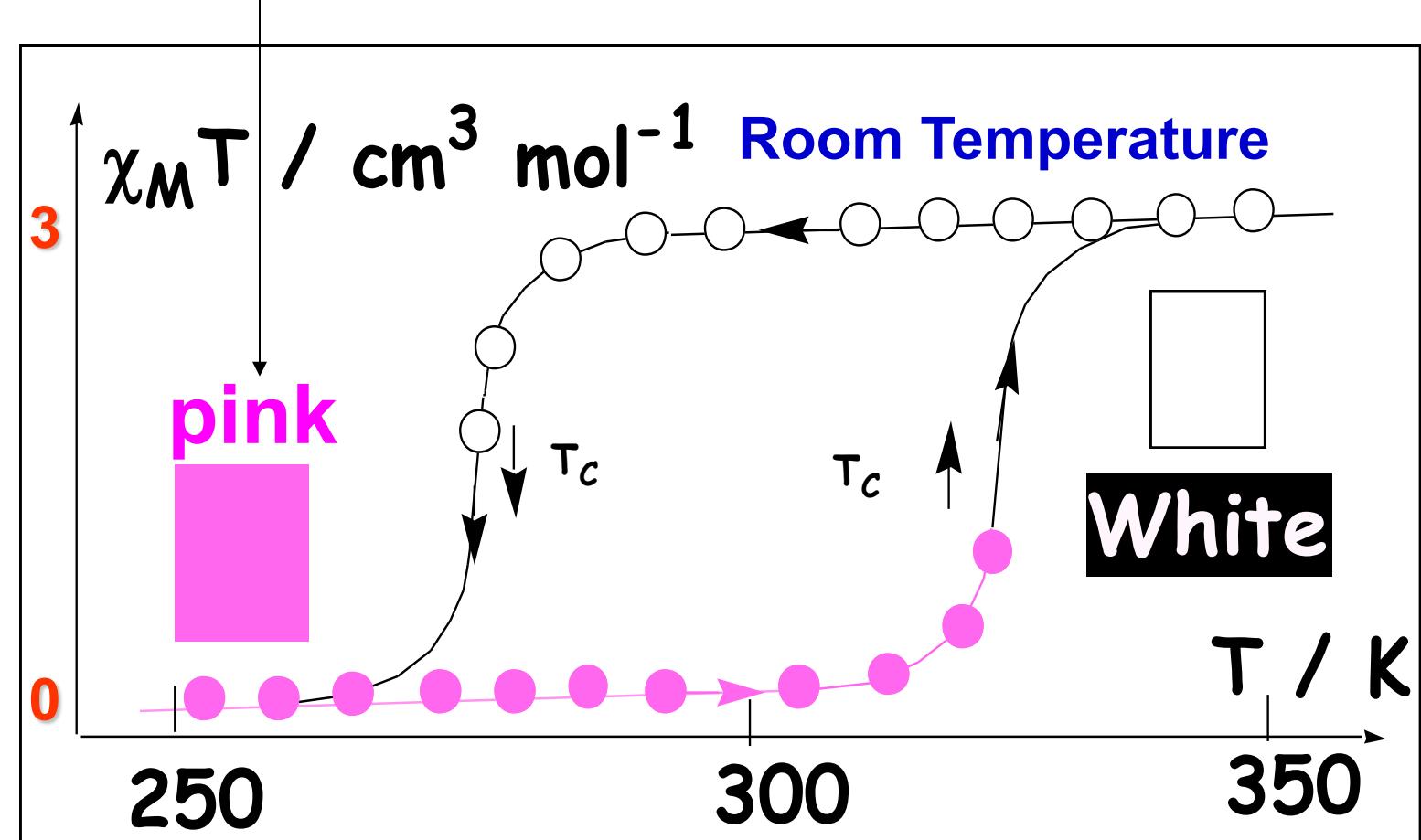
Ligands which cause a small splitting are *Weak field ligands* (Δ_o in the range $7000 - 30000 \text{ cm}^{-1}$) and those cause a large splitting are *Strong field ligands* ($\text{CFSE typically} > 30000 \text{ cm}^{-1}$)

$[\text{CrCl}_6]^{3-}$	13640 cm^{-1}	163 kJ/mol
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17830	213
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21680	259
$[\text{Cr}(\text{CN})_6]^{3-}$	26280	314

From basic science to real time applications: Story on HS-LS complexes

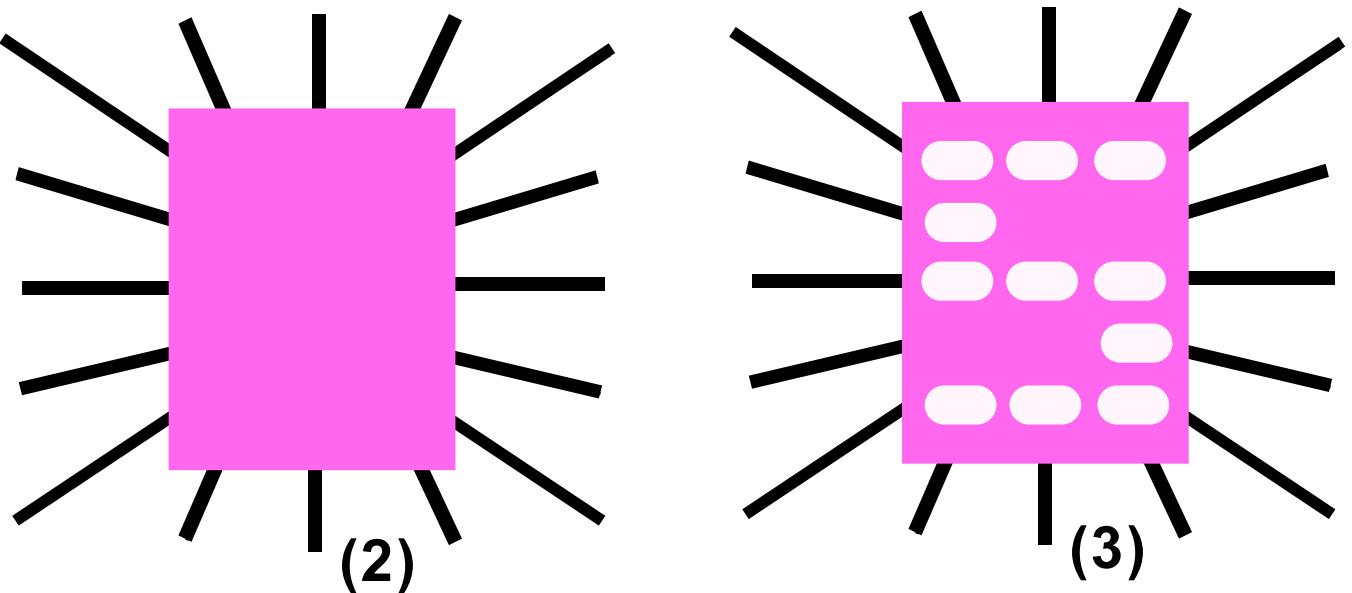


A Fe(II) HS-LS compound: Colour change



Application of Spin-Crossover complexes

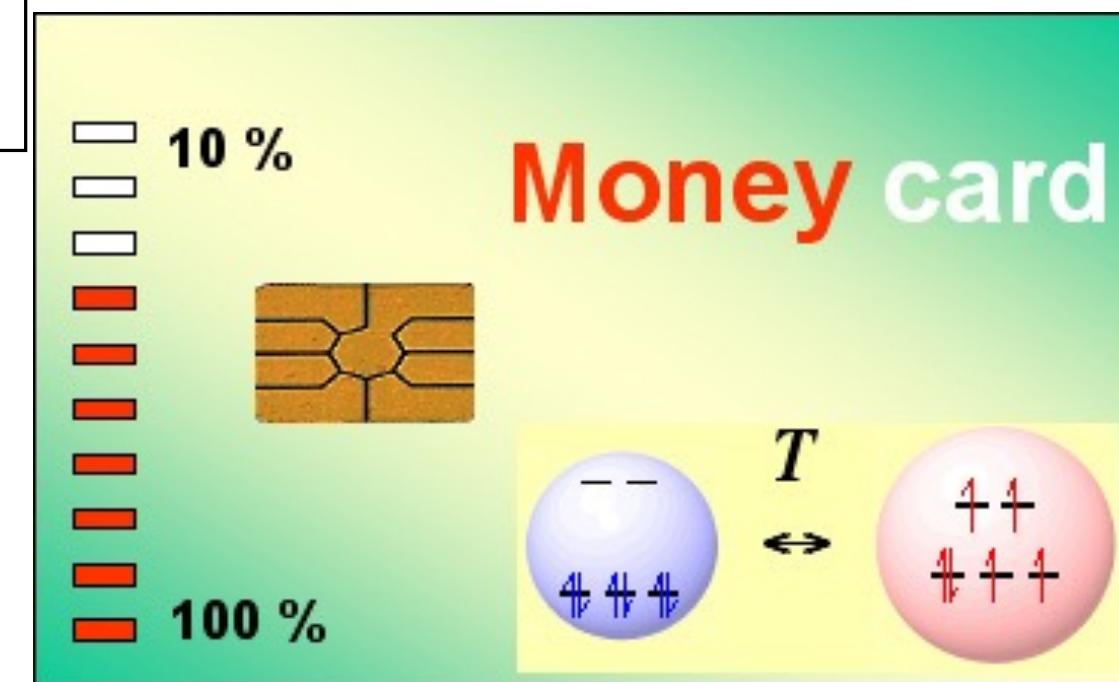
Display device



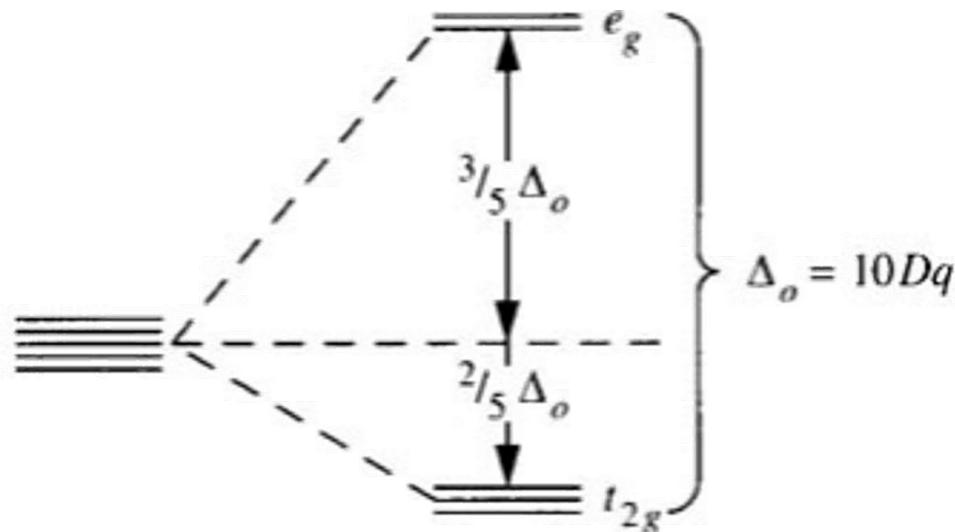
Compound in
Low spin state
(Thin Layer)

Display

LS-HS transition (Spin crossover) tuneable with light (or Temperature or Pressure): Applications



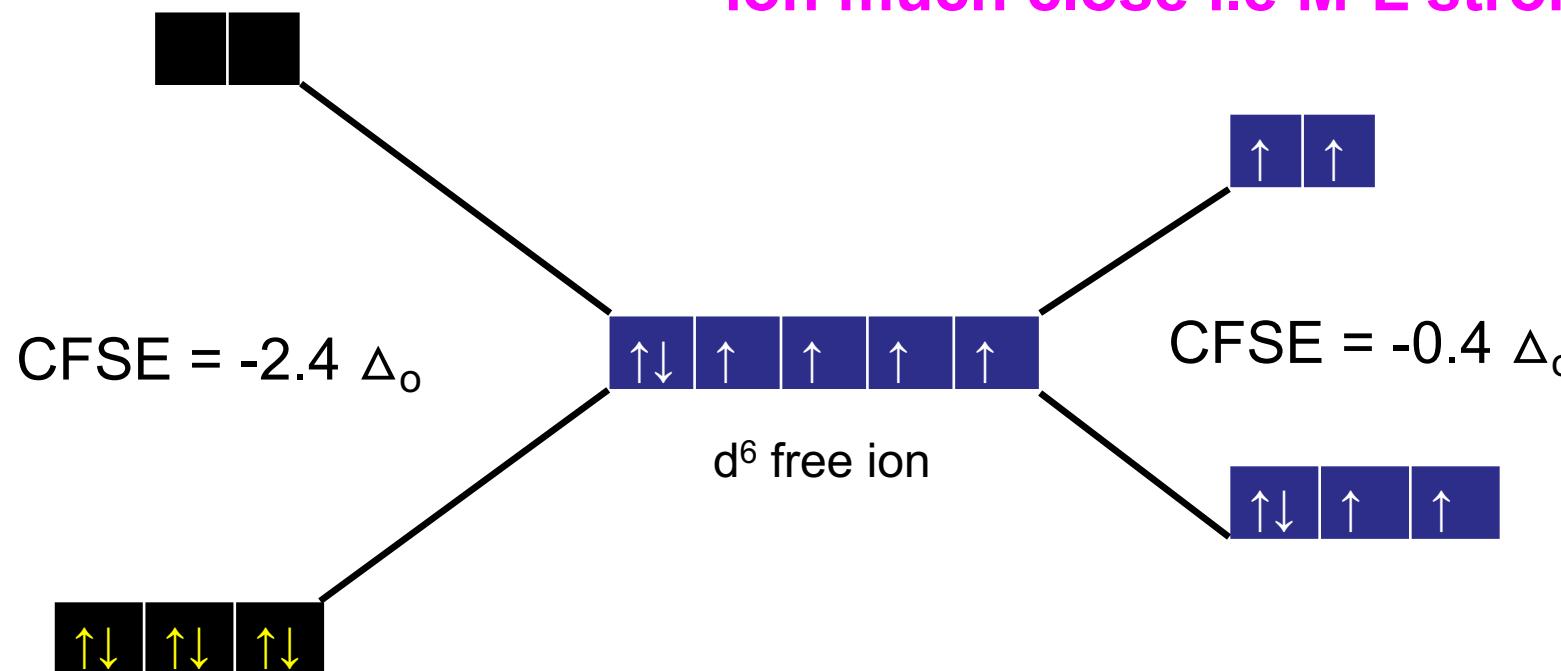
Application of CFT / Thermodynamic stability of complexes (CFSE)



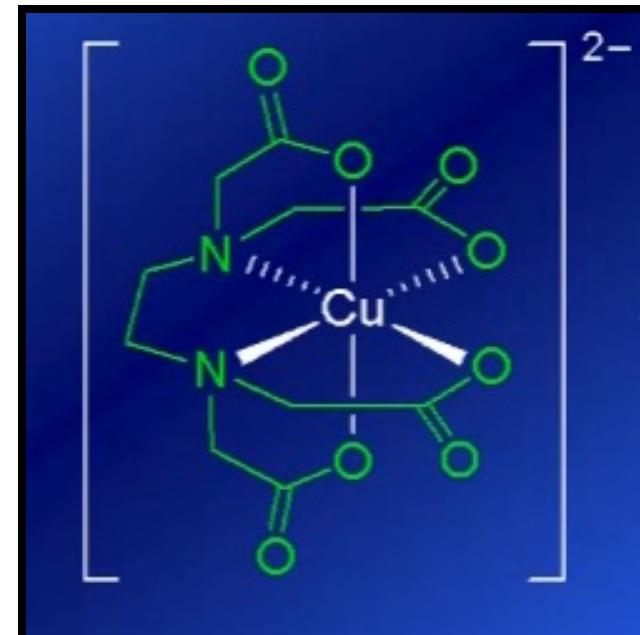
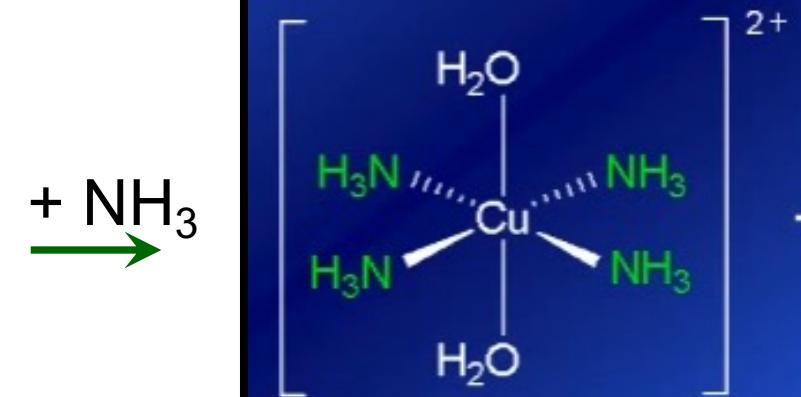
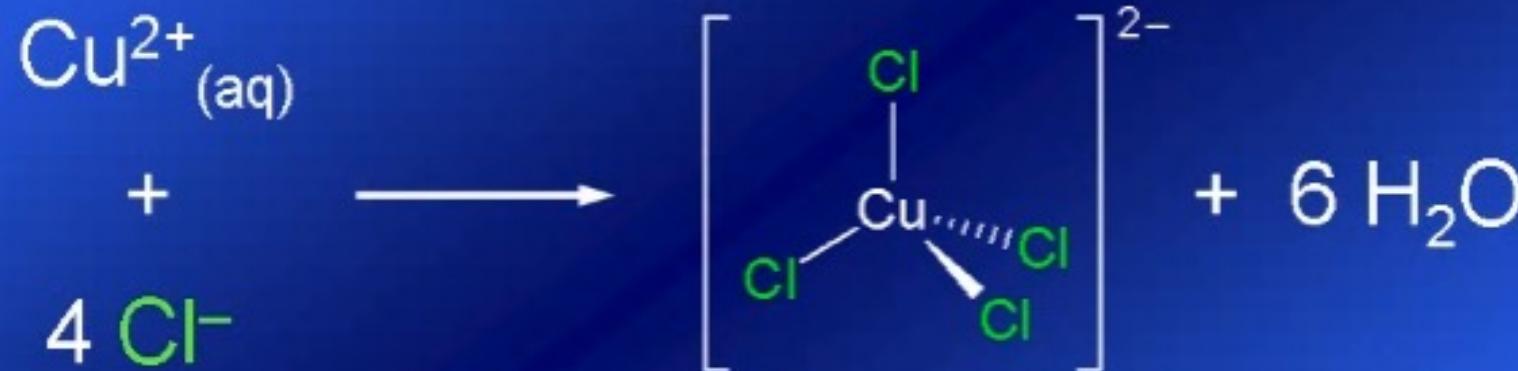
$$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g) \Delta_o$$

Where $n(t_{2g})$ and $n(e_g)$ are the number of electrons occupying the respective levels.

