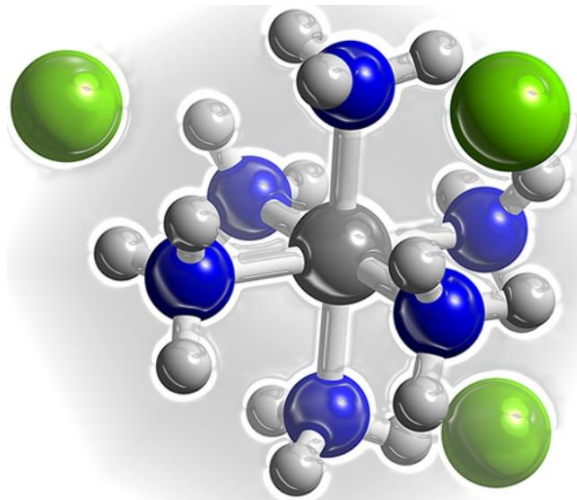
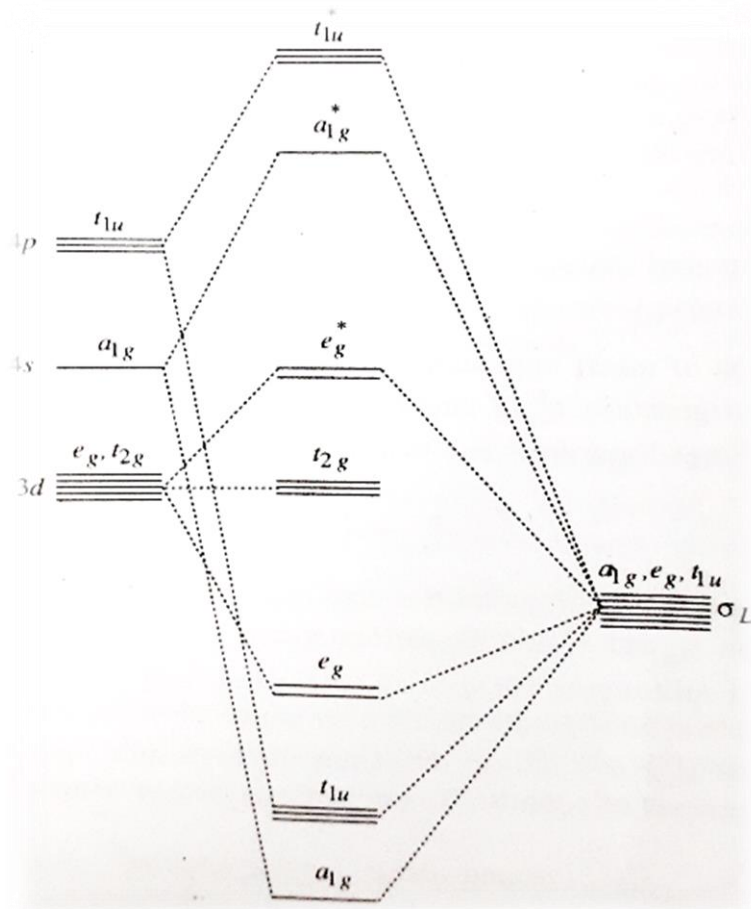


# Ligand Field Theory



Presented  
By

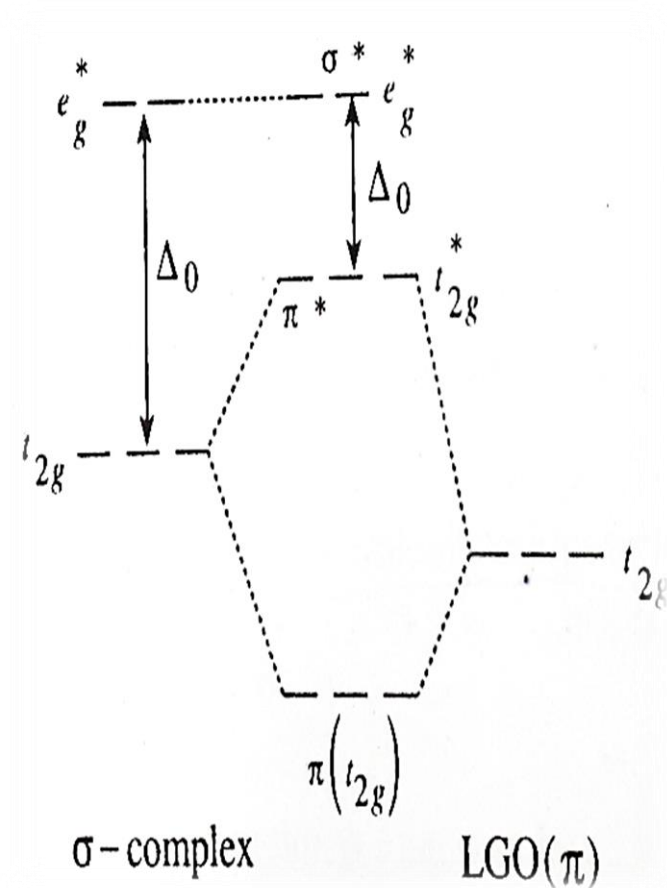
**DR. KAUSTAB MANDAL**

Assistant Professor

Department of Chemistry

Ramakrishna Mission Vivekananda Centenary College

Kolkata- 700 118 (Mobile: 8777 313491)



# What is Ligand Field Theory?

**Ligand Field Theory (LFT)** represents the application of molecular orbital theory to transition metal complexes. According to **LFT**, valence atomic orbitals of central metal/metal ion [(n-1)d, ns and np ) combine with the appropriate **Ligand Group Orbitals (LGOs)** to form **Symmetry Adopted Linear Combinations (SALCs)**.

**LFT also known as Adjusted Crystal Field Theory.**

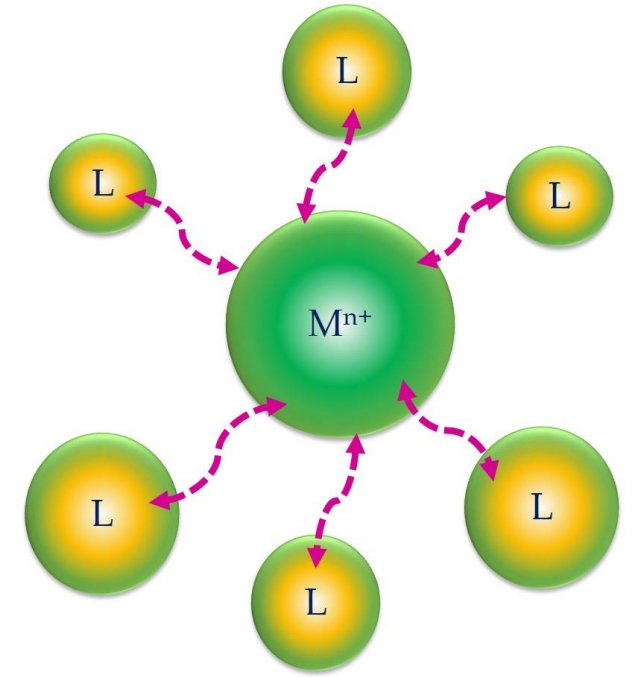
# CFT *vs* LFT

## CFT description

Metal/ metal ion forms complex with the ligands by electrostatic attraction force only. Ligands are considered as point negative charge or point dipole. The orbitals of ligands are not taken into consideration.

## LFT description

Metal/ metal ion forms complex with the ligands by the overlap of suitable orbitals. The orbitals of ligands (LGOs) are taken into consideration.

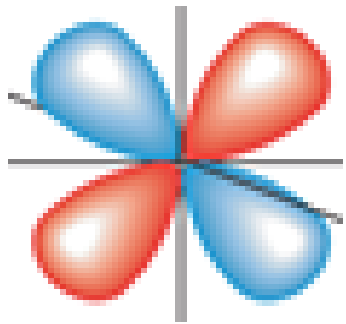


# Evidence of Metal-Ligand Orbital Overlap

## Nephelauxetic effect

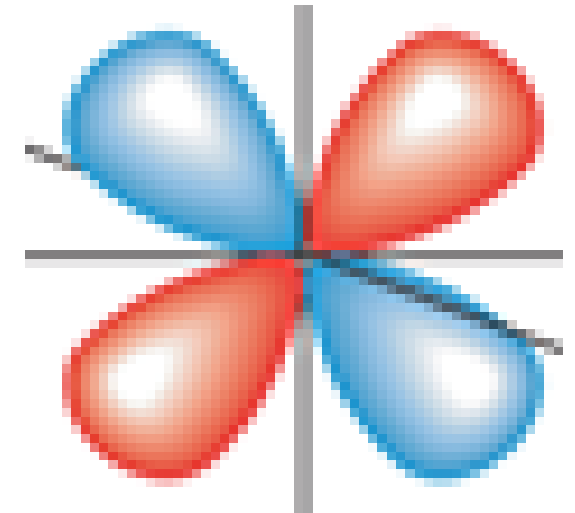
- Racah parameter (B) is found much smaller in the complexes compared to that in the free ions.

$$\beta \text{ (nephelauxetic constant)} = \frac{B_{\text{complex}}}{B_{\text{free ion}}}, \quad \beta \text{ is always less than 1.}$$



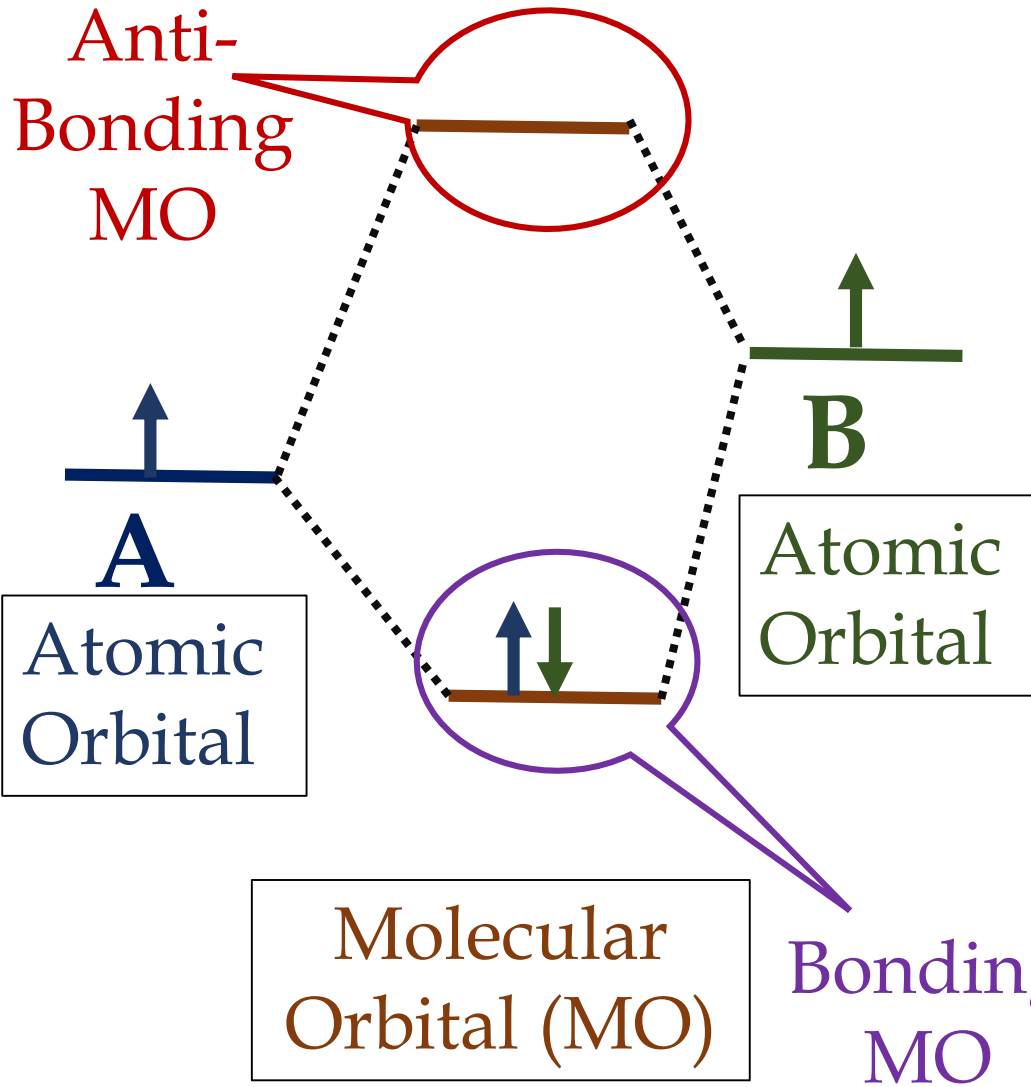
Free metal ion

Ligands with greater ability to delocalize metal electrons show higher nephelauxetic effect *i.e.* lower value of B, it indicates metal-ligand orbitals overlap.



Complex

# Atomic Orbital Overlap Concept



- ❖ Bonding MO is nearer to atomic orbital of A. Bonding MO mostly bear the character of A; large portion of electron cloud of covalent bond is near to atom A. A is the negative end of bond dipole.
- ❖ Anti-bonding MO is nearer to atomic orbital of B. Anti-bonding MO mostly bear the character of B; small portion of electron cloud of covalent bond is near to atom B. B is the positive end of bond dipole.
- ❖ Ionic nature of the compound increases with increasing energy difference between the AOs of A and B.

# Ligand Field Theory...

- ❖ LFT is the application of Molecular Orbital Theory (MOT).
- ❖ Metal-Ligand bond overlap may result in  $\sigma$  bond and  $\pi$  bond formation.
- ❖ In  $\sigma$  bonding, LGOs have perfect symmetry for head-on overlap with the metal's atomic orbitals.
- ❖ The  $\sigma$ -MOs formed by coordination result from the donation of two electrons by each  $\sigma$ -donor ligand.
- ❖ In  $\pi$  bonding, the ligand has filled or empty orbitals of  $\pi$  symmetry around the M-L axis.

## LFT for Octahedral Complex ( $\sigma$ bond description)

- ❖ In octahedral complex, ligands approach along the X, Y and Z axes. Metal orbitals having  $\sigma$  symmetry combine with the LGOs having  $\sigma$  symmetry to form bonding and anti-bonding MOs.
- ❖ For 1<sup>st</sup> transition series, the available metal orbitals to overlap with LGOs are (i) five 3d, (ii) one 4s and (iii) three 4p orbitals.

### Symmetry properties of six $\sigma$ bonding atomic orbitals present in metal:

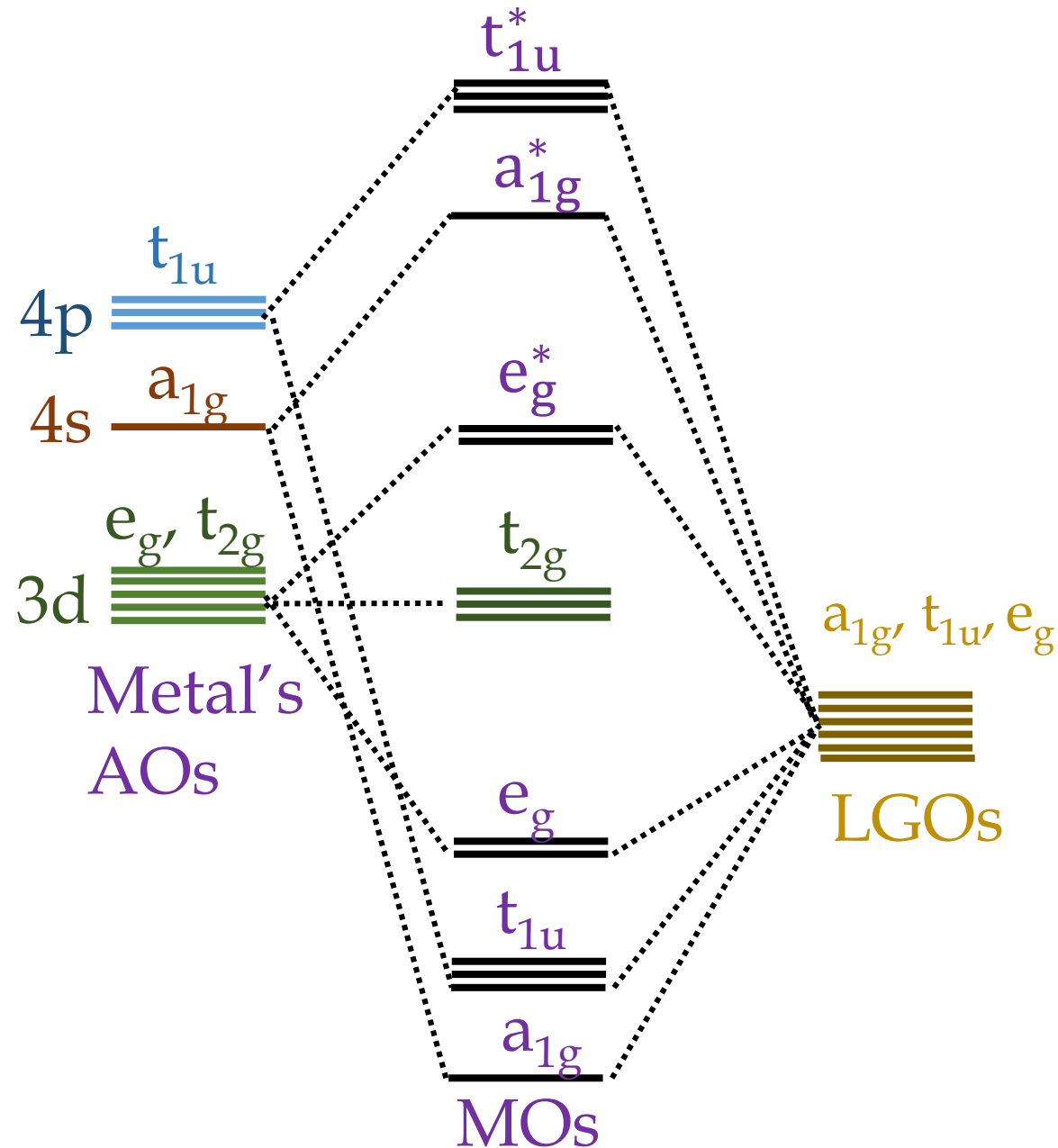
Atomic orbitals	Irreducible representation	
4s	$a_{1g}$ (spherically symmetrical).	} These comes from Group Theory.
$4p_x, 4p_y, 4p_z$	$t_{1u}$ (a set of three equivalent orbital).	
$3d_{(x^2-y^2)}, 3d_{z^2}$	$e_g$ (a pair of equivalent orbital).	

$3d_{xy}, 3d_{xz}$  and  $3d_{yz}$  (irreducible representation:  $t_{2g}$ ) orbitals projecting their lobes between the Cartesian coordinates. These are not suitable for  $\sigma$ -bonding; remain as non-bonding orbitals.

# LFT for Octahedral Complex ( $\sigma$ bond description)

## Energy order:

- ❖ Energy order of atomic orbitals:  $(n-1)d < ns < np$
- ❖ In general,  $\sigma$  symmetry orbitals of LGOs have lower energy compared to the metal valence orbitals.
- ❖ 3d orbitals are large and diffuse compared to the 4s and 4p orbitals. Hence, the 4s and 4p orbitals make better overlap to the LGOs compared to 3d orbitals. As a result, the bonding MOs  $a_{1g}$  and  $t_{1u}$  are more stabilized compared to the bonding MOs of  $e_g$  symmetry.