Since there are no electrons in the e_g orbitals (low spin), ligands can approach the metal ion much close i.e M-L strong (than in HS)



Stability of complex due to chelation effect

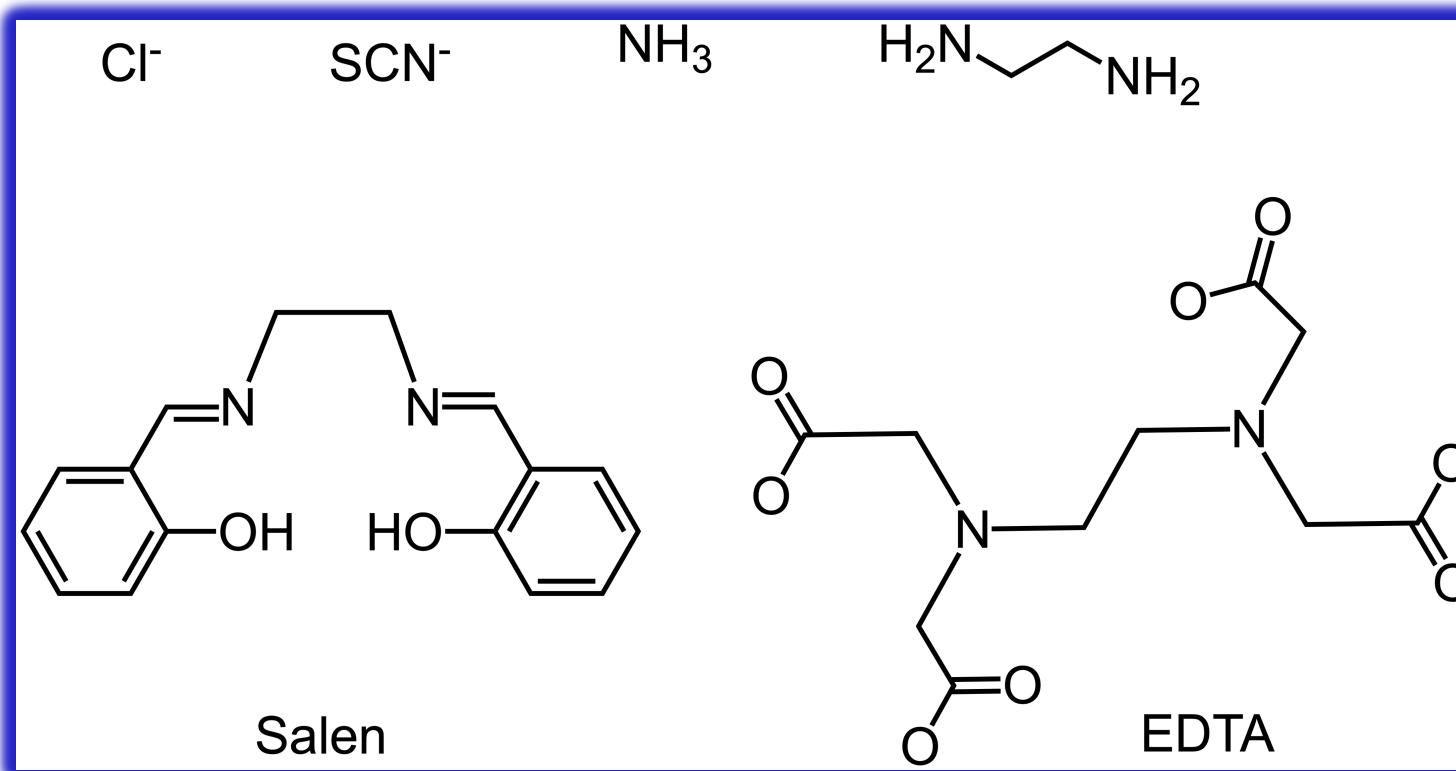


+ EDTA

Demonstration

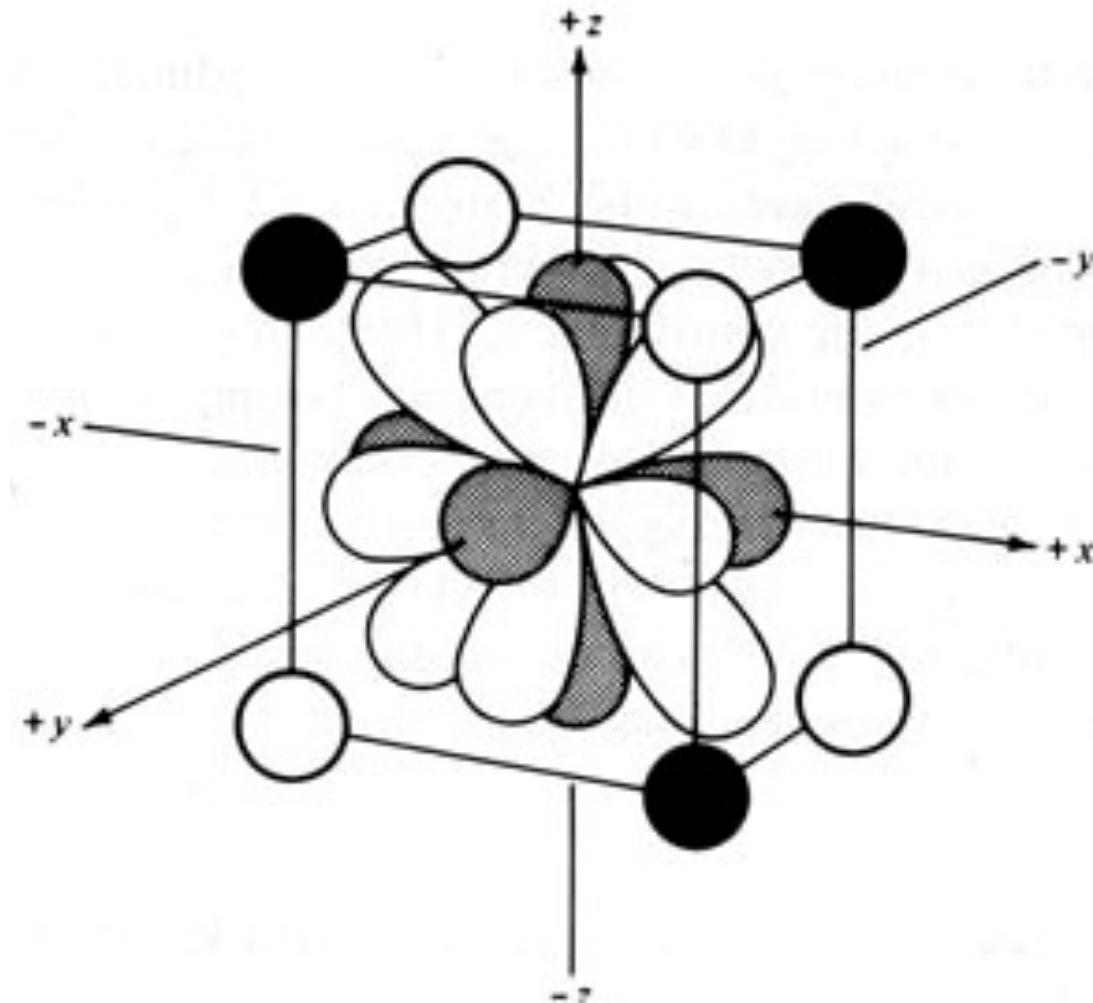
Spectrochemical Series/Chelate effect

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-$, $\text{F}^- < \text{urea}$, $\text{OH}^- < \text{ox}$, $\text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}$, $\text{NH}_3 < \text{en} < \text{bpy}$, $\text{phen} < \text{NO}_2^- < \text{CH}_3^-$, $\text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$.

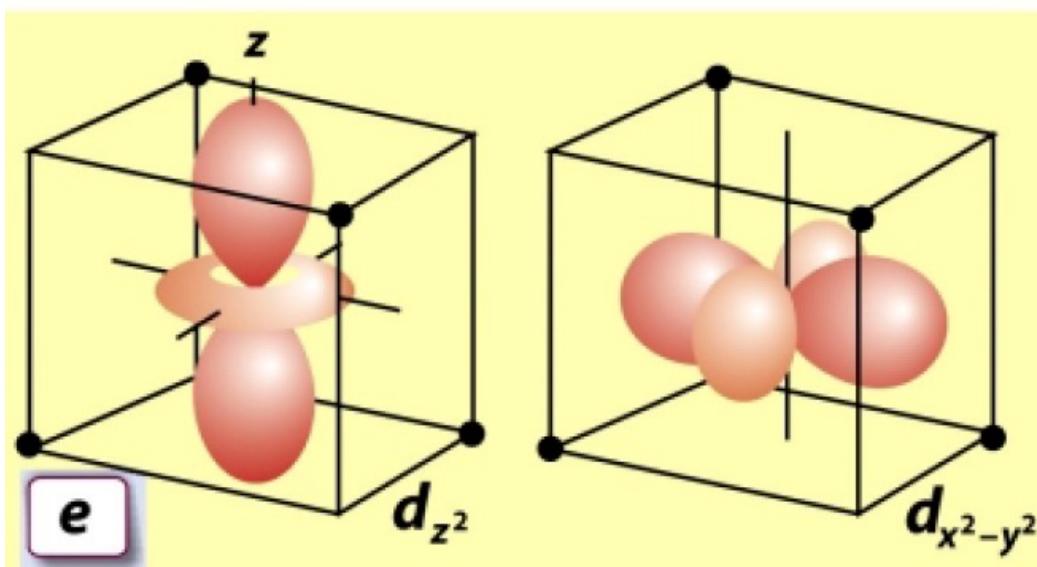
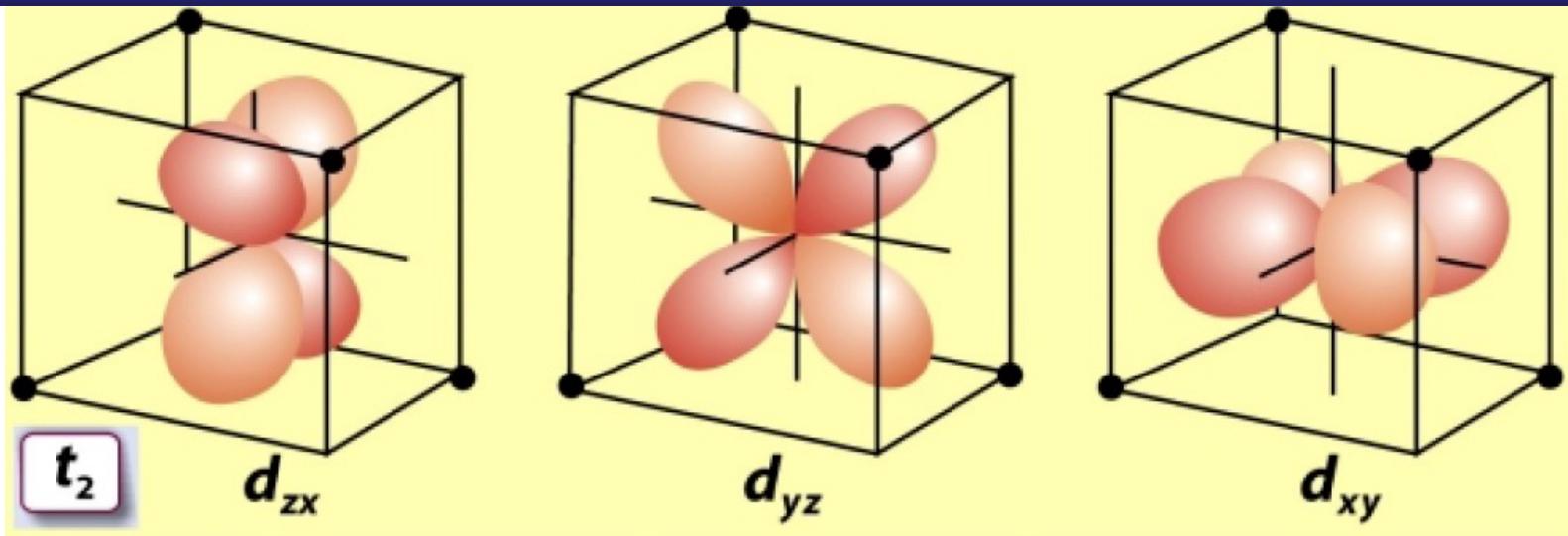


Tetrahedral Field- Considerations

- Imagine a tetrahedral molecule inside a cube with metal ions at the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.
- The two 'e' orbitals point to the center of the face of the cube while the three 't₂' orbitals point to the center of the edges of the cube.



Tetrahedral complexes



The three ' t_2 ' orbitals
point to the center of the
edges of the cube
 $109^\circ 28' / 3 = 35^\circ 16'$.

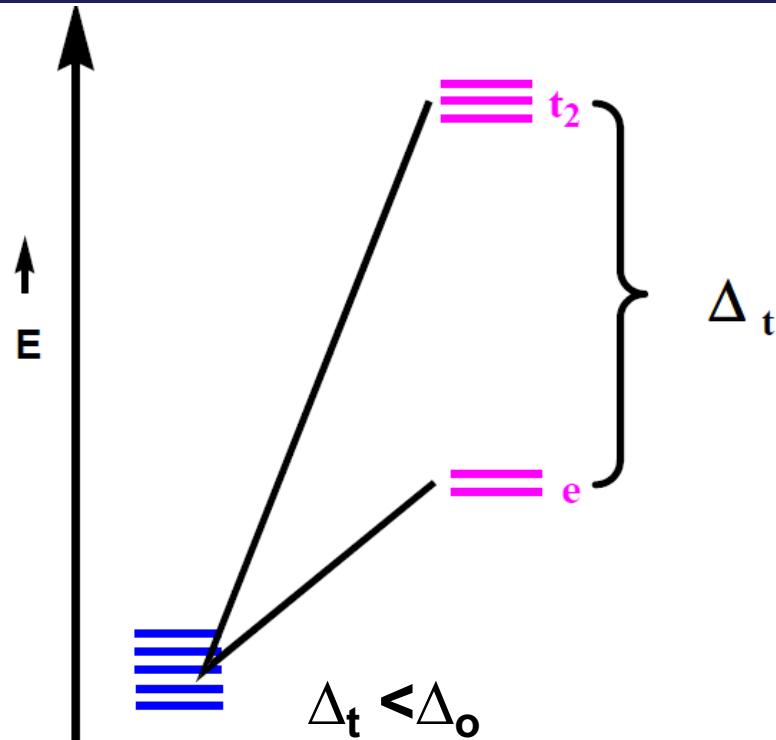
The two 'e' orbitals
point to the center of
the face of the cube
 $109^\circ 28' / 2 = 54^\circ 44'$.

figure 19-8

Shriver & Atkins Inorganic Chemistry, Fourth Edition

2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Tetrahedral complexes



Thus the t_2 orbitals are nearer to the direction of approach of the ligands than the e orbitals. Hence, t_2 orbitals have higher energy compared to e -orbitals

In Td four ligands $\sim 2/3$ of Oh field

In Td the ligands do not coincide with d-orbitals $\sim 2/3$
Hence,

$$\Delta_t \approx 4/9 \Delta_o$$

Due to this, tetrahedral complexes are high-spin, in general.