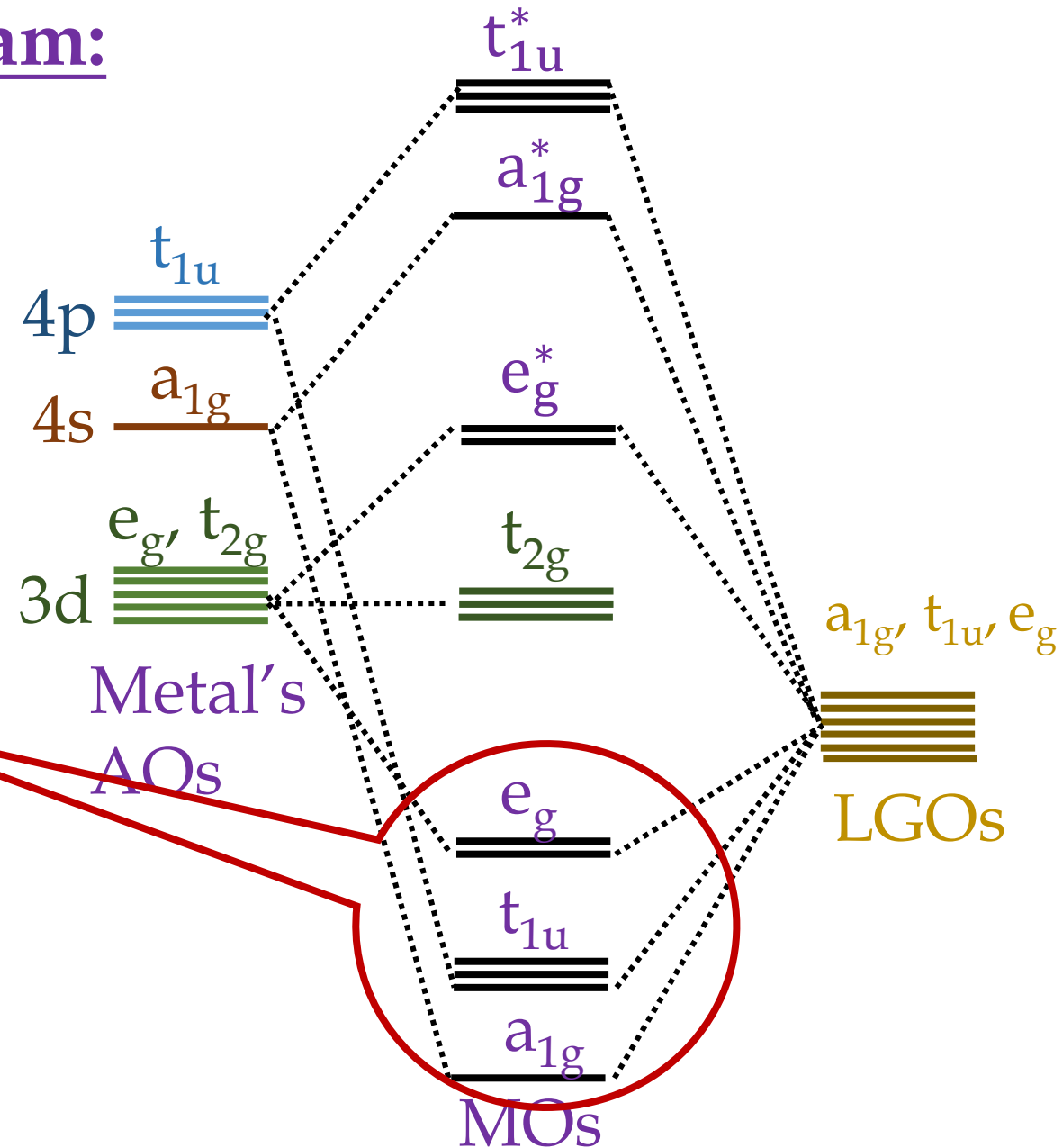




# LFT for Octahedral Complex ( $\sigma$ bond description)

## Molecular Orbitals (MOs) Diagram:

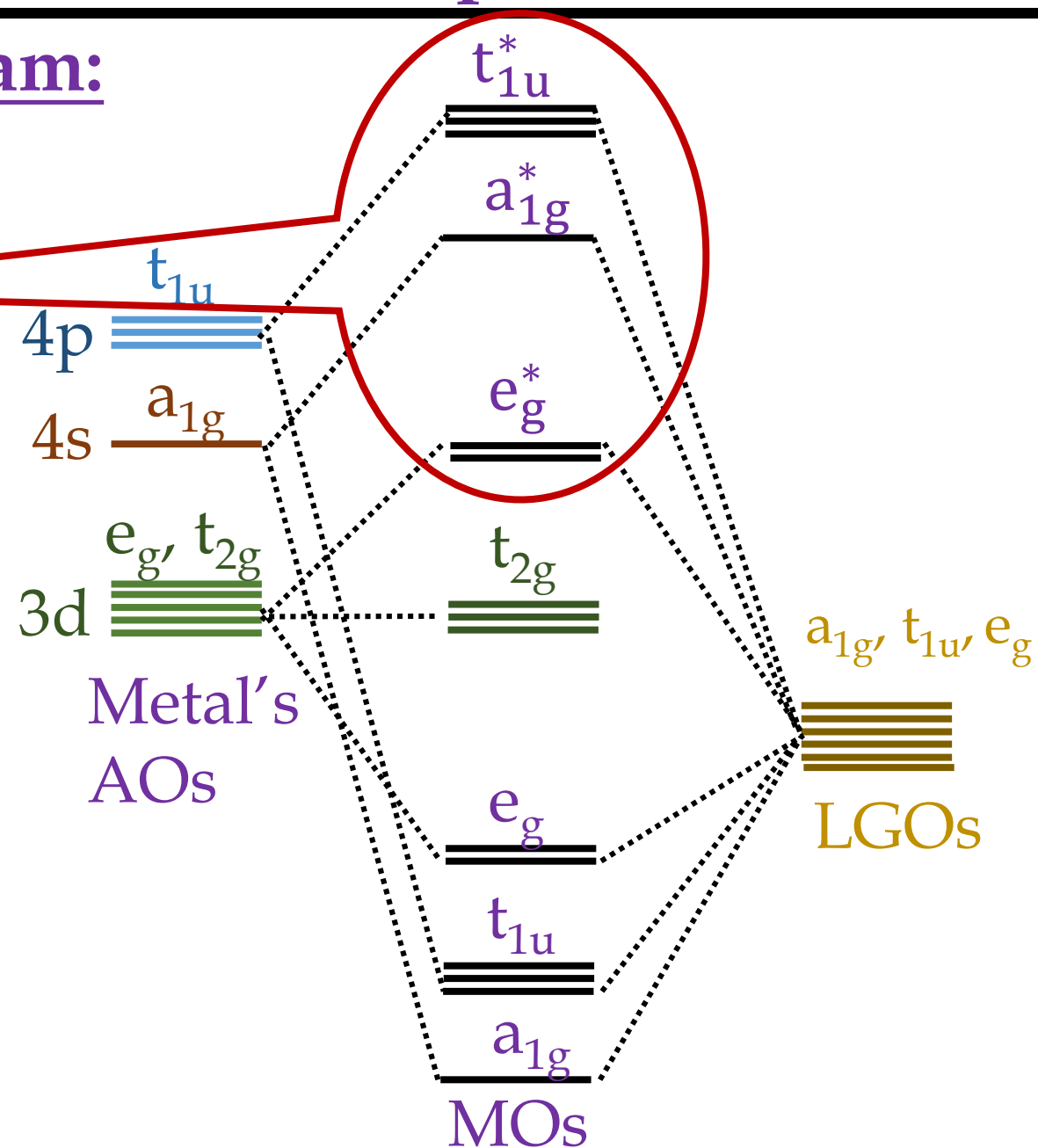
These are bonding MOs. Six bonding MOs are closer in energy to the lower energy ligand orbitals. Hence bonding MOs are expected to have greater ligand character. It implies some polarity in the metal-ligand bond.



# LFT for Octahedral Complex ( $\sigma$ bond description)

## Molecular Orbitals (MOs) Diagram:

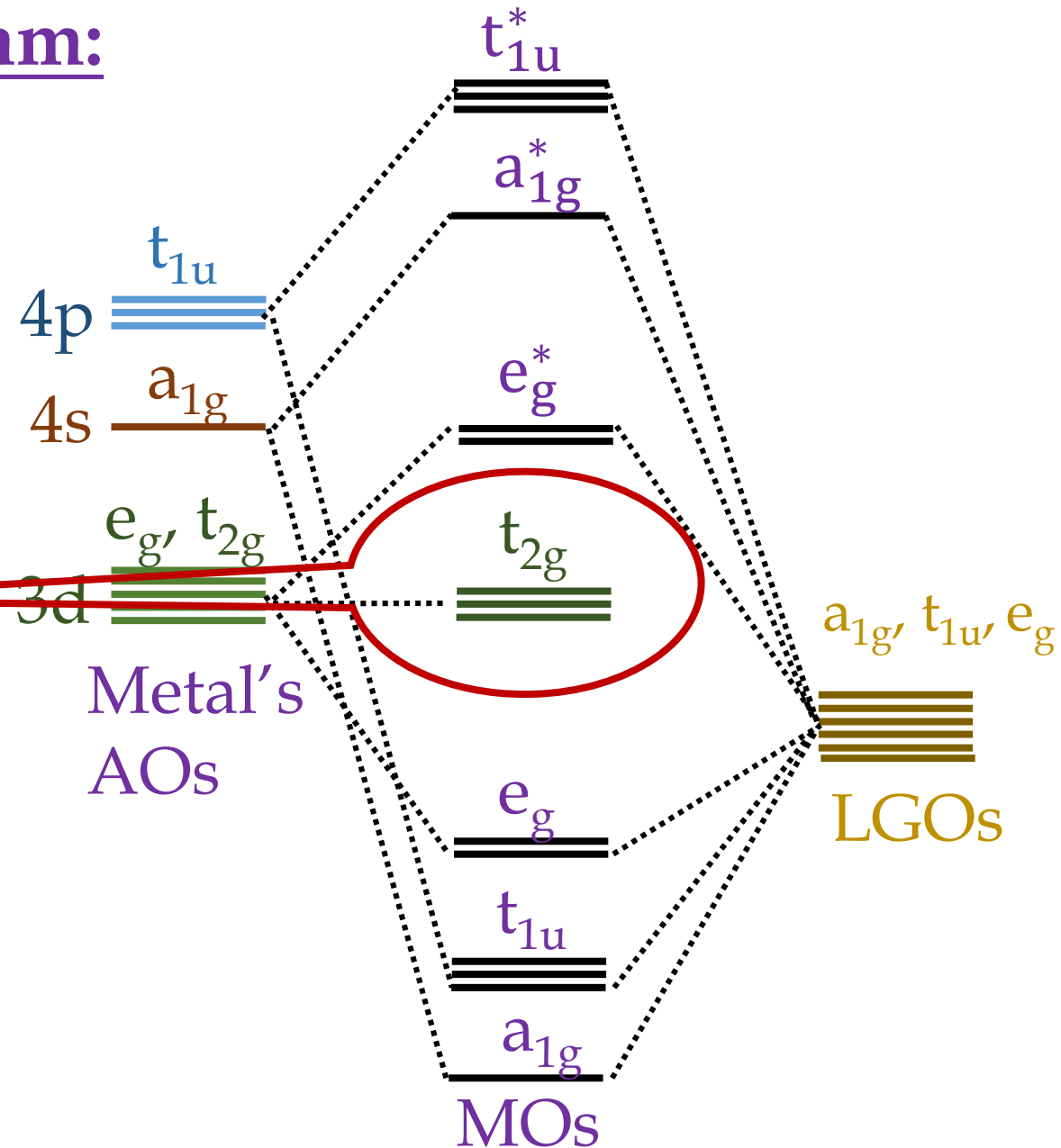
These are anti-bonding MOs. The anti-bonding MOs are expected to resemble the metal orbitals more to which they are close in energy.