Complex	Δ_T/cm^{-1}
VCl_4	9010
$[\text{CoCl}_4]^{2-}$	3300
$[\text{CoBr}_4]^{2-}$	2900

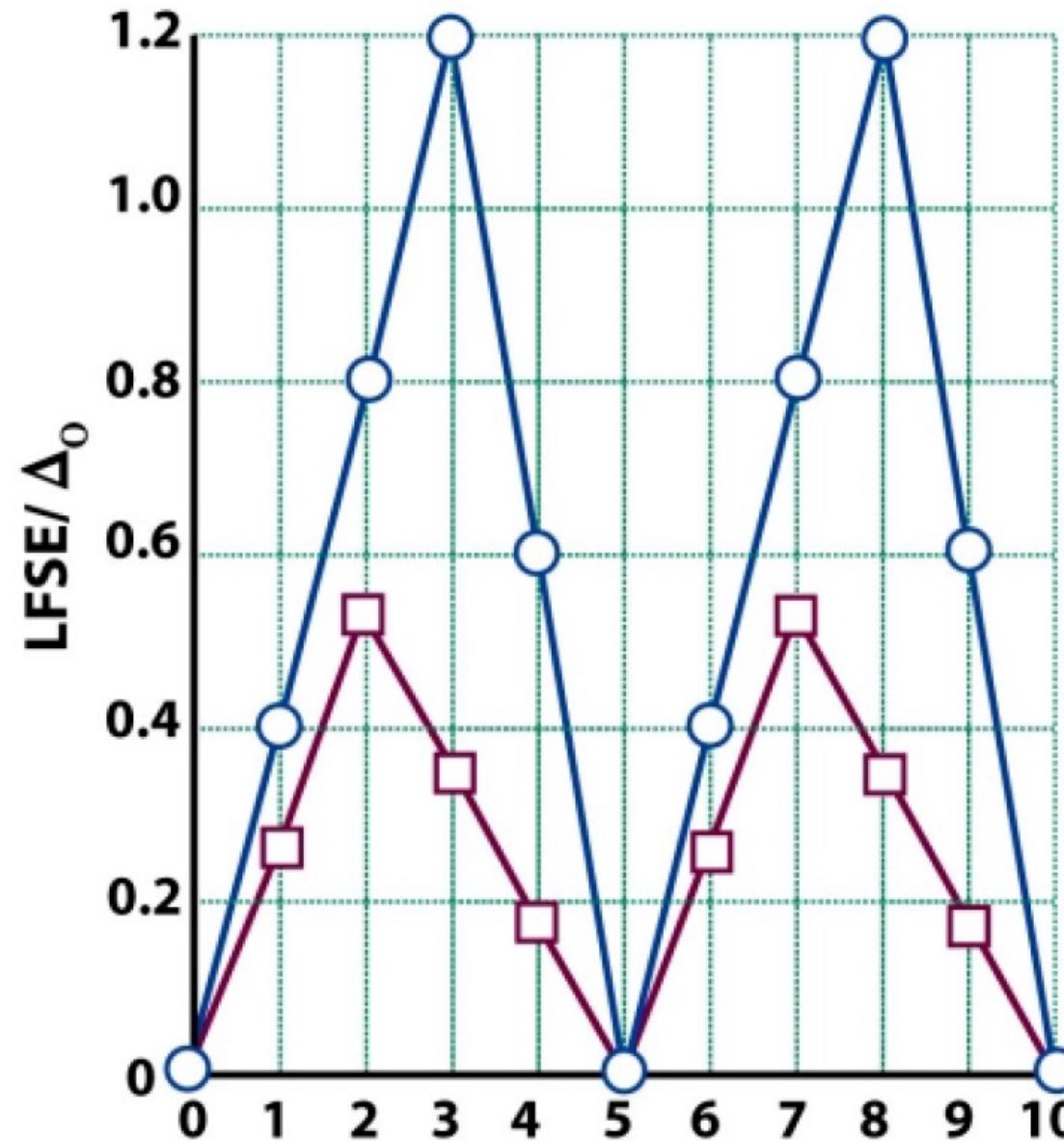
$[\text{CoI}_4]^{2-}$	2700
$[\text{Co(NCS)}_4]^{2-}$	4700

Table 19.2 Ligand-field stabilization energies*

d^n	Example	Octahedral			Tetrahedral			
		N	LFSE		N	LFSE		
d^0		0	0		0	0		
d^1	Ti ³⁺	1	0.4		1	0.6		
d^2	V ³⁺	2	0.8		2	1.2		
d^3	Cr ³⁺ , V ²⁺	3	1.2		3	0.8		
		Strong-field		Weak-field				
d^4	Cr ²⁺ , Mn ³⁺	2	1.6		4	0.6	4	0.4
d^5	Mn ²⁺ , Fe ³⁺	1	2.0		5	0	5	0
d^6	Fe ²⁺ , Co ³⁺	0	2.4		4	0.4	4	0.6
d^7	Co ²⁺	1	1.8		3	0.8	3	1.2
d^8	Ni ²⁺		2	1.2			2	0.8
d^9	Cu ²⁺		1	0.6			1	0.4
d^{10}	Cu ⁺ , Zn ²⁺	0	0		0	0		

* N is the number of unpaired electrons; LFSE is in units of Δ_0 for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx 0.45\Delta_0$.

O_h vs. T_d CFSE



Application of CFSE: Determination of Spinels Structures

Spinel is the name given to the mineral MgAl_2O_4 .

It has a common structural arrangement shared by many oxides of the transition metals with formula AB_2O_4 .

In the **normal spinel**

The oxygens form a cubic close packed array

The Mg(II) (A-type) sit in tetrahedral sites

The Al(III) (B-type) sit in octahedral sites



An **inverse spinel** is an alternative arrangement where half of the trivalent ions swap with the divalent ions so that the Mg(II) now occupy octahedral sites ie $\text{B}(\text{AB})\text{O}_4$.



Spinels- Use of CFSE

There are several transition metal oxides which have the formula AB_2O_4 and crystallize in spinel or inverse spinel structure. E.g. $FeCr_2O_4$, $ZnAl_2O_4$, Co_3O_4 , Mn_3O_4 , Fe_3O_4 , $NiFe_2O_4$ etc.

CFSE is highly useful to determine whether a structure would be normal or inverse

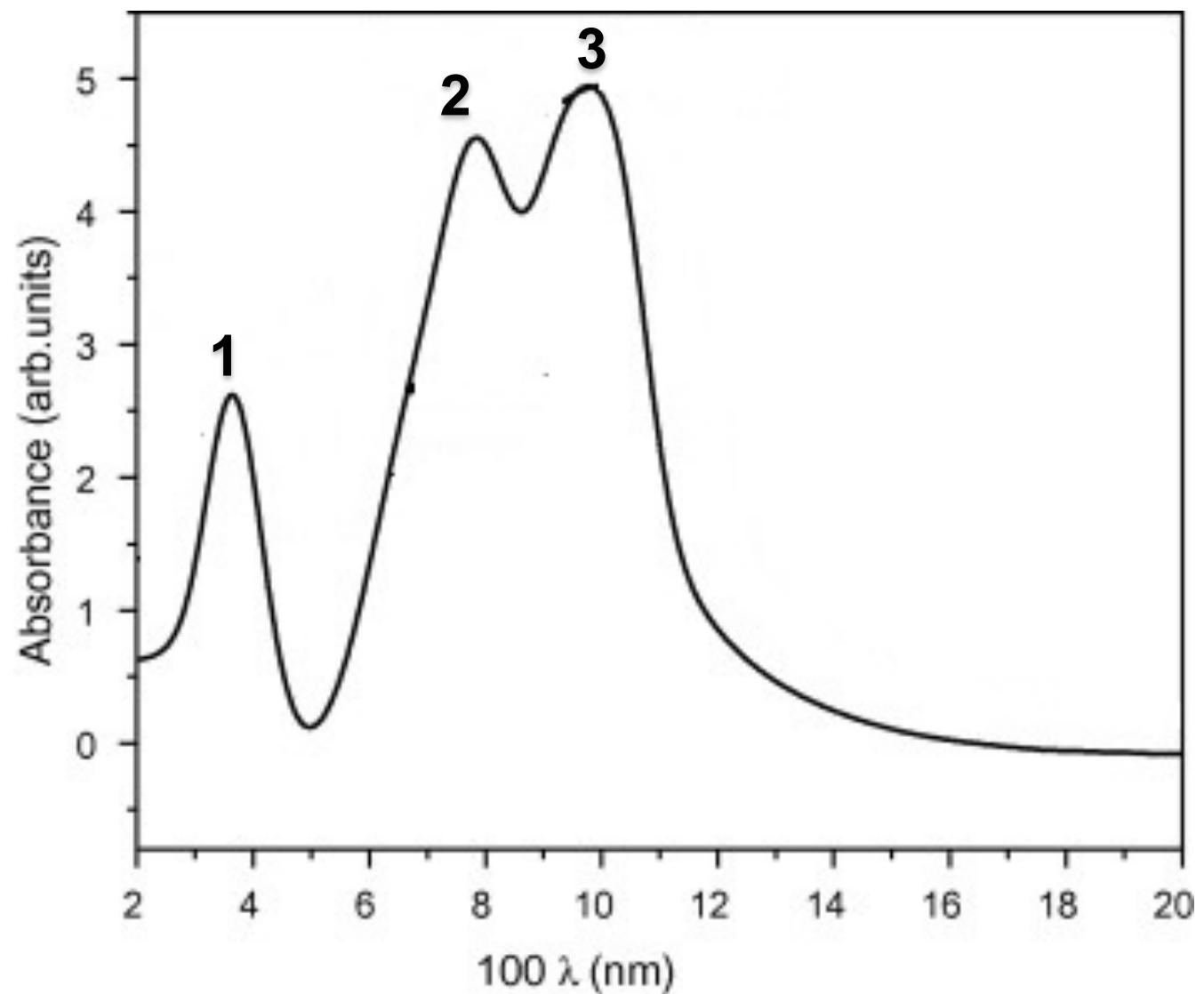
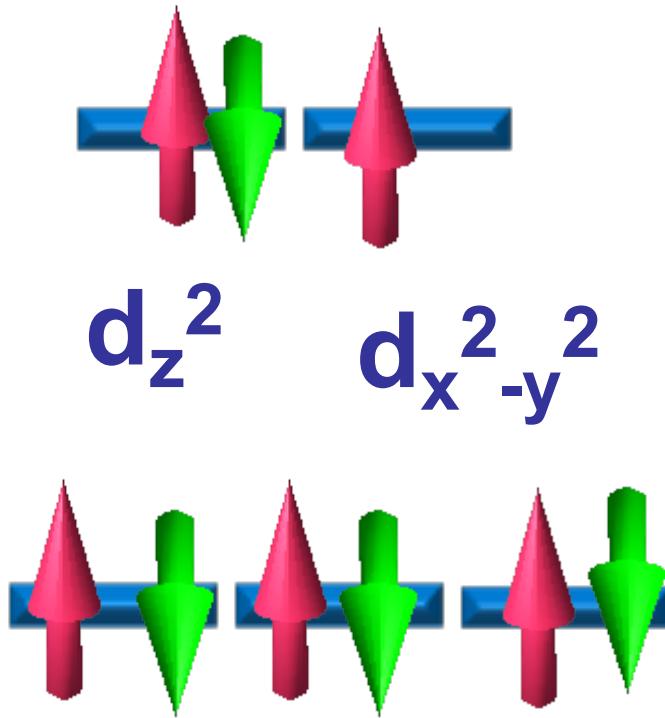
If M^{3+} ion has a higher CFSE in an octahedral field compared to M^{2+} ion, **normal spinel** will result.

If M^{2+} ion has a higher CFSE in an octahedral field compared to M^{3+} ion, **inverse spinel** will result.

normal $[M^{II}]_{\text{tet}}[M^{III}M^{III}]_{\text{oh}}O_4$; **inverse** $[M^{III}]_{\text{tet}}[M^{II}M^{III}]_{\text{oh}}O_4$

Absorption spectra of d⁹ octahedral complexes

Can we explain this?

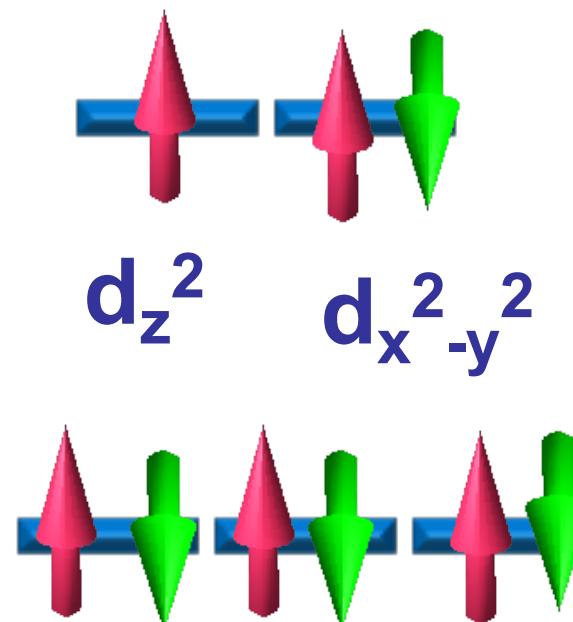
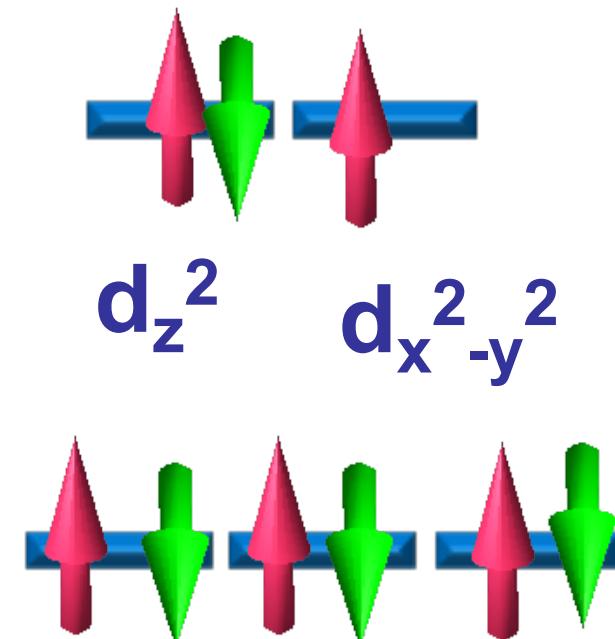


Case of degeneracy: Jahn-Teller distortion

Jahn-Teller Distortion:

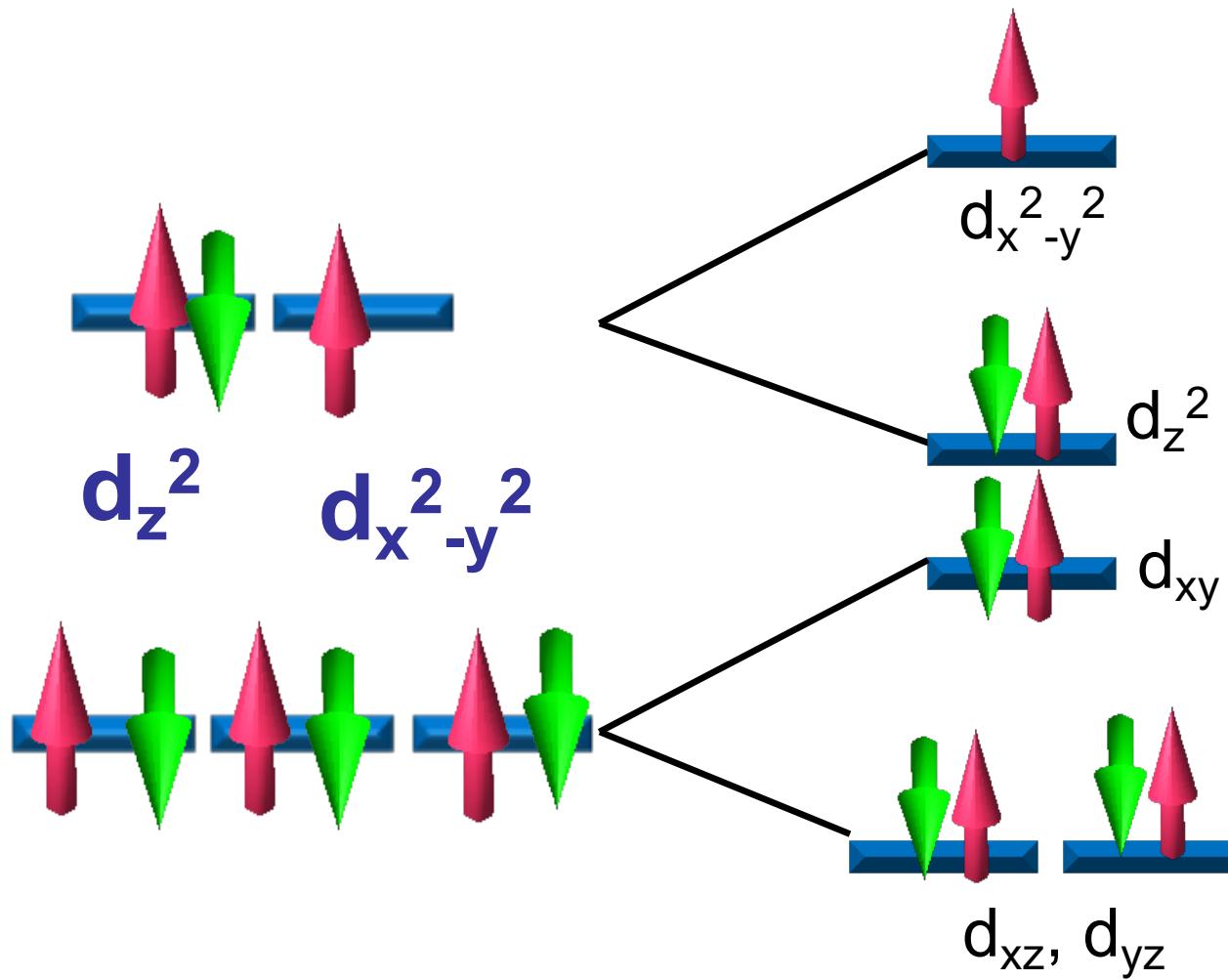
Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy.