# LFT for Octahedral Complex ( $\sigma$ bond description)

## Molecular Orbitals (MOs) Diagram:

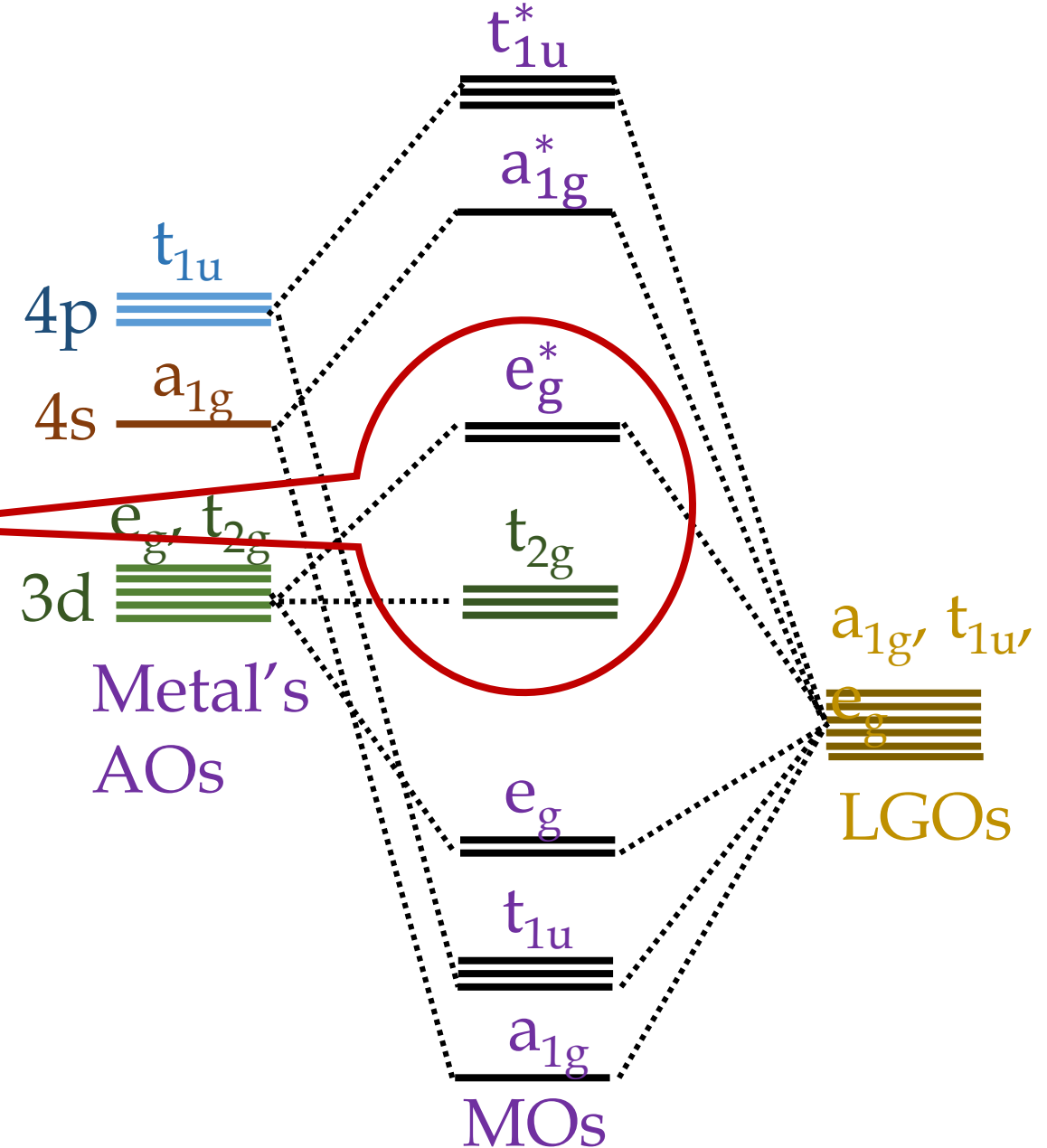
These are non-bonding orbitals. Any electron present in the non-bonding  $t_{2g}$  orbitals will have only metal character in absence of  $\pi$  bonding.



# LFT for Octahedral Complex ( $\sigma$ bond description)

## Molecular Orbitals (MOs) Diagram:

Central part consisting of  $t_{2g}$  and  $e_g^*$  Mos corresponds to  $t_{2g}$  and  $e_g$  level in CFT where they were considered as pure metal orbitals. Here the orbitals have greater metal character. The energy gap between  $t_{2g}$  and  $e_g^*$  corresponds to crystal field splitting energy ( $\Delta_0$ ).

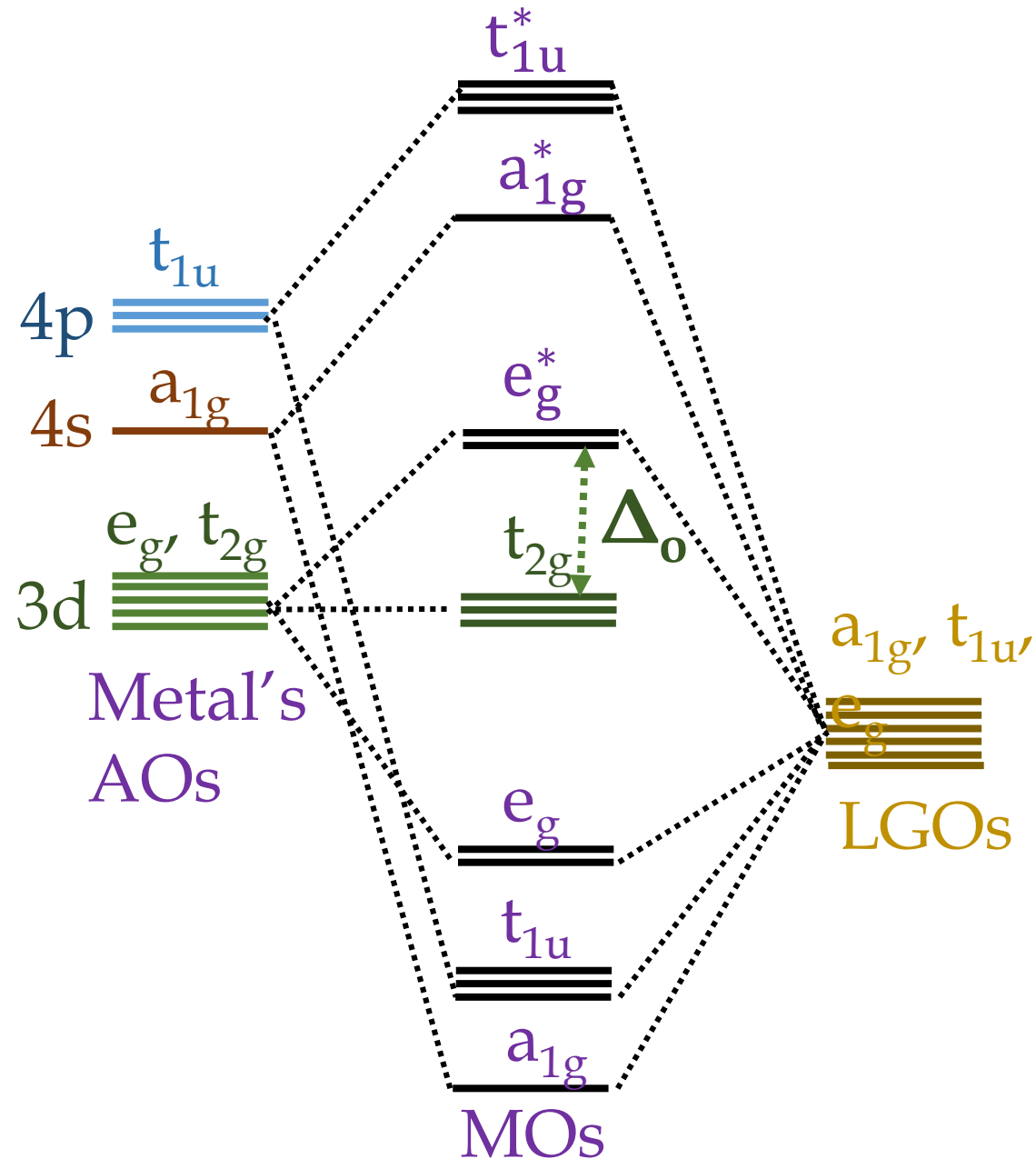


# LFT for Octahedral Complex ( $\sigma$ bond description)

## Molecular Orbitals (MOs) Diagram:

### Filling of MOs:

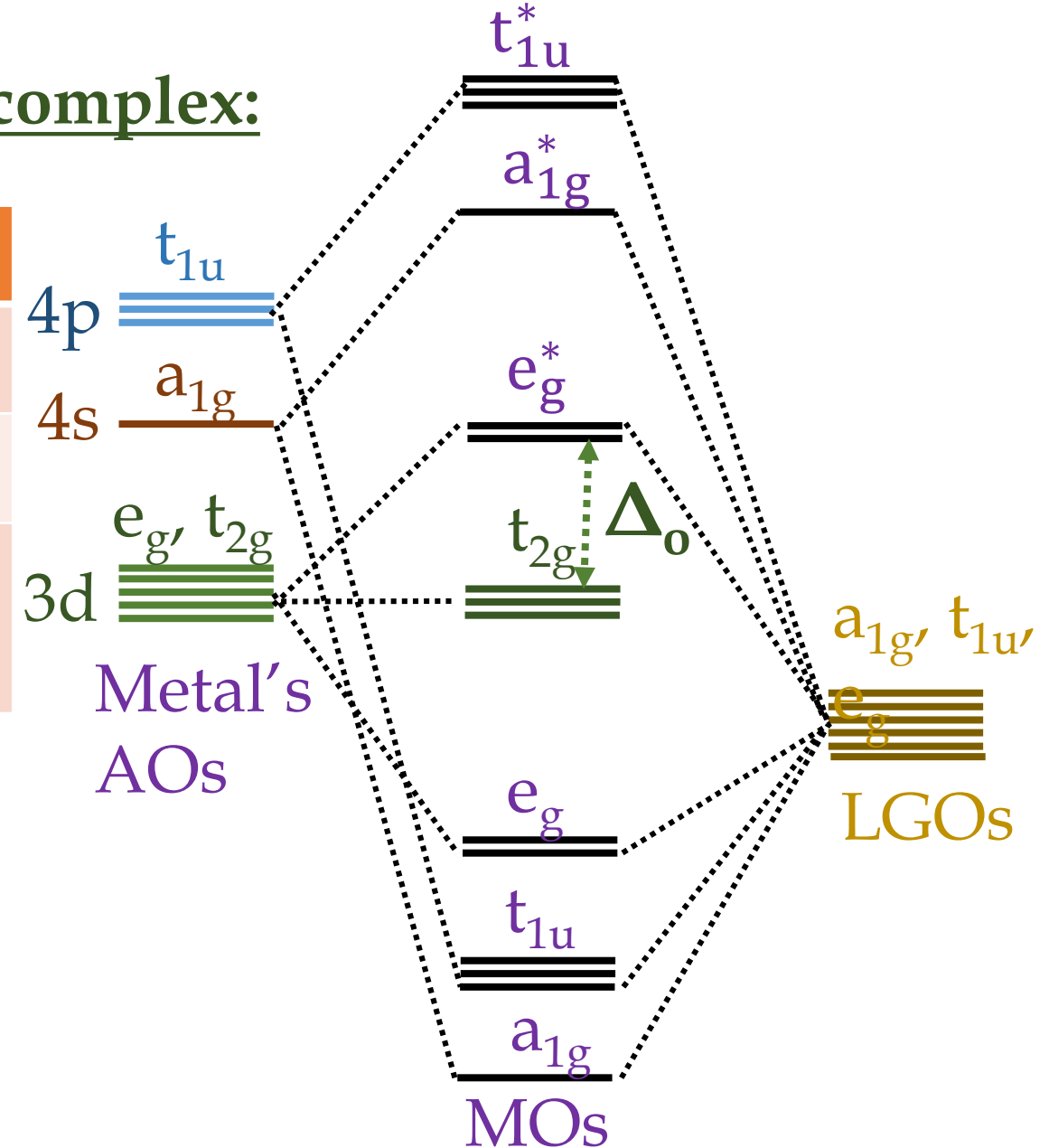
- Six lower energy LGOs donate twelve electrons ( $6 \times 2$ ). These twelve electrons filled the six bonding MOs ( $a_{1g}$ ,  $t_{1u}$  and  $e_g$ ).
- Metal's d electrons go to the non-bonding  $t_{2g}$  and anti-bonding  $e_g^*$  according to the energy sequence.
- High spin or low spin configuration depends on relative value of pairing energy and  $\Delta_o$ .



# LFT for Octahedral Complex ( $\sigma$ bond description)

## Electronic configuration of octahedral complex:

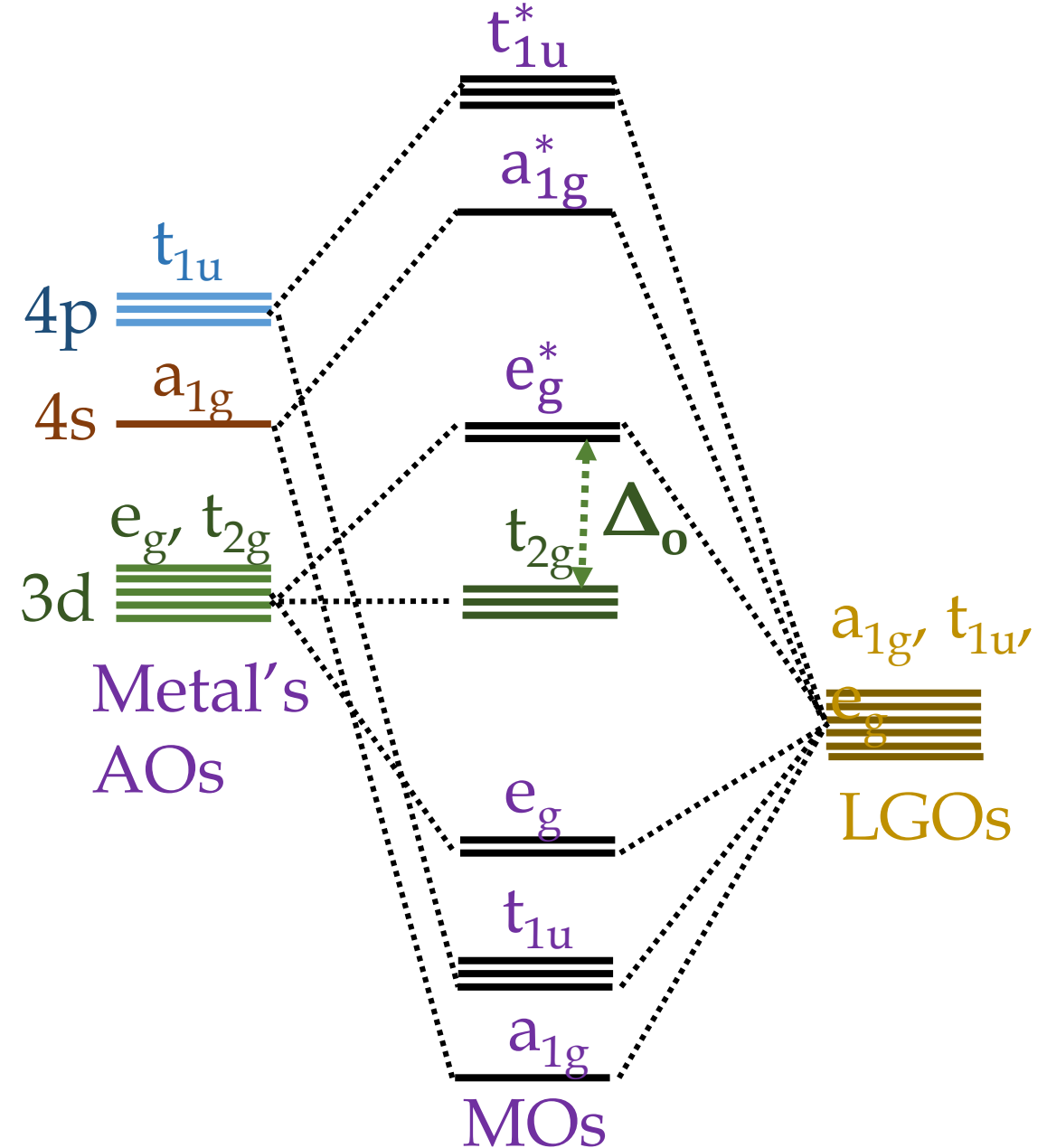
Complex	Electronic configuration
$[\text{Ti}(\text{OH}_2)_6]^{3+}$	$a_{1g}^2 t_{1u}^6 e_g^4 t_{2g}^1$
$[\text{Co}(\text{NH}_3)_6]^{3+}$	$a_{1g}^2 t_{1u}^6 e_g^4 t_{2g}^6$ (low spin)
$[\text{CoF}_6]^{3-}$	$a_{1g}^2 t_{1u}^6 e_g^4 t_{2g}^4 e_g^{*2}$ (high spin)



# LFT for Octahedral Complex ( $\sigma$ bond description)

## Electronic spectra:

Electronic spectra of complex may be explained from MO energy level diagram. For  $d^1$  metal complexes like  $[\text{Ti}(\text{OH}_2)_6]^{3+}$ , the ground state electronic configuration is  $t_{2g}^1 e_g^*{}^0$  and the first excited state corresponds to  $t_{2g}^0 e_g^*{}^1$ . Hence the complex is expected to absorb electromagnetic radiation.



# LFT for Octahedral Complex ( $\sigma$ bonding along with $\pi$ bond)

## $\pi$ bonding in the metal-ligand bond

- ❖ The extent of  $\pi$  bonding is determined by the symmetry of the orbitals as well as match in size and energy of the orbitals.
- ❖ The metal and ligand orbitals which are perpendicular to the inter-nuclear axis can take part in  $\pi$  bonding.
- ❖  $\pi$  bonding may involve  $\pi$  donor effect as well as  $\pi$  acceptor effect.
- ❖ The  $t_{2g}$  metal orbitals form  $\pi$  bonds with LGOs of matching symmetry.