Example: Cu(II) Oh complex – d⁹ configuration



Degenerate electronic state: Complex undergoes distortion

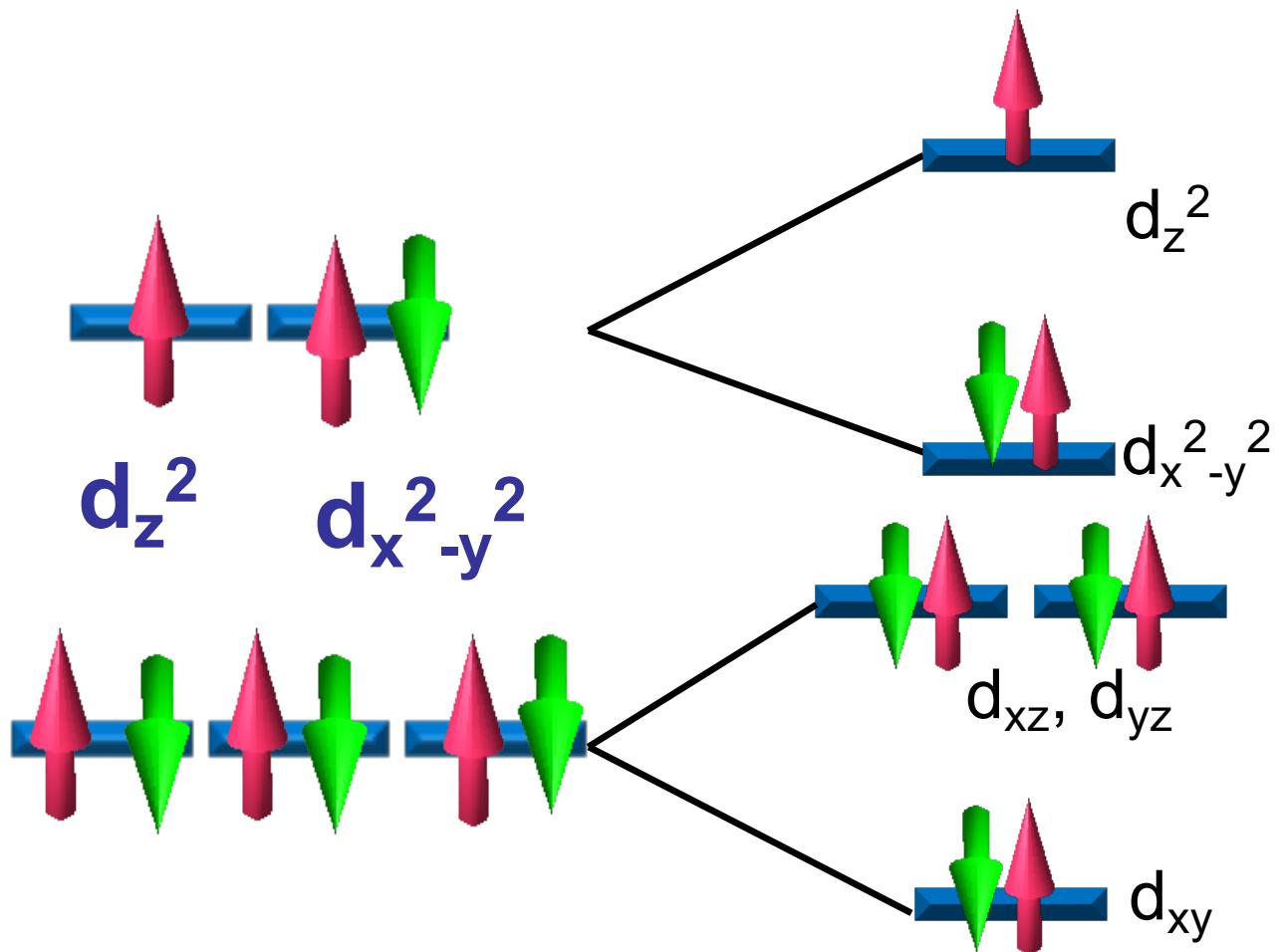
Axial elongation: Jahn-Teller distortion



As ligands approached along the axis in O_h

- ❖ The ligands can not approach Cu(II) ion closely along z-axis because d_z^2 orbital contains two electron (i.e. due to the ligand e^- and metal e^- repulsion), hence stabilized
- ❖ While along xy plane ligands can approach towards Cu(II) ion much more closer than the z-axis, since $d_{x^2-y^2}^2$ orbital consists of only one unpaired electron. Therefore, destabilized.
- ❖ Distortion felt even in t_{2g} orbitals, where all the z-component of the orbitals (d_{xz} and d_{yz}) stabilized since ligands along z-axis do not come closer to the Cu(II) ion.
- ❖ Consequently Cu(II)-L bond lengths along z-axis is longer than Cu(II)-L bond lengths along xy-plane (i.e. axially elongated or tetragonal elongation geometry around Cu(II) ion).

Axial compression: Jahn-Teller distortion

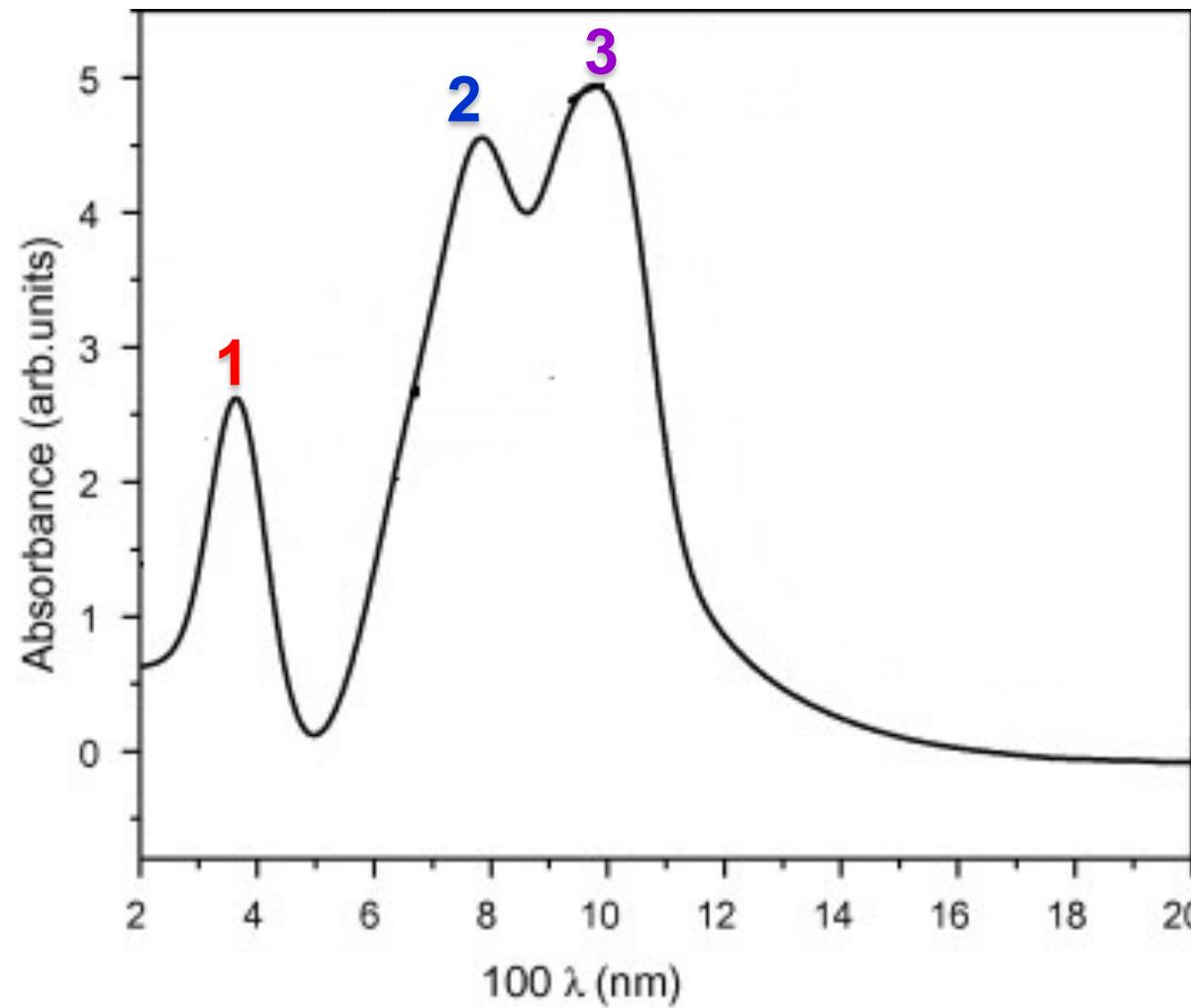
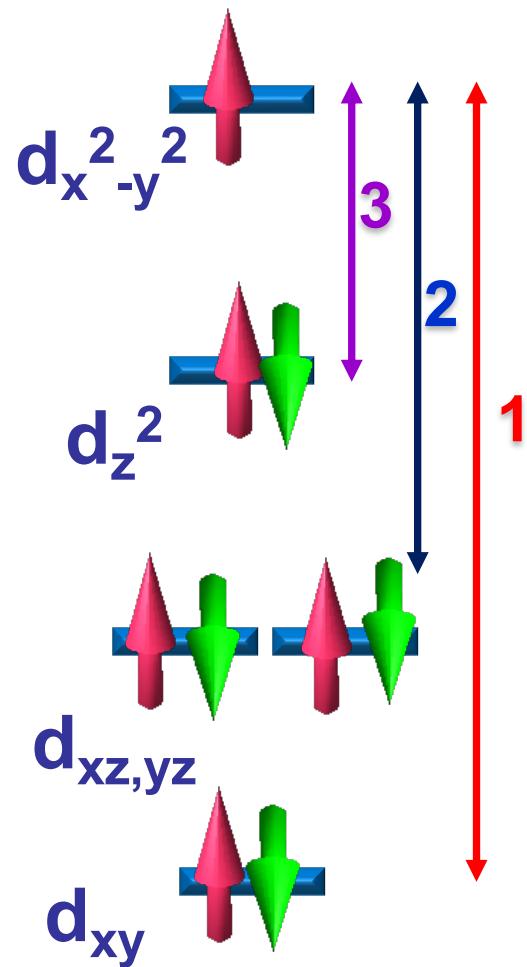


As ligands approached along the axis in O_h

- ❖ The ligands can not approach $\text{Cu}(\text{II})$ ion closely along xy -plane because $d_{x^2-y^2}$ orbital contains two electron (i.e. due to the ligand e^- and metal e^- repulsion)
- ❖ While along d_{z^2} axis ligands can approach toward $\text{Cu}(\text{II})$ ion much more closer than the xy -plane, since d_{z^2} orbital consists of only one unpaired electron.
- ❖ Distortion felt in t_{2g} orbitals as well, where all z-component of the orbitals (d_{xz} and d_{yz}) destabilized since ligands along z-axis come closer to metal ion.
- ❖ Consequently $\text{Cu}(\text{II})$ -L bond lengths along z-axis is shorter than $\text{Cu}(\text{II})$ -L bond lengths along xy -plane (i.e. axially compressed or tetragonal compression geometry around $\text{Cu}(\text{II})$ ion).

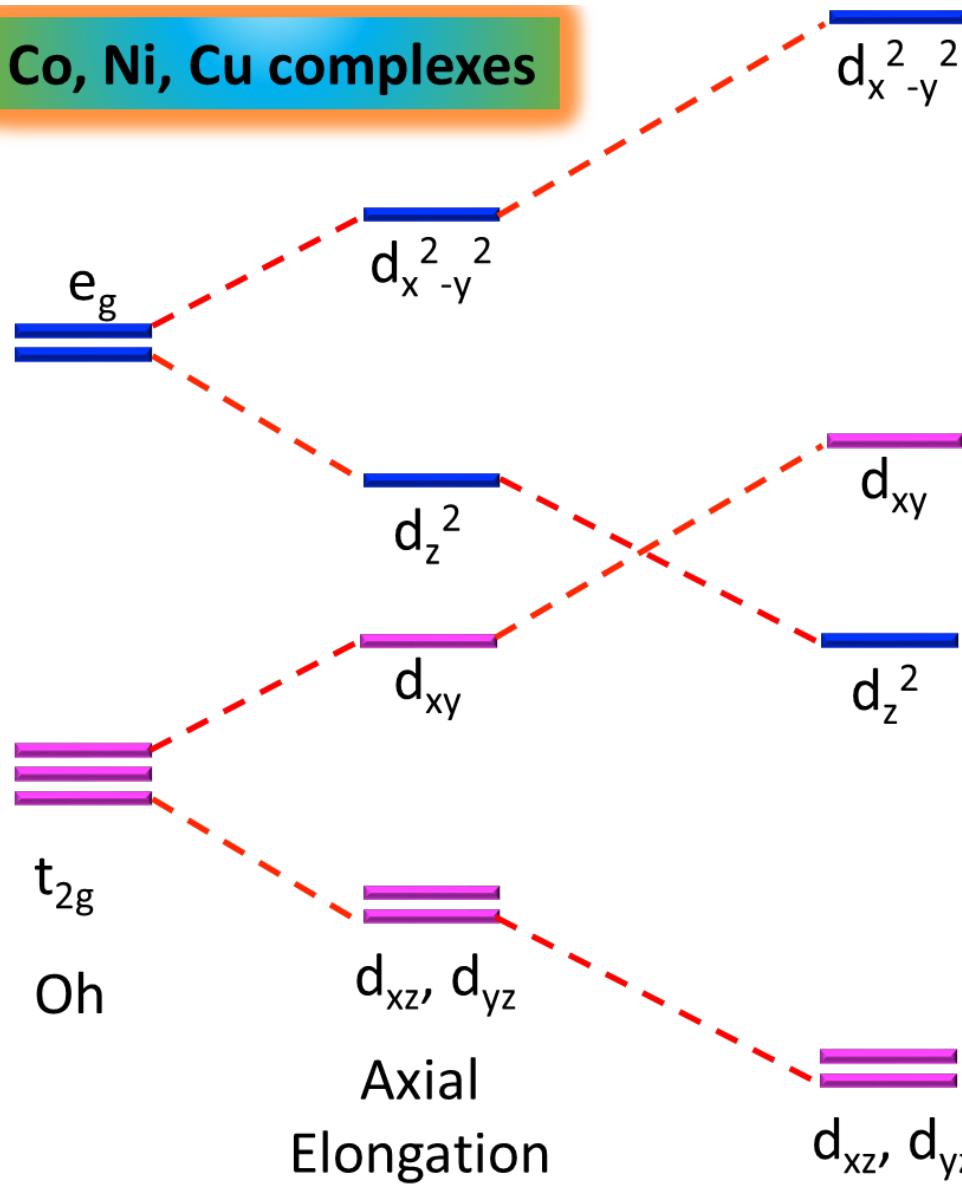
Absorption spectra of d⁹ octahedral complexes

Rationale for 3 transitions!