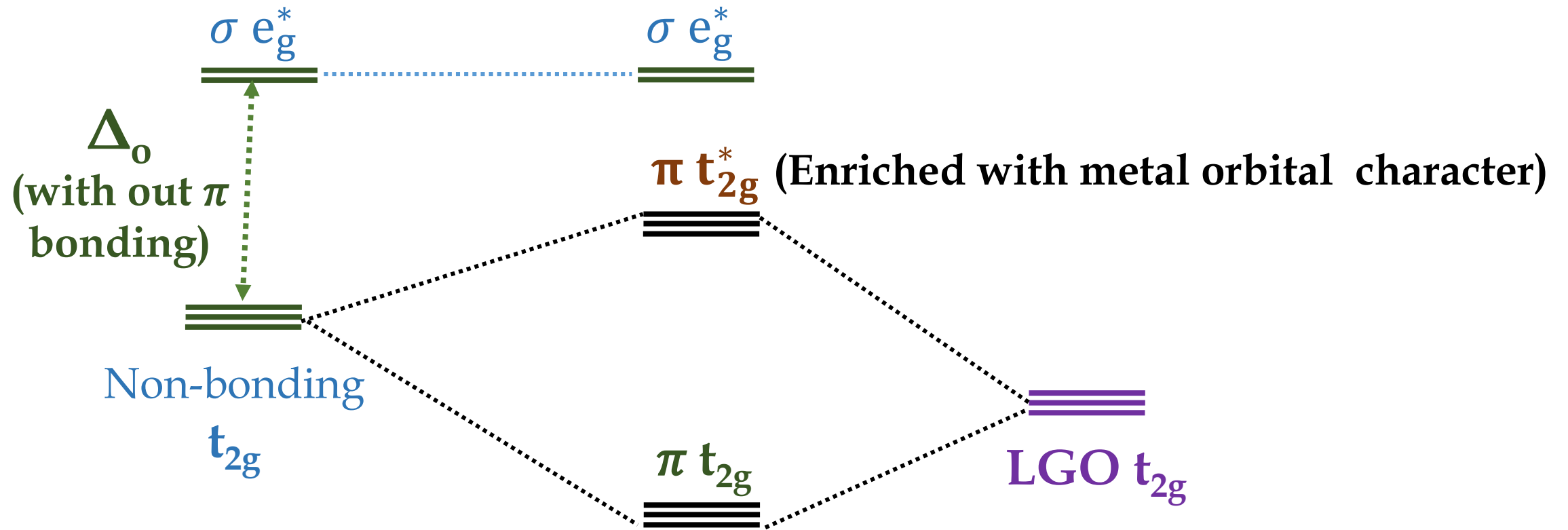
**The effect of  $\pi$  interaction on the final energy level diagram mainly depend upon two factors:**

- (i) The relative energies of ligand  $\pi$  orbitals and the metal  $t_{2g}$  orbitals.
- (ii) Whether the ligand  $\pi$  orbitals are filled or empty.



# Effect of $\pi$ bonding

Case 1. Filled ligand  $\pi$  orbitals of lower energy than the metal  $t_{2g}$  orbitals.

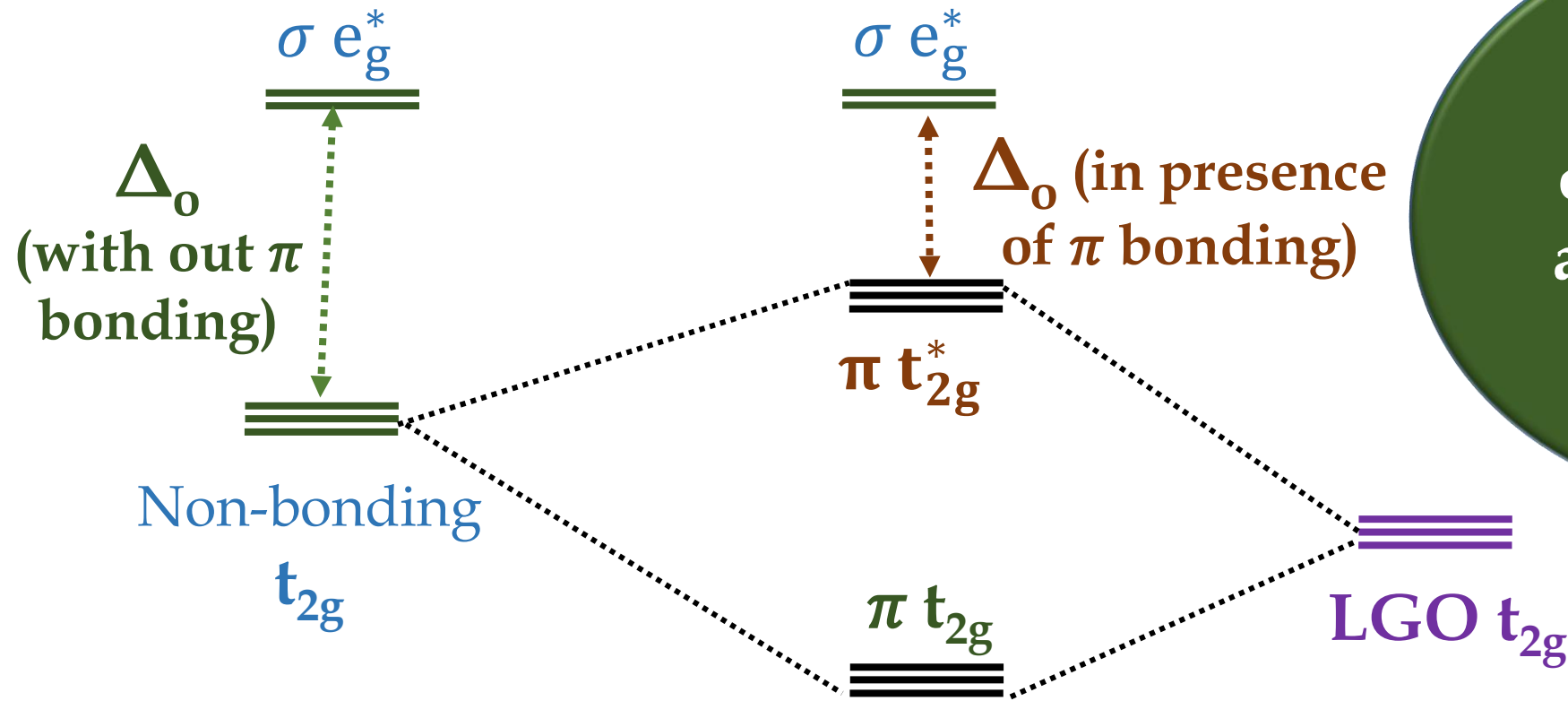


$\sigma$  bond  
description only

$\sigma$  bonding along  
with  $\pi$  bond

# Effect of $\pi$ bonding

Case 1. Filled ligand  $\pi$ -orbitals of lower energy than the metal  $t_{2g}$  orbitals.



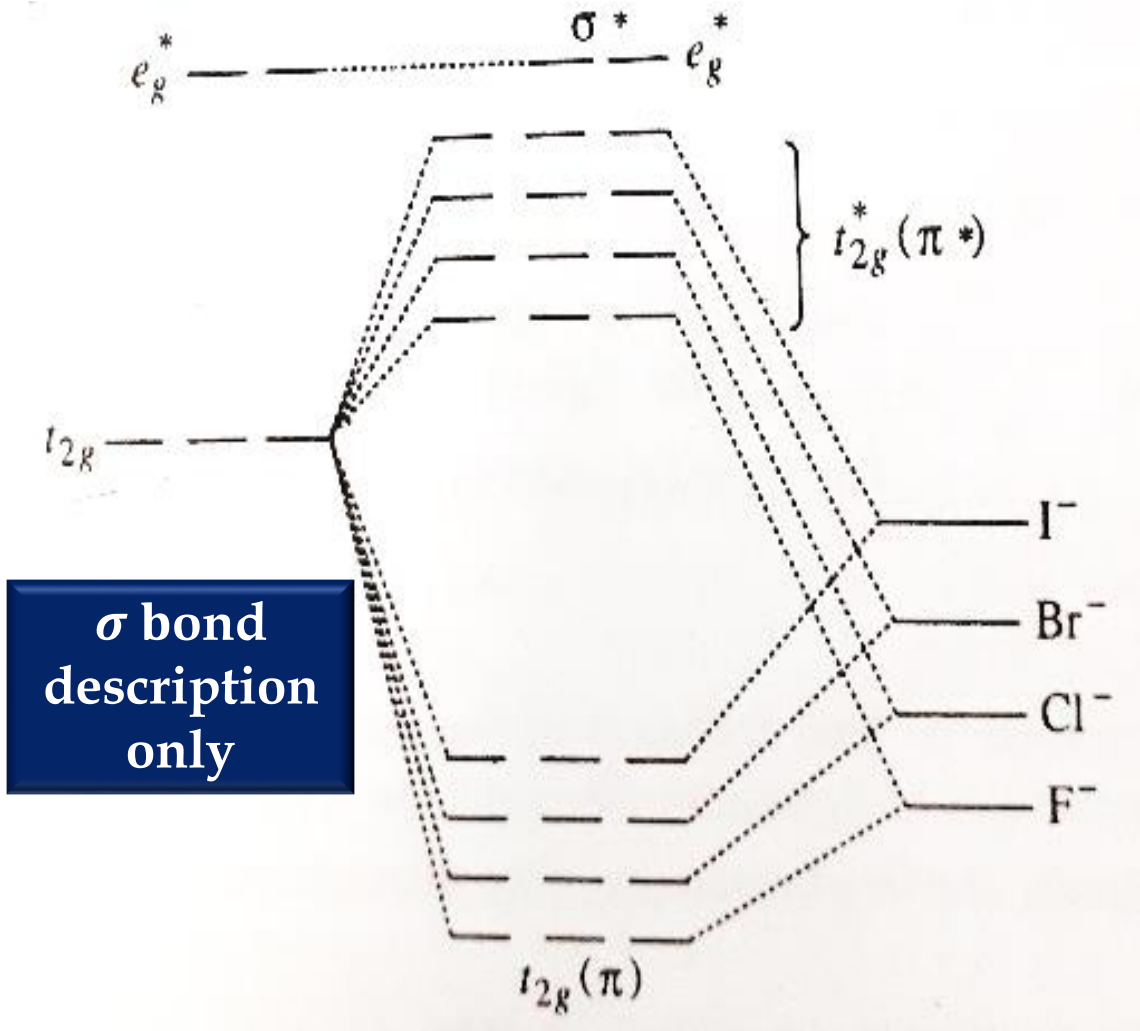
In general,  $\pi$ -donor ligands are weak field ligands.

$\sigma$  bond description only

$\sigma$  bonding along with  $\pi$  bond

# Effect of $\pi$ bonding

## Relative positions of the halides in the spectrochemical series:

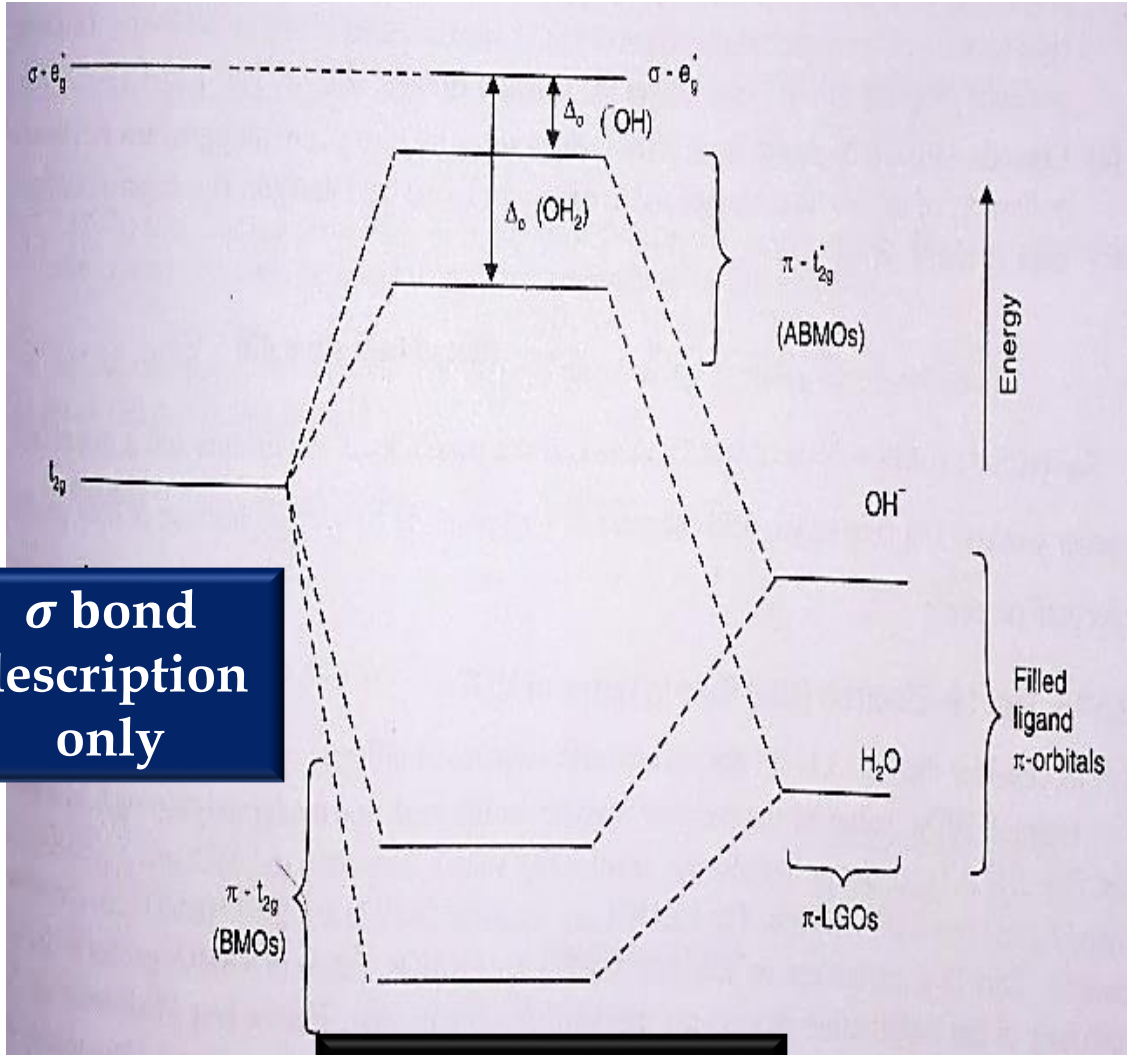


- $\pi$ -donor halides are weak field ligands.
- Among the halide ions,  $\pi$ -orbital of  $I^-$  has the highest energy which results highest energy  $\pi t_{2g}^*$  MOs. Hence,  $I^-$  is the weakest ligand among the halides.
- $F^-$  has the lowest energy which results lowest energy  $\pi t_{2g}^*$  MOs. Hence,  $F^-$  is the strongest ligand among the halides.
- Order of ligand field strength of the halide ions is:  $I^- < Br^- < Cl^- < F^-$ .

With the increase of  $\pi$ -donor properties of the ligands,  $10Dq$  value decreases.

# Effect of $\pi$ bonding

## Why $\text{OH}^-$ is weaker ligand than $\text{H}_2\text{O}$ ?



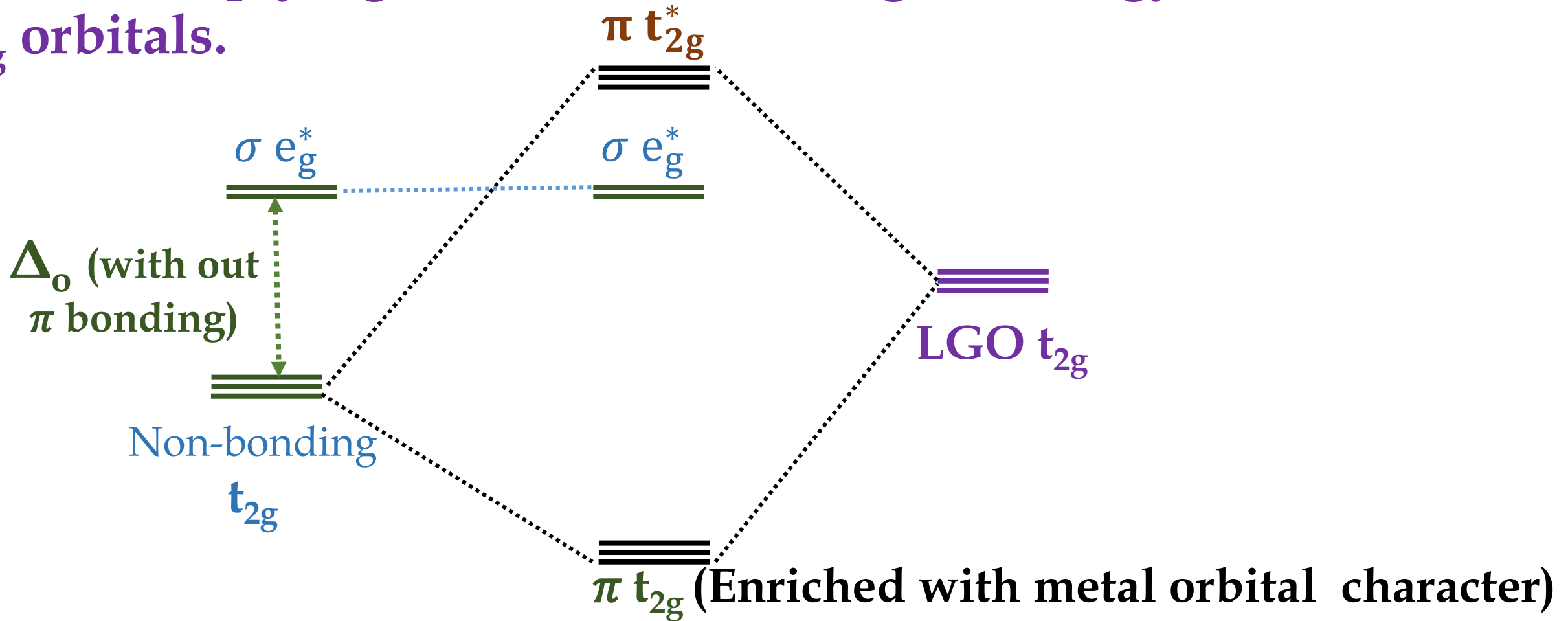
**$\sigma$  bond  
description  
only**

**$\sigma$  bonding along  
with  $\pi$  bond**

- OH<sup>-</sup> ion has three lone pairs of electrons; one lone pair is involved in  $\sigma$ -donation while other two lone pairs are involved in  $\pi$ -donation.
- H<sub>2</sub>O has two lone pairs of electrons; one lone pair is involved in  $\sigma$ -donation while other lone pair is involved in  $\pi$ -donation.
- So, OH<sup>-</sup> is better  $\pi$ -donor than H<sub>2</sub>O i.e. the energy of filled  $\pi$ -orbital of OH<sup>-</sup> is higher than that of H<sub>2</sub>O.
- Anti-bonding  $t_{2g}^*$  MOs of metal-OH<sup>-</sup> complex has higher energy comparing to that of metal-H<sub>2</sub>O complex.
- Hence OH<sup>-</sup> is weaker ligand than H<sub>2</sub>O.

# Effect of $\pi$ bonding

Case 2. Empty ligand  $\pi$  orbitals of higher energy than the metal  $t_{2g}$  orbitals.