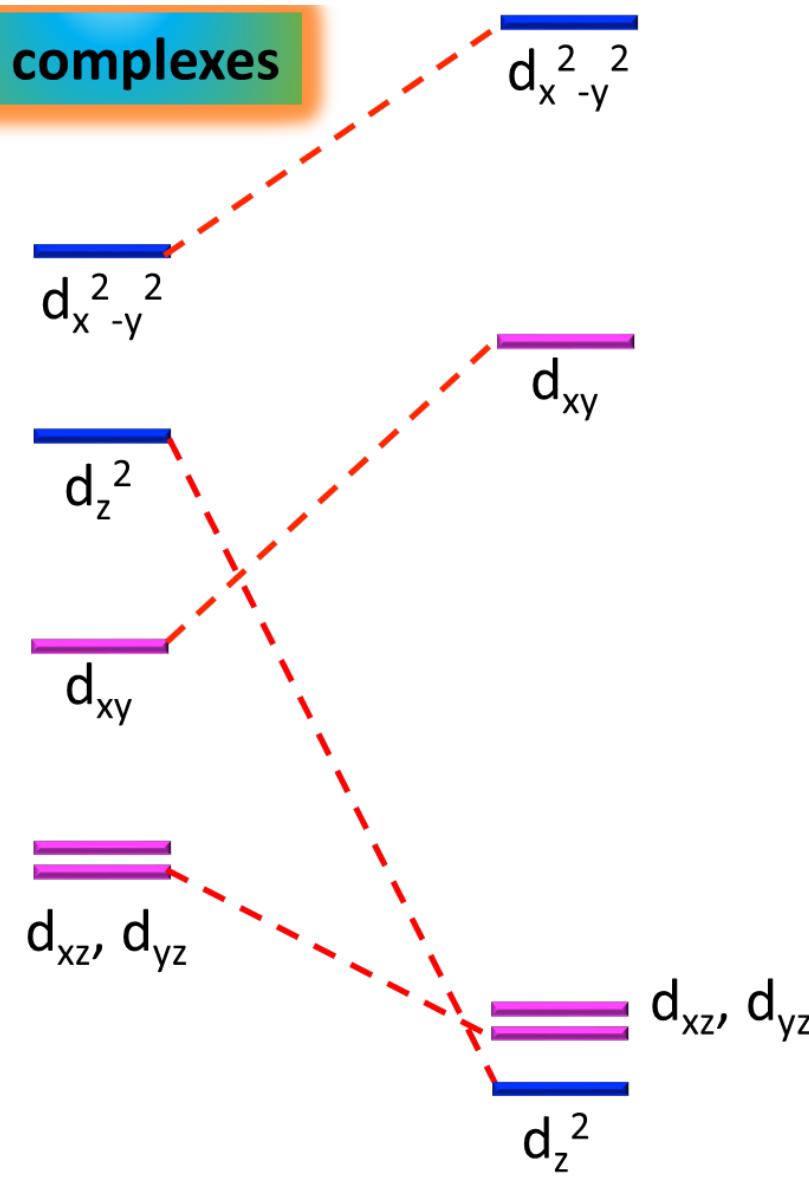


Crystal field splitting for square planar complexes

Co, Ni, Cu complexes



Pt complexes

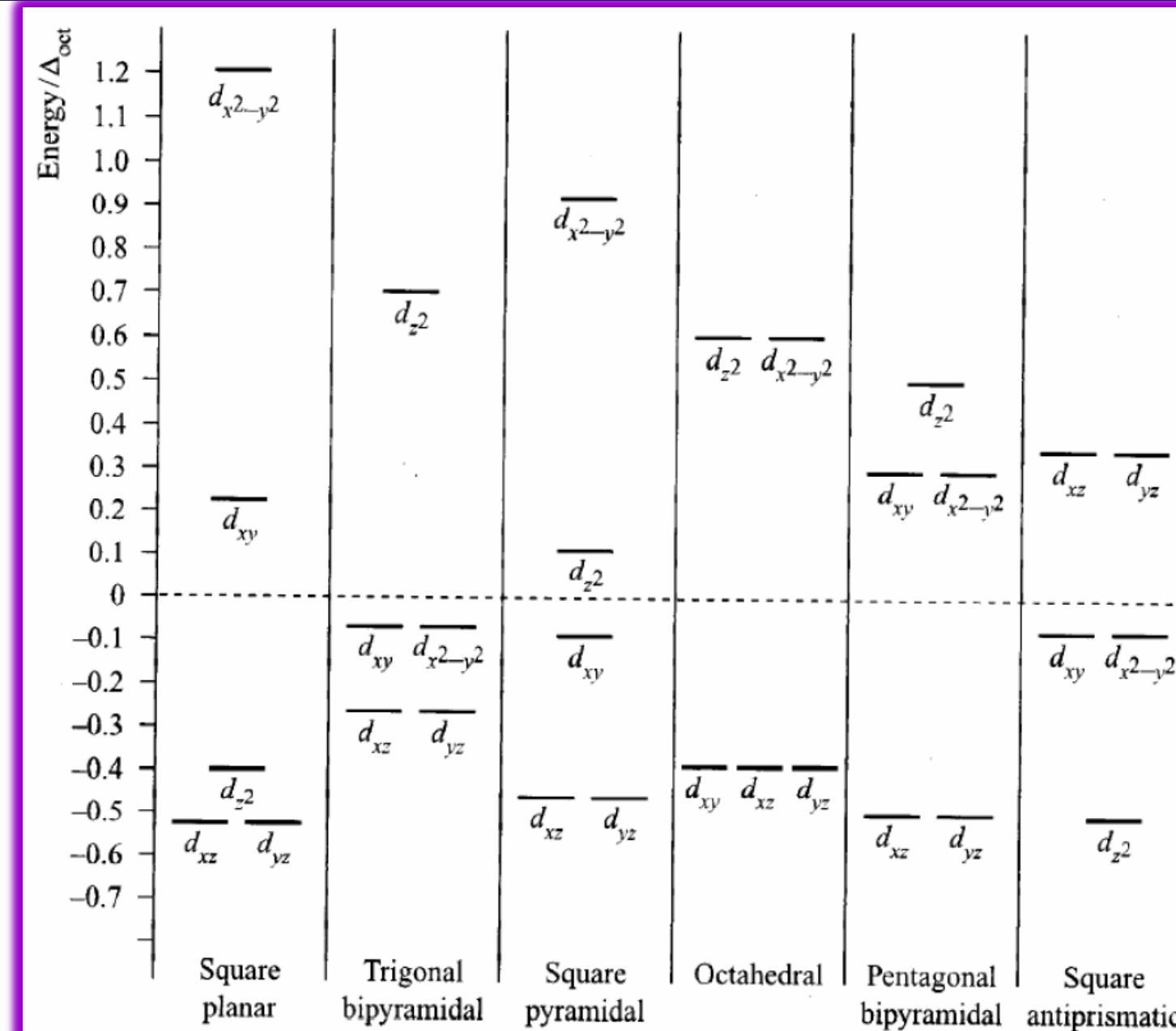


Examples:

Elongation

Ni^{2+} , Pd^{2+} , Pt^{2+} , Cu^{3+} , Ag^{3+} , Au^{3+}

Crystal field splitting for other geometries

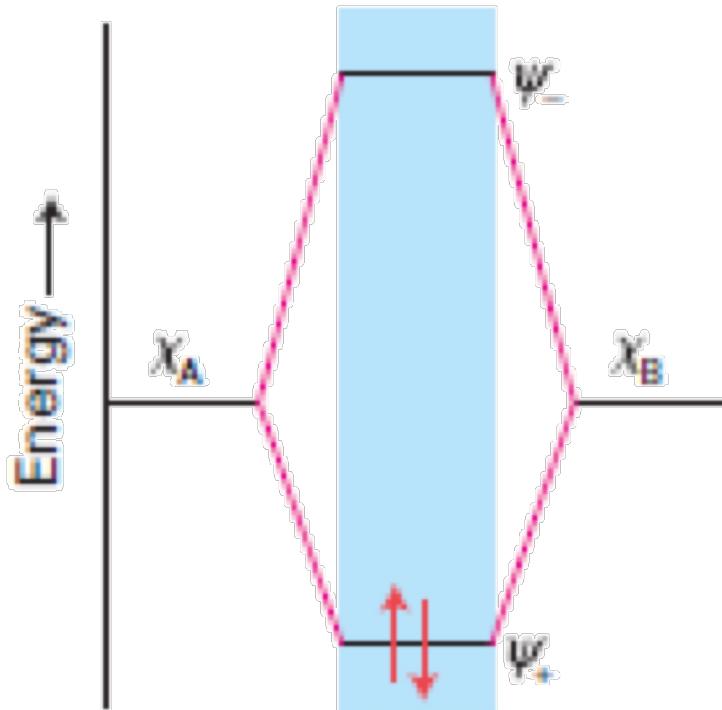


Limitation of CFT

- ✓ The ligand spectrochemical series was not explained by CFT
- ✓ CFT could not account for the M-L covalancy

Ligand Field Theory (Molecular Orbital Theory)

The building up principle is used in conjunction with a **molecular orbital energy level** constructed from **metal orbital** and **Linear Combinations** of ligand orbitals



Schematic representation of molecular orbital construction using the linear combination of atomic orbitals (χ_A and χ_B)

Linear combination of atomic orbitals (LCAO)

LCAO:

This modelling of a molecular orbital in terms of contributing atomic orbitals is called the linear combination of atomic orbitals (LCAO) approximation i.e. **only the valence shell atomic orbitals are used to form molecular orbitals.**

Simple example: Molecular orbitals of H_2 molecule

$$\Psi = c_A \chi_A + c_B \chi_B$$

Where

χ_A = Hydrogen atomic orbital ($1s$) of atom A

χ_B = Hydrogen atomic orbital ($1s$) of atom B

c = Coefficient in the linear combination extent to which each atomic orbital contributes to molecular orbital

- ❖ Greater the c value, greater the contribution of atomic orbital to the molecular orbital

Bonding and Anti-bonding molecular orbital

$$\Psi = c_A \chi_A + c_B \chi_B$$

χ_A and χ_B in the above equation represent 1s orbital of hydrogen, both atomic orbitals contribute equally to the molecular orbital

Under this situation

$$\Psi_{\pm} = \chi_A \pm \chi_B$$

$\Psi_+ = \chi_A + \chi_B \Rightarrow$ **Constructive interference** of two atomic orbitals (**Energy of the molecule lowered compared to the atomic orbital**) (**Bonding MO**)

$\Psi_- = \chi_A - \chi_B =$ **Destructive interference** of two atomic orbitals (**Energy of the molecule increased compared to the atomic orbital**) (**Antibonding MO**)

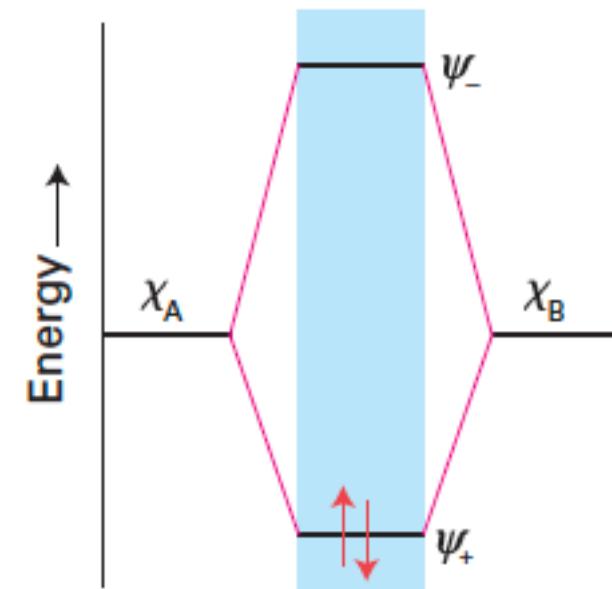


Fig. 2.10 The molecular orbital energy level diagram for H_2 and analogous molecules.

Non-Bonding orbital

Nonbonding molecular orbital

It is a molecular orbital that has the same energy as the initial atomic orbitals. In this case, occupation of this orbital neither stabilizes nor destabilizes the molecule and so it is described as a **nonbonding orbital**.

σ and π Orbital

Molecular orbitals are classified as σ or π according to their rotational symmetry about the internuclear axis, and (in centrosymmetric species) as g or u according to their symmetry with respect to inversion.

σ and π Orbital

σ Orbital

σ orbitals formed by allowing overlap between atomic orbitals that have cylindrical symmetry around the internuclear axis, which is conventionally labelled z.

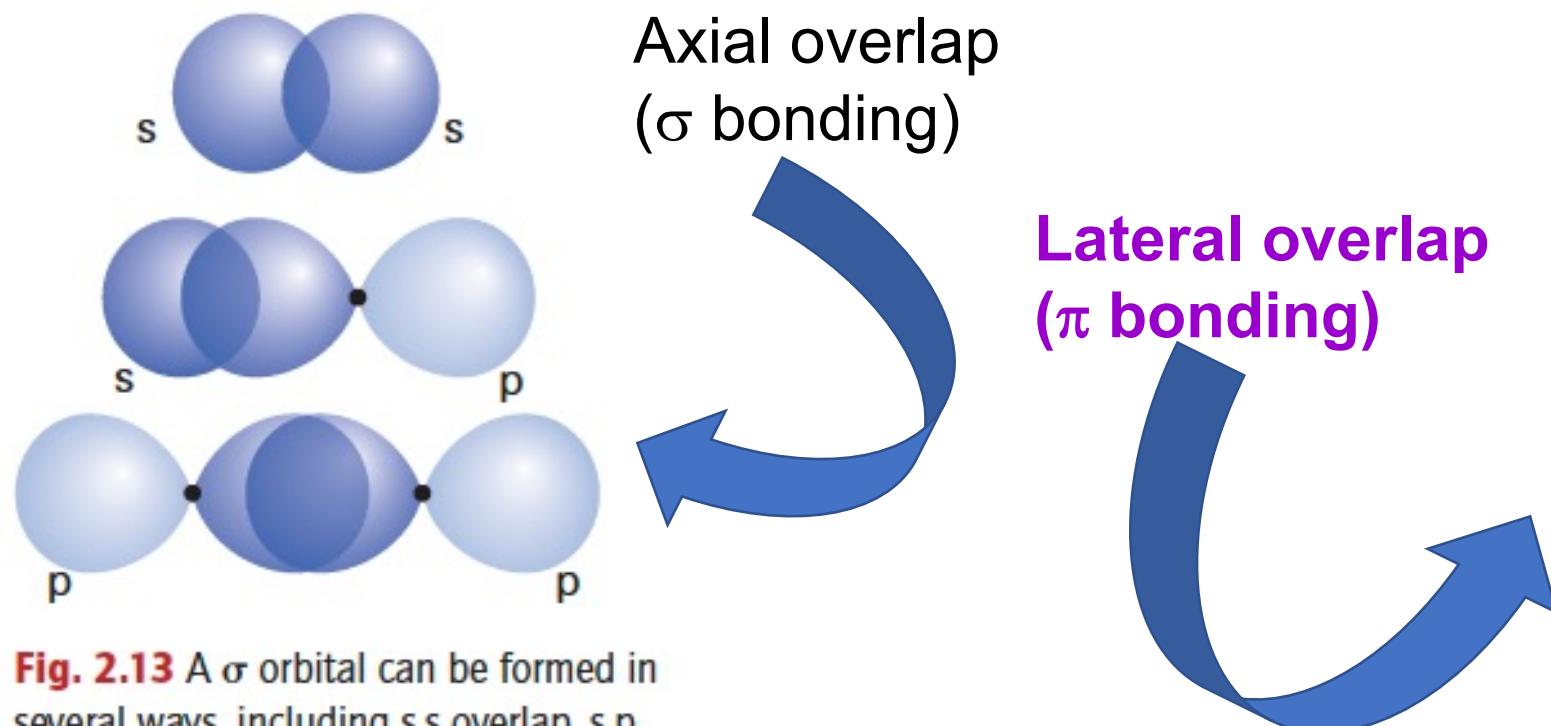


Fig. 2.13 A σ orbital can be formed in several ways, including s,s overlap, s,p overlap, and p,p overlap, with the p orbitals directed along the internuclear axis.

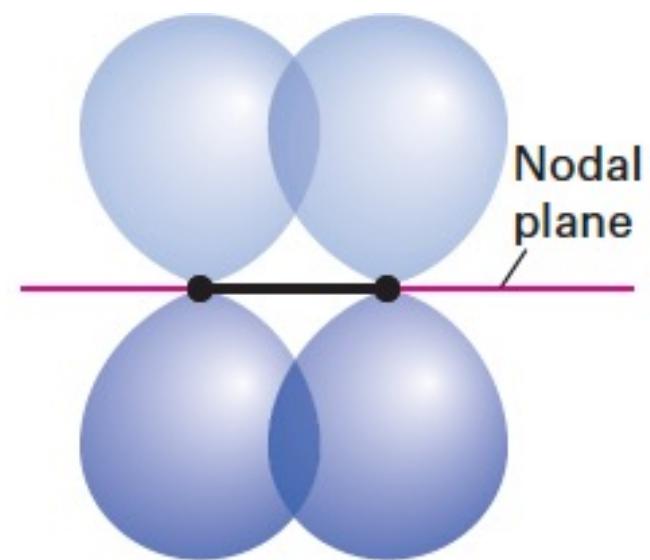


Fig. 2.14 Two p orbitals can overlap to form a π orbital. The orbital has a nodal plane passing through the internuclear axis, shown here from the side.

g and u formalism (with respect to inversion symmetry)

The operation of inversion consists of starting at an arbitrary point in the molecule, travelling in a straight line to the centre of the molecule, and then continuing an equal distance out on the other side of the centre. This procedure is indicated by the arrows in Figs 2.15 and 2.16. The orbital is designated g (for gerade, even) if it is identical under inversion, and u (for ungerade, odd) if it changes sign.

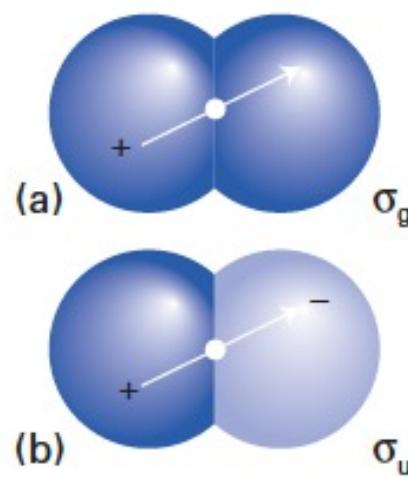


Fig 2.15 (a) Bonding and (b) antibonding σ interactions with the arrow indicating the inversions.

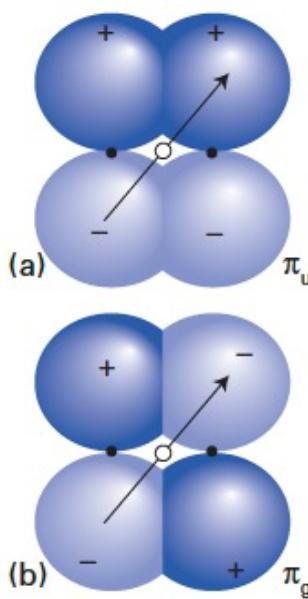
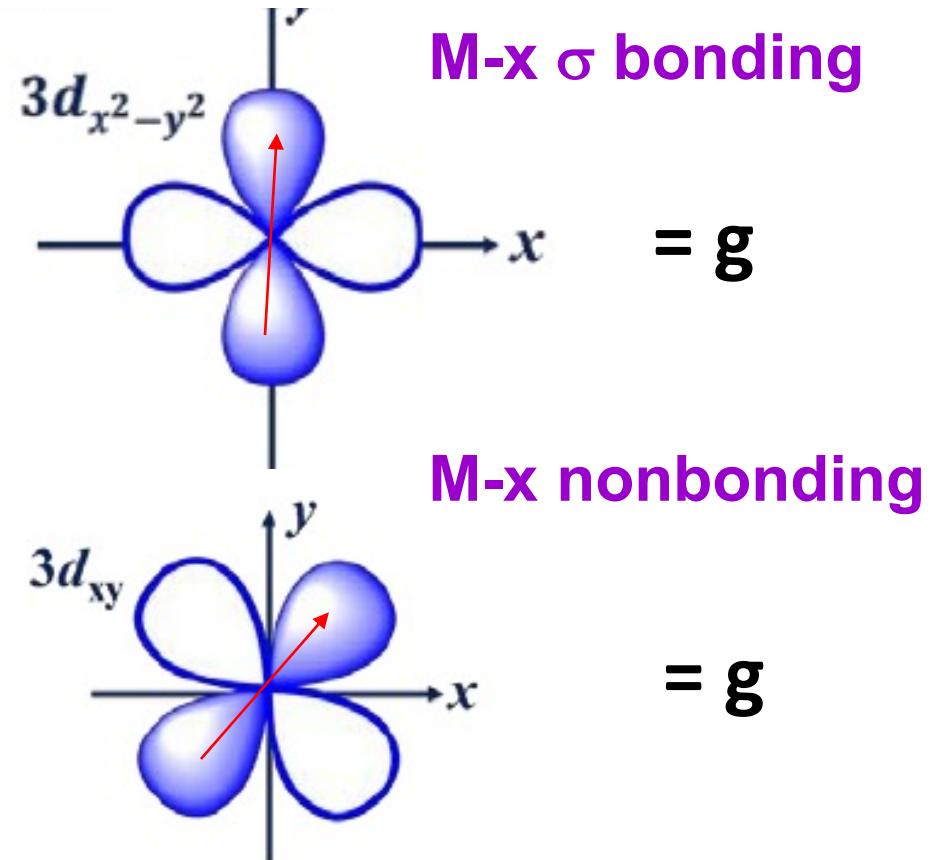


Fig 2.16 (a) Bonding and (b) antibonding π interactions with the arrow indicating the inversions.



Molecular Orbital of heterodiatomic molecule

The molecular orbitals of heteronuclear diatomic molecules differ from those of homonuclear diatomic molecules in having unequal contributions from each atomic orbital.

$$\psi = c_A \chi_A + c_B \chi_B \quad \text{But } c_A^2 > c_B^2 \text{ OR } c_A^2 < c_B^2$$

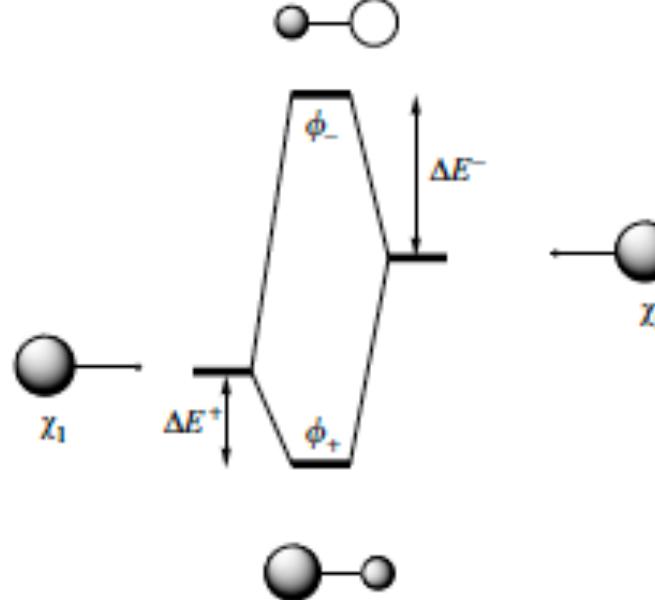


Figure 1.2. Interaction diagram for two orbitals with different energies.

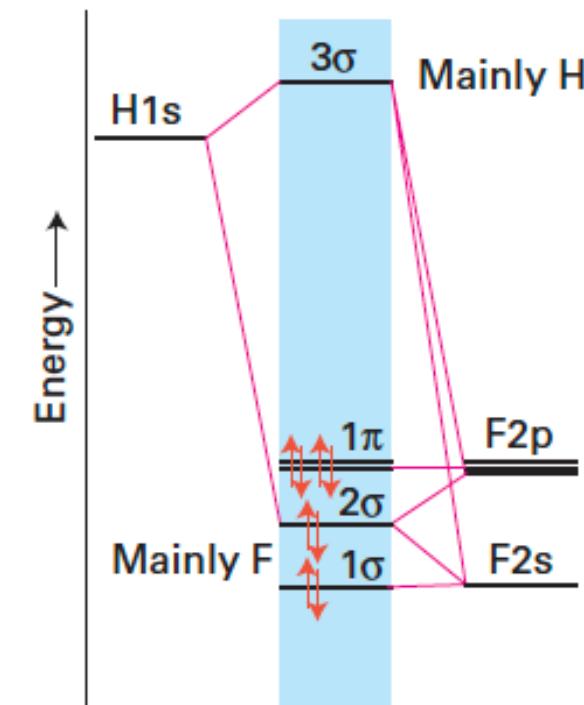


Fig. 2.21 The molecular orbital energy level diagram for HF. The relative positions of the atomic orbitals reflect the ionization energies of the atoms.

The 1σ bonding orbital is predominantly F2s in character as the energy difference between it and the H1s orbital is large. It is, therefore, confined mainly to the F atom and essentially nonbonding.

The 2σ orbital is more bonding than the 1σ orbital and has both H1s and F2p character.

The 3σ orbital is antibonding, and principally H1s in character: the 1s orbital has a relatively high energy (compared with the fluorine orbitals) and hence contributes predominantly to the high energy antibonding molecular orbital.

Take home message from the MO's of simple diatomic molecules

- ❖ MO's are constructed as linear combination of atomic orbitals (Valence orbitals)
- ❖ Each MO can accommodate maximum of two electrons (Pauli's exclusion principle and Hund's rule followed)
- ❖ From n-number atomic orbitals, n-number of molecular orbital can be constructed
- ❖ Electron filling up of MO's follows the same rules that are followed to fill the atomic orbitals (Hund's rule or building-up principle)

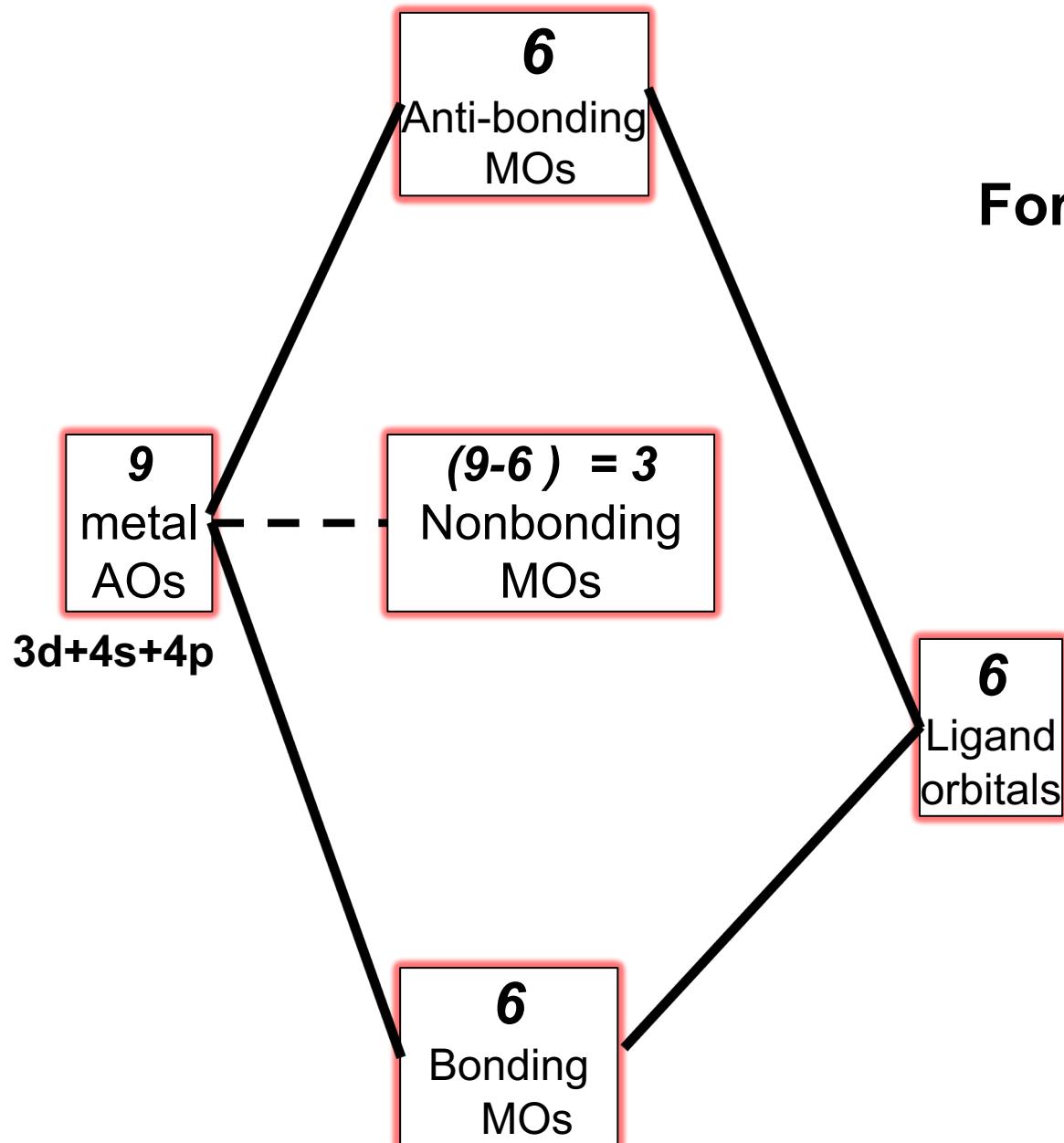
WE WILL EXTEND THESE PRINCIPLES TO EXPLAIN THE ELECTRONIC STRUCTURE AND BONDING OF THE ML_6 OCTAHEDRAL COMPLEXES

General consideration for constructing MO of ML_6 σ -bonding

To construct MO:

- ❖ Valence atomic orbitals of 3d metal ions are considered (3d, 4s and 4p orbitals)
- ❖ Specific combination of atomic orbitals of ligands are used to build MO's of a given symmetry (called Symmetry Adopted Linear Combination (SALC)). In simpler terms, ligand orbitals are placed in certain symmetry so as to have maximum overlap with metal atomic orbitals.
- ❖ Energetic of MO's based on the overlap (metal and ligand atomic orbitals)
- ❖ Filling up of electrons into the MO's

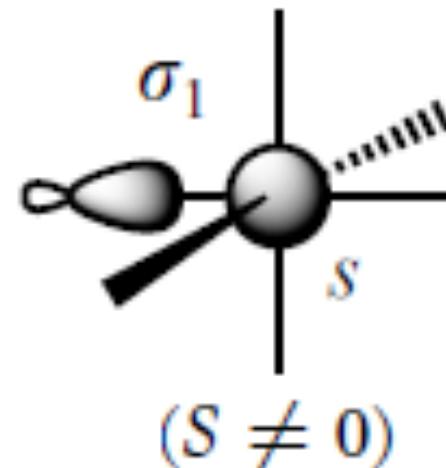
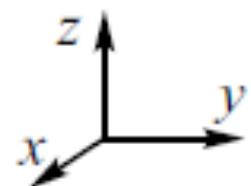
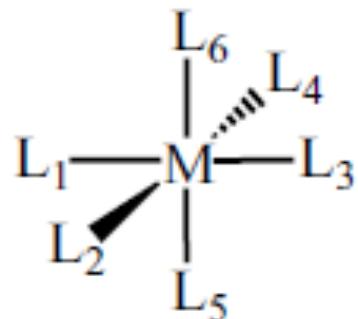
General interaction diagram (M-L₆ σ bonding)



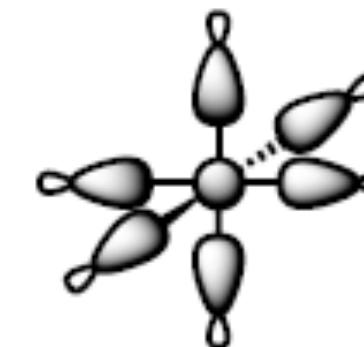
For stability, total number of electron desired is,

$$N_t = (2 \times 6) + 2 \times (9 - 6)$$
$$12 + 6 = 18 \text{ electrons}$$

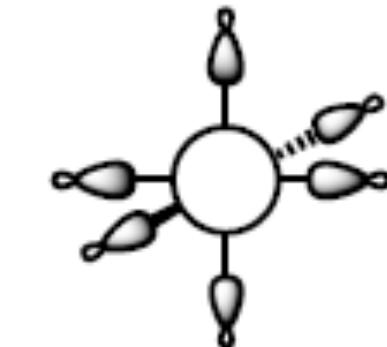
Metal-Ligand Combinations decided by overlap (S)



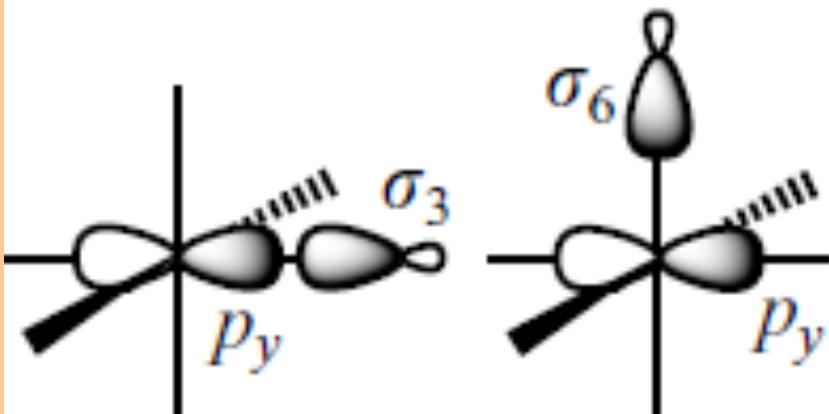
$(S \neq 0)$



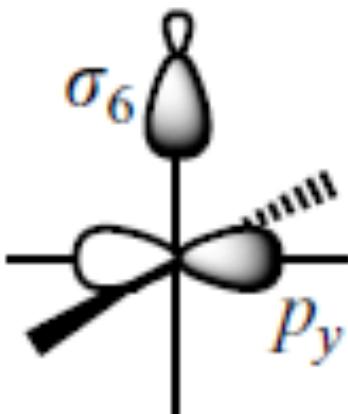
(bonding)



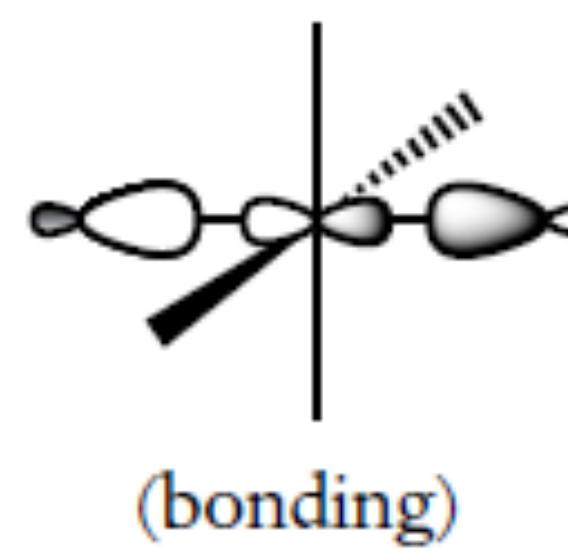
(antibonding)



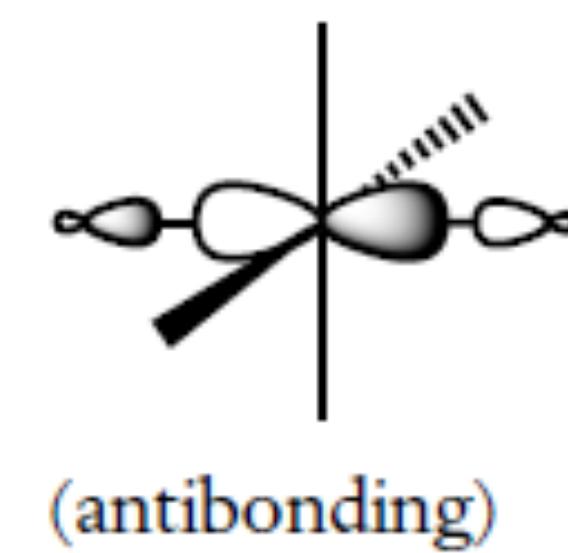
$(S \neq 0)$



$(S = 0)$

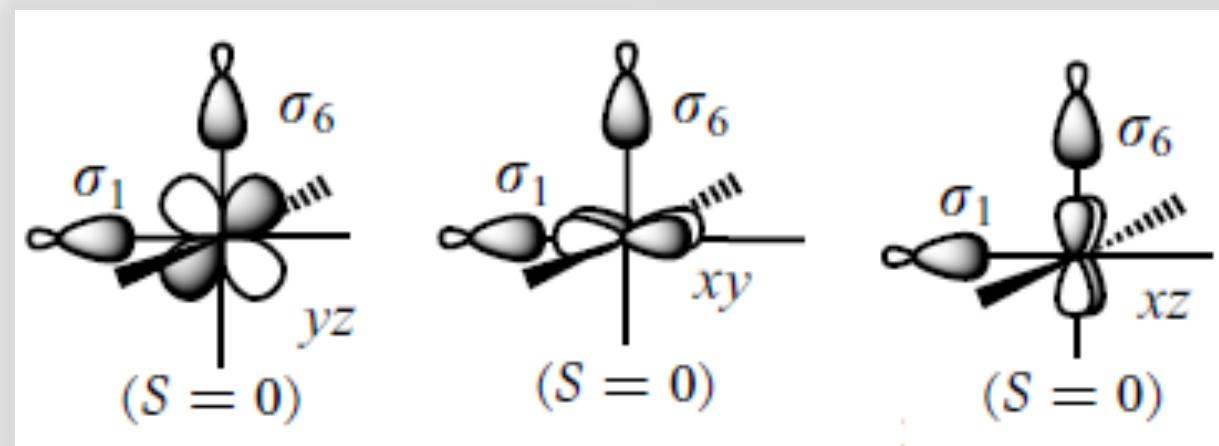
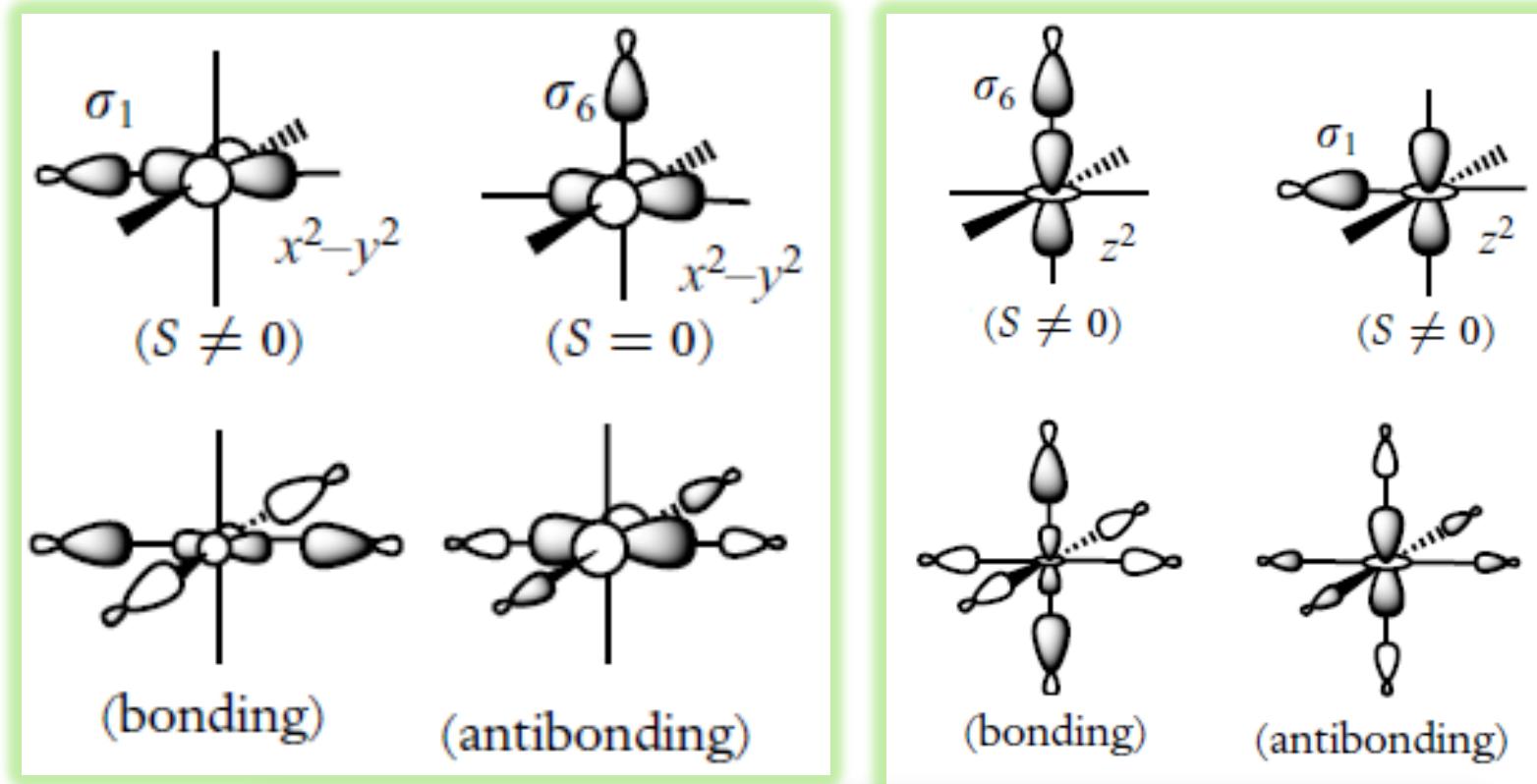


(bonding)



(antibonding)

Metal-Ligand Combinations decided by overlap (S)



M-L $\rightarrow \sigma$ -bonding

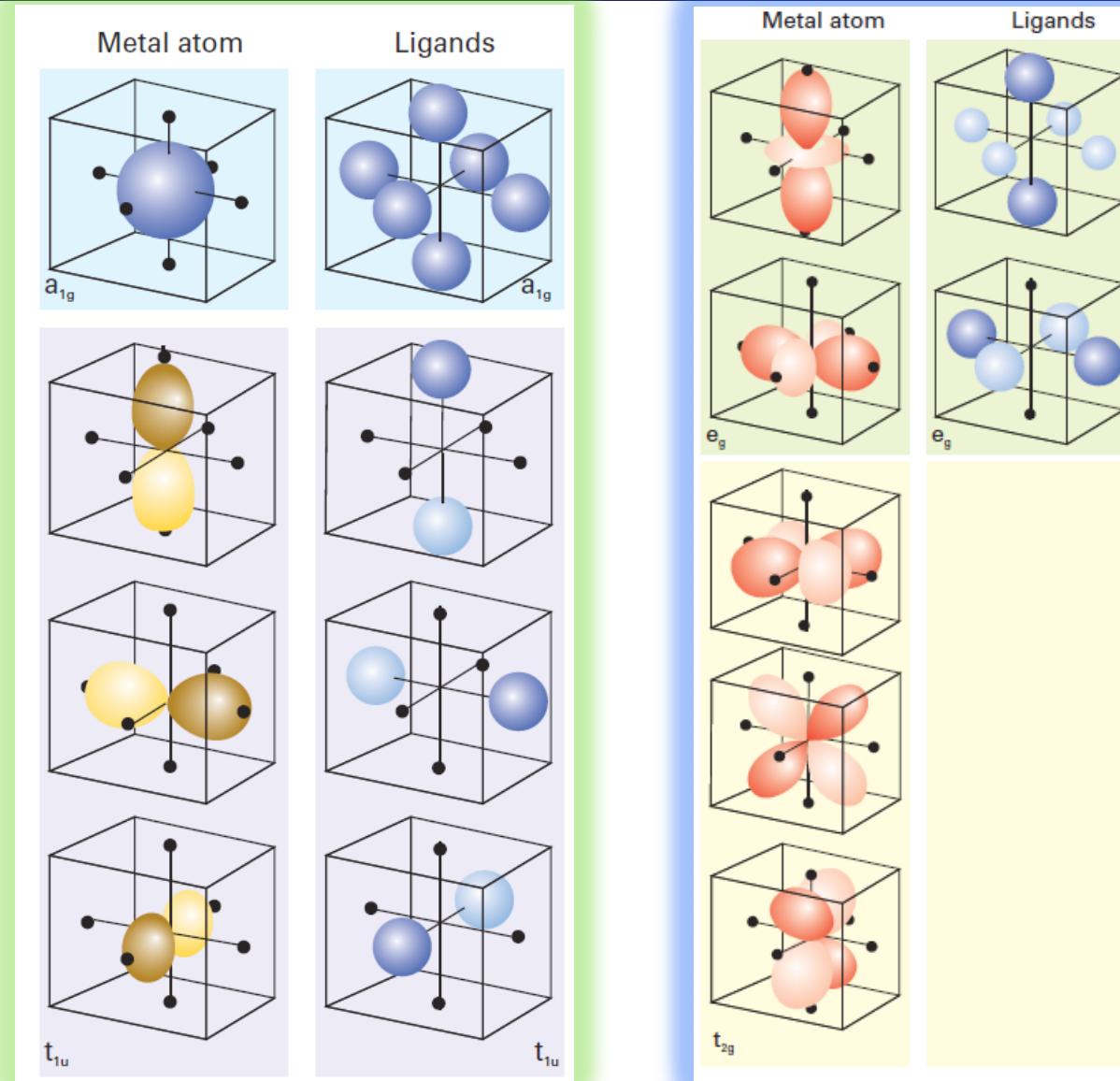
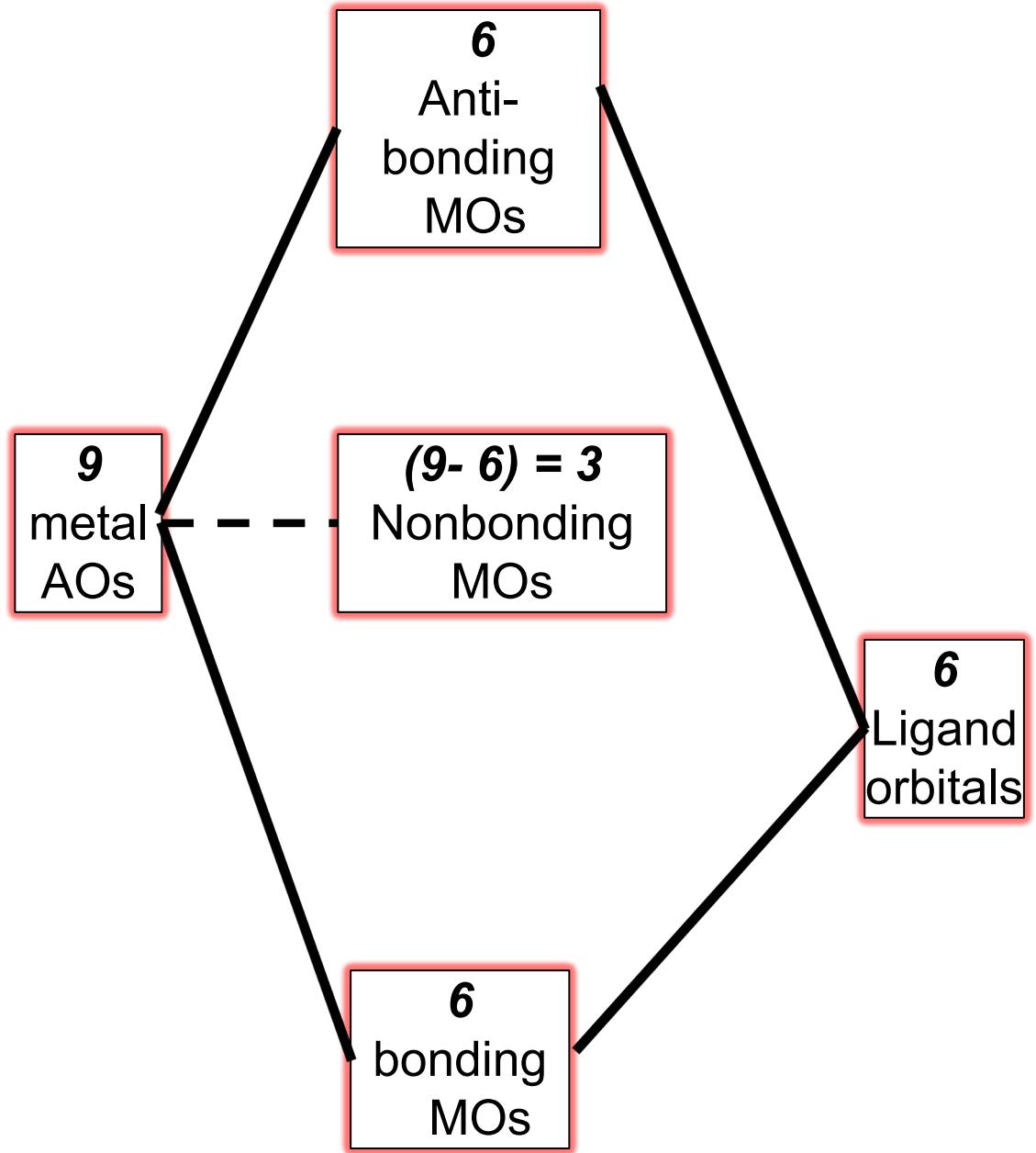


Figure 20.15 Symmetry-adapted combinations of ligand orbitals (represented here by spheres) in an octahedral complex. For symmetry-adapted orbitals in other point groups, see *Resource section 5*.



M-L \rightarrow σ -bonding

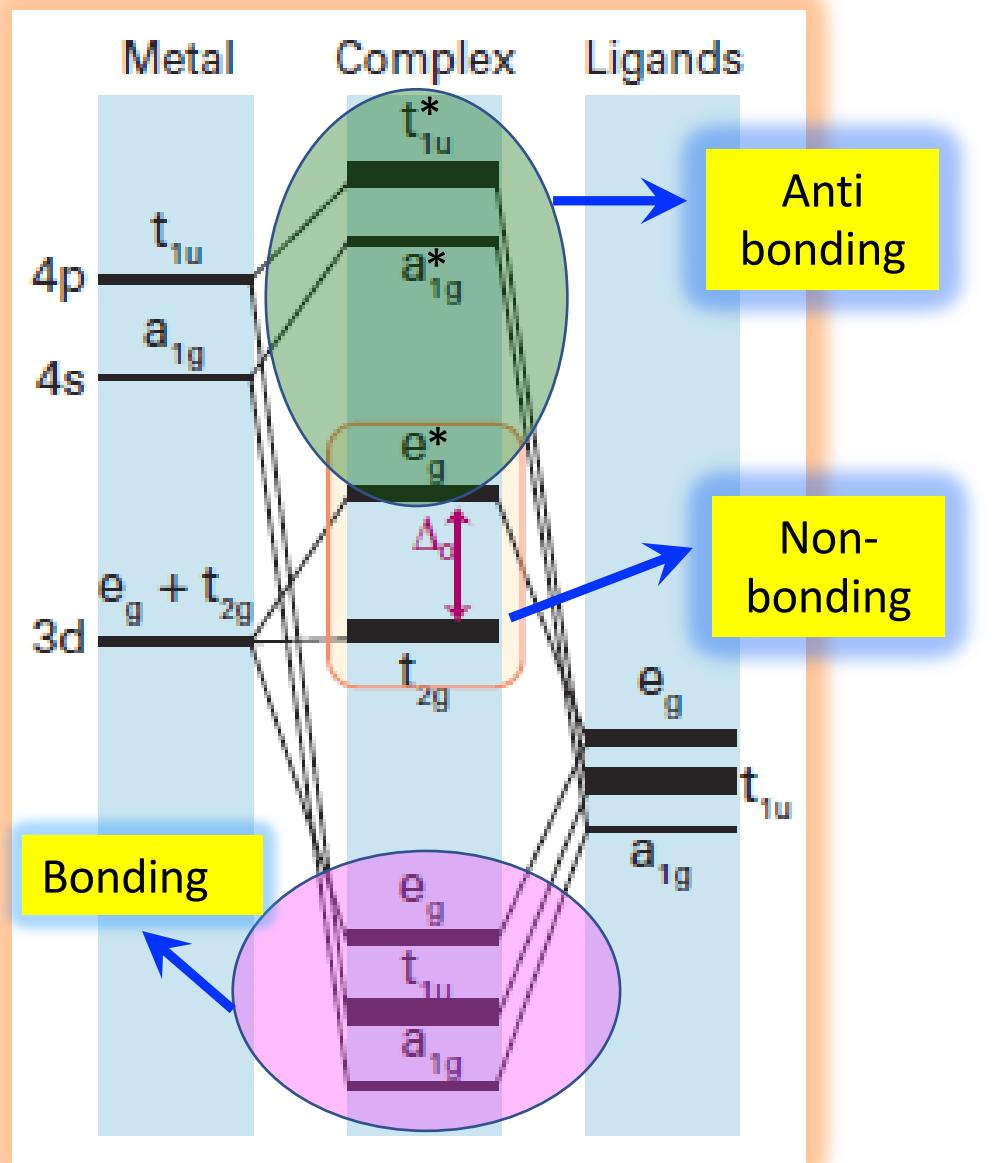
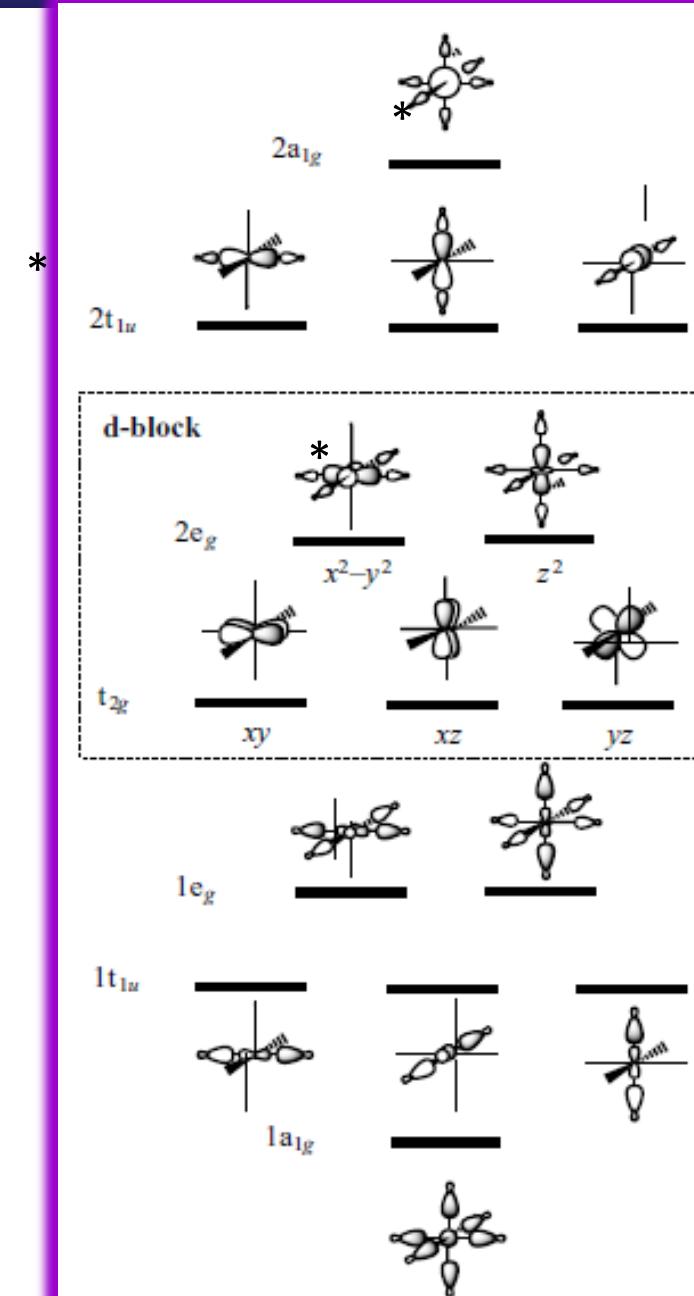
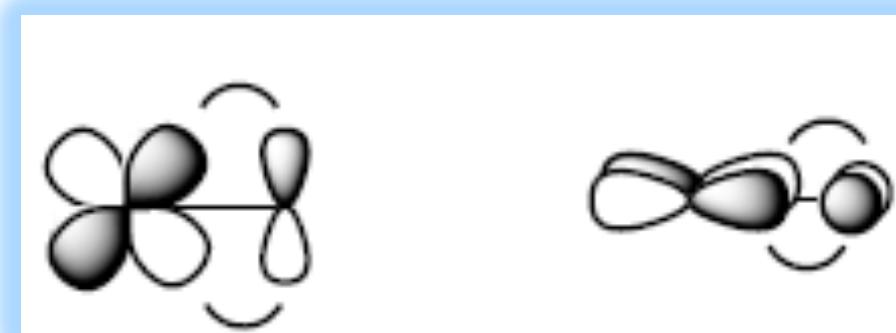
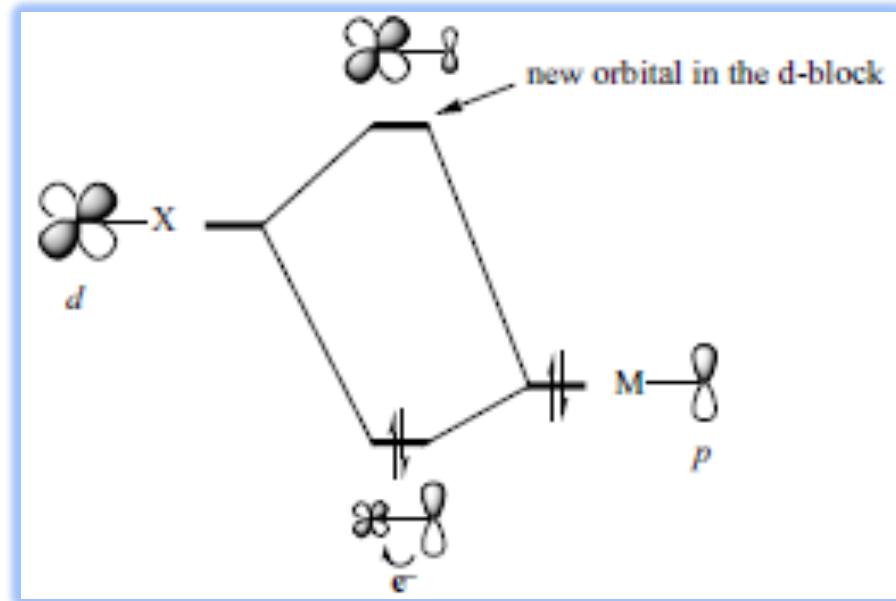


Figure 20.16 Molecular orbital energy levels of a typical octahedral complex. The frontier orbitals are inside the tinted box.



Influence of π -bonding on Non-bonding Orbital (t_{2g}) in O_h complexes

π -Donor ligands decrease Δ_o whereas π -acceptor ligands increase Δ_o ; the spectrochemical series is largely a consequence of the effects of π bonding when such bonding is feasible.



In O_h geometry: The non-bonding d-orbital (t_{2g}) will interact with the suitable ligand with π/π^* molecular orbital.

π -Donors decreases Δ_o

Example: $[ML_5Cl]$ with only one π -donor

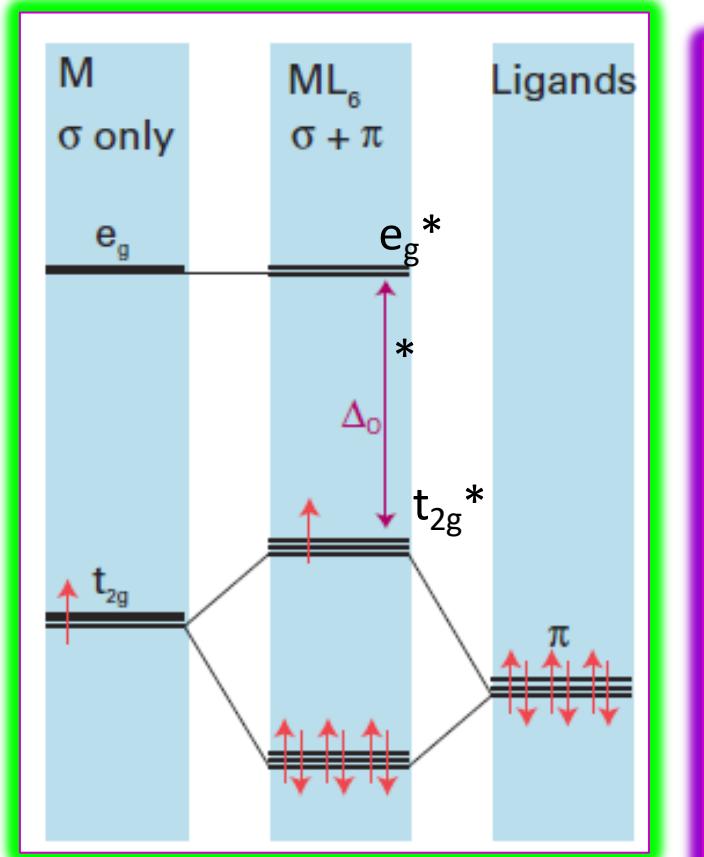
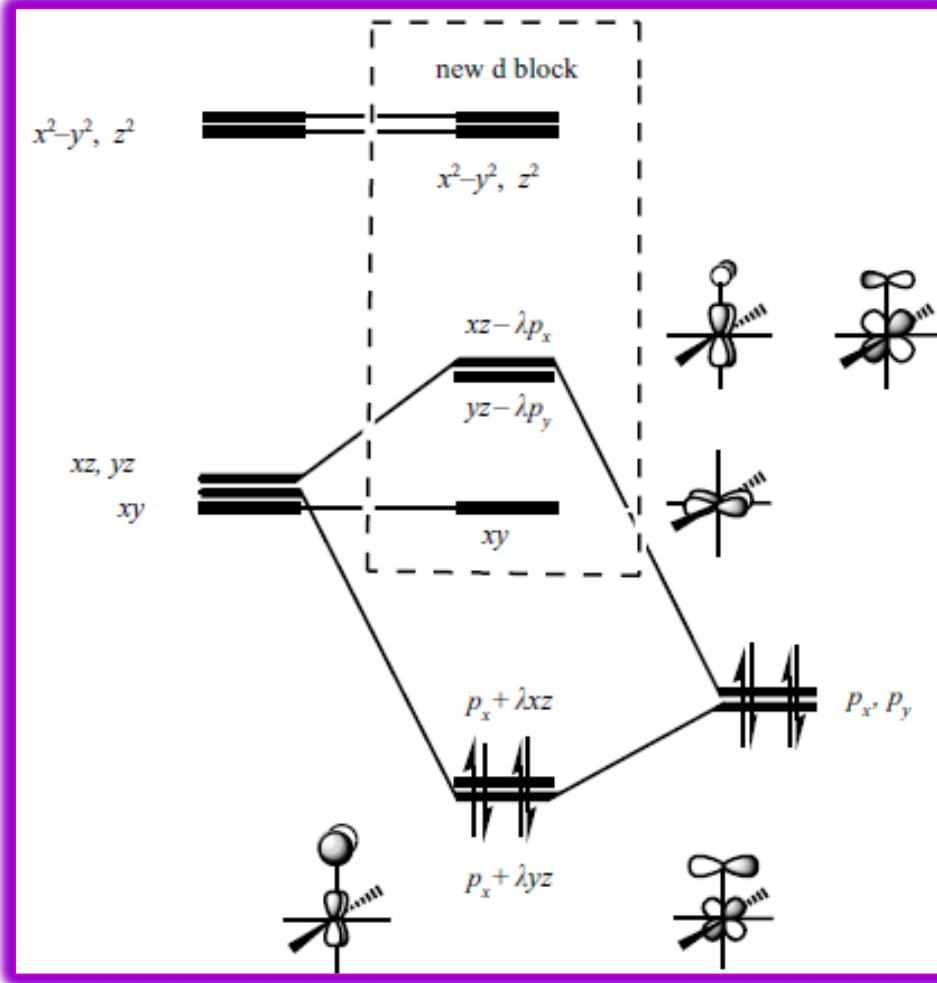


Figure 20.20 The effect of π -bonding on the ligand-field splitting parameter. Ligands that act as π donors decrease ΔO . Only the π orbitals of the ligand are shown.



- ❖ π - donor ligand (HOMO) of an atomic orbital energy will be lower than the energy of non-bonding t_{2g} molecular orbital.
- ❖ The interaction of π -donor with t_{2g} orbital lead to bonding (mostly ligand in character) and anti-bonding (mostly metal in character).
- ❖ The π - donor ligand raises the energy of non-bonding t_{2g} level to anti-bonding t_{2g}^* orbital.
- ❖ Consequently, the energy gap between the t_{2g}^* and e_g^* becomes small i.e Δ_o is small.
- ❖ Examples: I⁻, Br⁻, Cl⁻ and F⁻

π -Acceptors increases Δ_o

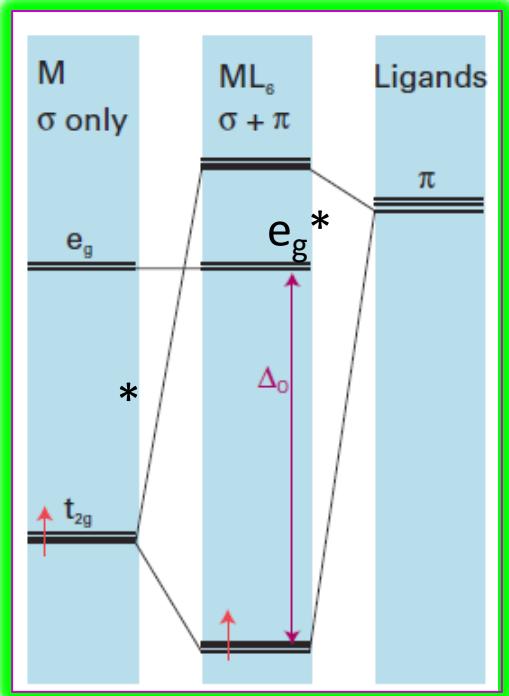
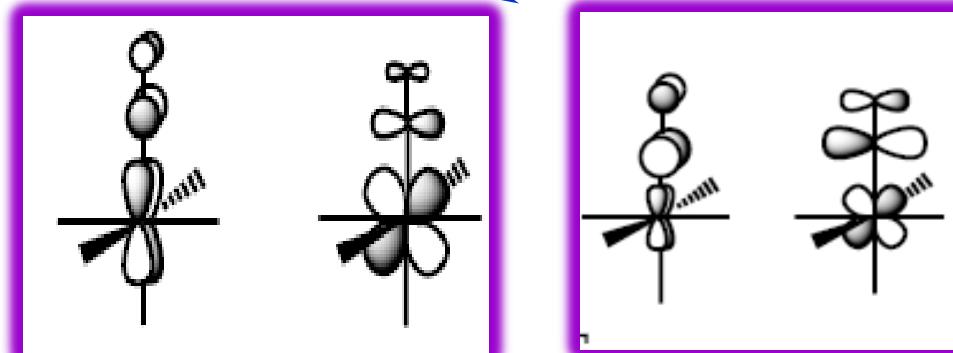
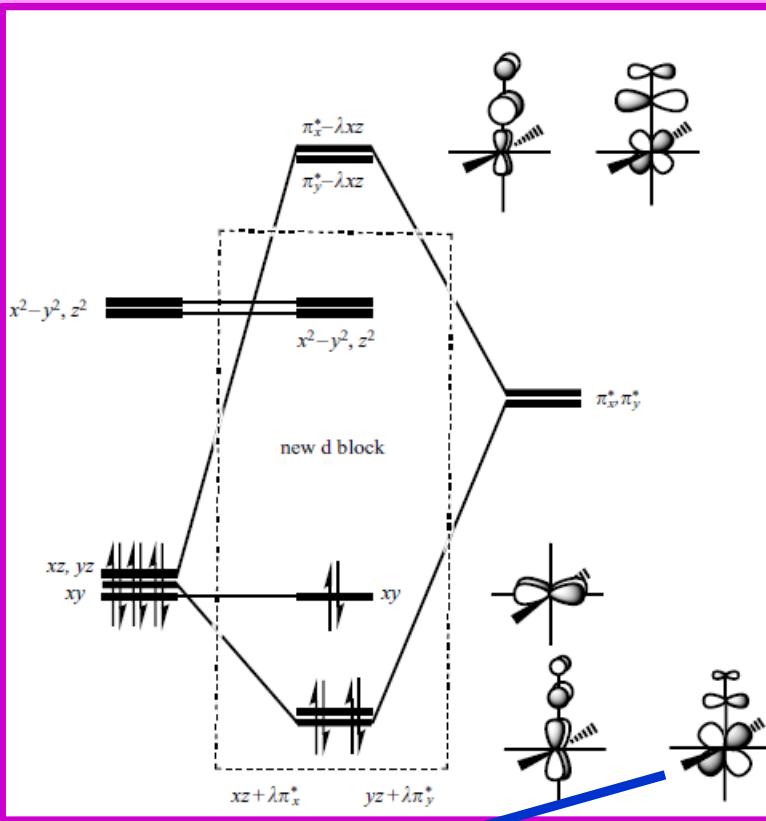


Figure 20.21 Ligands that act as π -acceptors increase Δ_o . Only the π orbitals of the ligand are shown.



- ❖ π - acceptor ligand (LUMO) of an atomic orbital energy will be higher than the energy of non-bonding t_{2g} molecular orbital.
- ❖ The interaction of π -acceptor with t_{2g} orbital lead to bonding (mostly metal in character) and anti-bonding (mostly ligand in character).
- ❖ The π - acceptor ligand lower the energy of non-bonding t_{2g} level.
- ❖ Consequently, the energy gap between the t_{2g} and e_g^* becomes large i.e Δ_o is large.
- ❖ Examples: CO, CN, PR₃

Rationale for Spectro-chemical Series

π -donor ligand

I⁻, Br⁻, S²⁻, SCN⁻, Cl⁻, N³⁻, F⁻

Weak π -donor ligand

Urea, OH⁻, Ox²⁻, O²⁻, H₂O, NCS⁻, Py

No π -effect

NH₃, en, bpy, phen, NO₂⁻, CH₃⁻ and C₆H₅⁻

π -acceptor ligand

CN, CO, PR₃

I⁻ < Br⁻ < S²⁻ < SCN⁻ < Cl⁻ < N₃⁻, F⁻ < urea, OH⁻ < ox, O²⁻ < H₂O < NCS⁻ < py, NH₃ < en < bpy, phen < NO₂⁻ < CH₃⁻, C₆H₅⁻ < CN⁻ < CO.

π -bases < weak π -bases < no π -effect < π -acids

LFT:

- 1) Electronic structure and bonding
- 2) Spectroscopic properties
- 3) Magnetic properties etc.
- 4) Metal ligand covalency
- 5) Spectrochemical series