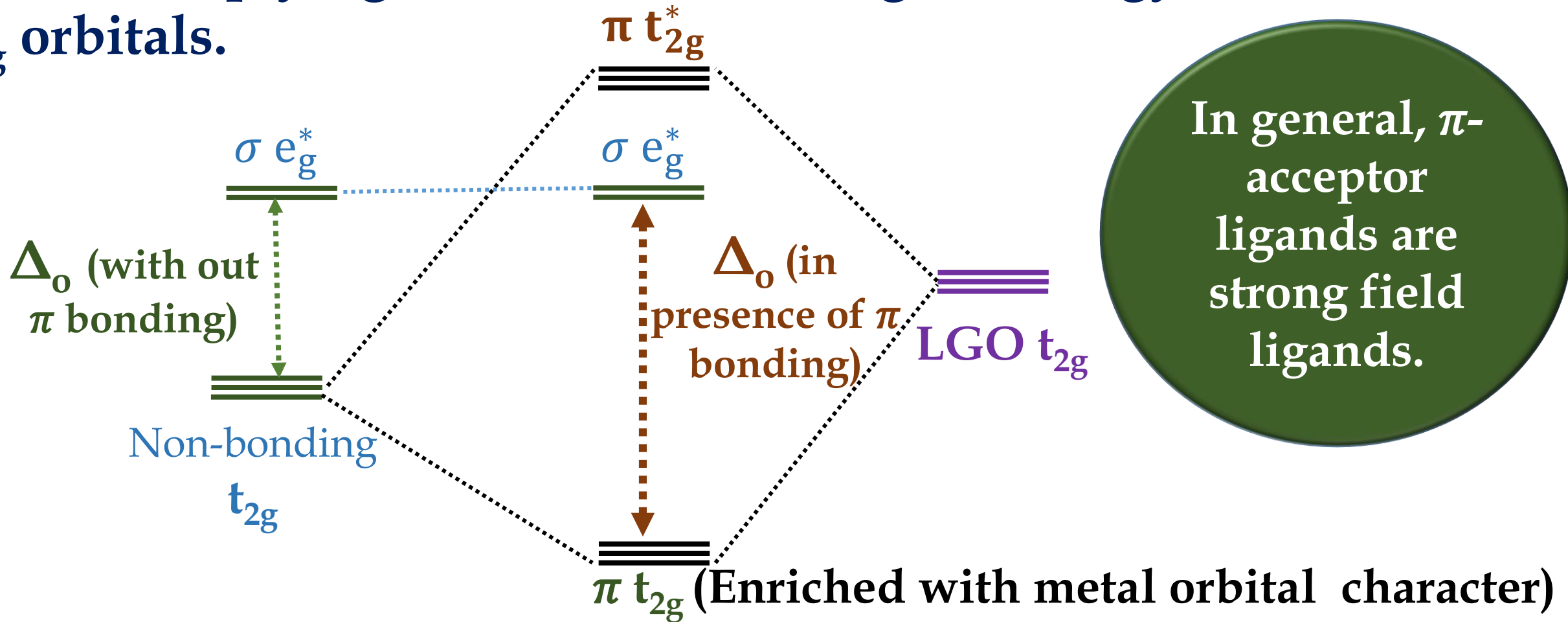


$\sigma$  bond description only

$\sigma$  bonding along with  $\pi$  bond

## Effect of $\pi$ bonding

**Case 2.** Empty ligand  $\pi$  orbitals of higher energy than the metal  $t_{2g}$  orbitals.



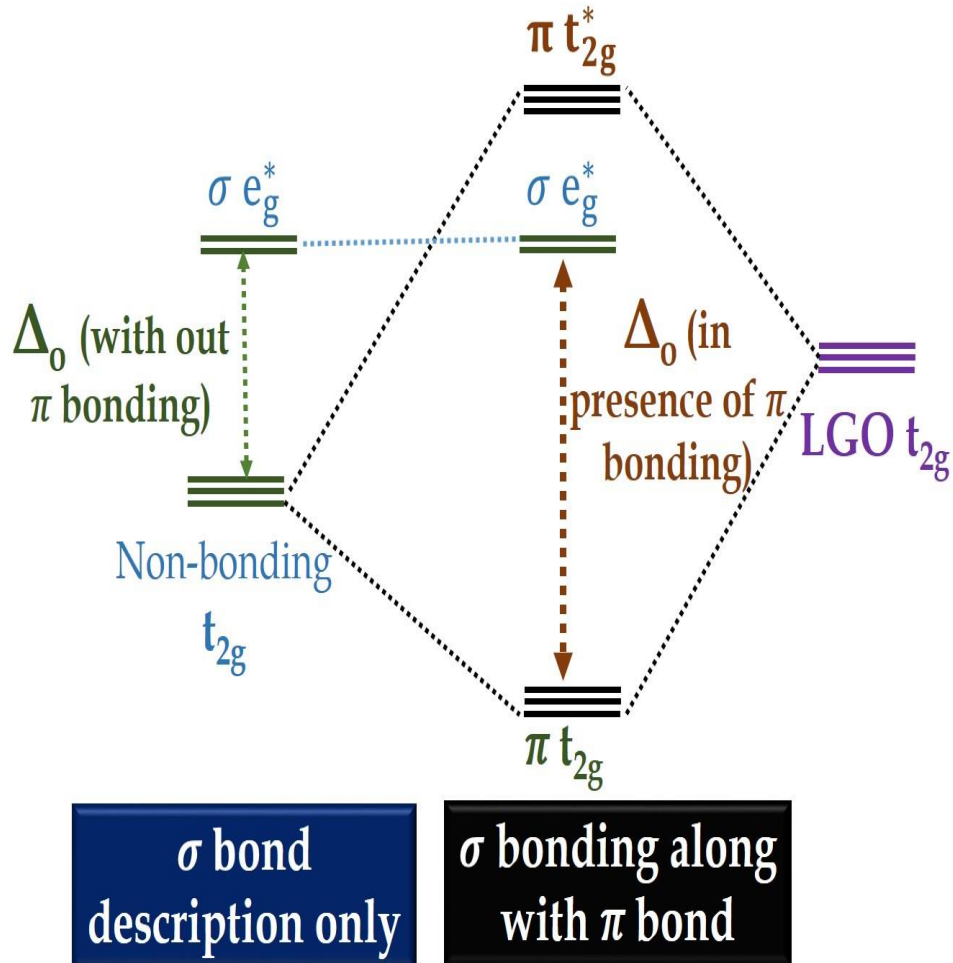
In general,  $\pi$ -acceptor ligands are strong field ligands.

$\sigma$  bond description only

$\sigma$  bonding along with  $\pi$  bond

## Effect of $\pi$ bonding

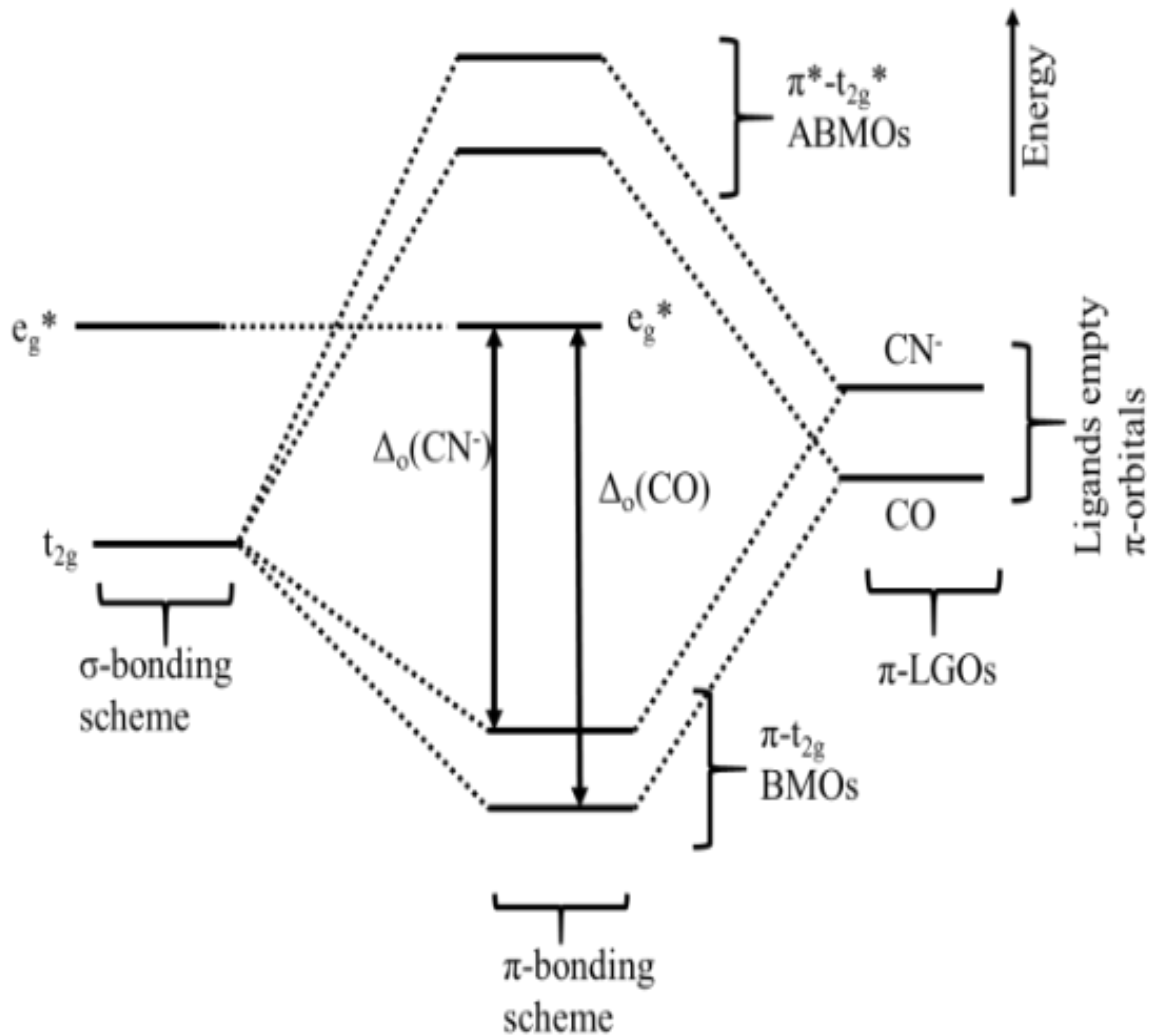
### Case 2. Empty ligand $\pi$ orbitals of higher energy than the metal $t_{2g}$ orbitals.



- CO,  $\text{CN}^-$ ,  $\text{C}_2\text{H}_4$  etc. have vacant  $\pi^*$  Mos.
- These ligands donate electrons to the metal through  $\sigma$  bonding and receives electron from the metal centre through  $\pi$  bonding. The  $\sigma$  donation and  $\pi$  acceptance work in a synergistic fashion.
- $\pi$  acid ligands construct the right portion of the spectrochemical series while the  $\pi$  donor ligands constitute the left portion.
- Purely good  $\sigma$  donor ligands (having no  $\pi$  bonding properties) constitute the middle portion of the series.

# Effect of $\pi$ bonding

## Why CO is stronger ligand than $\text{CN}^-$ ?

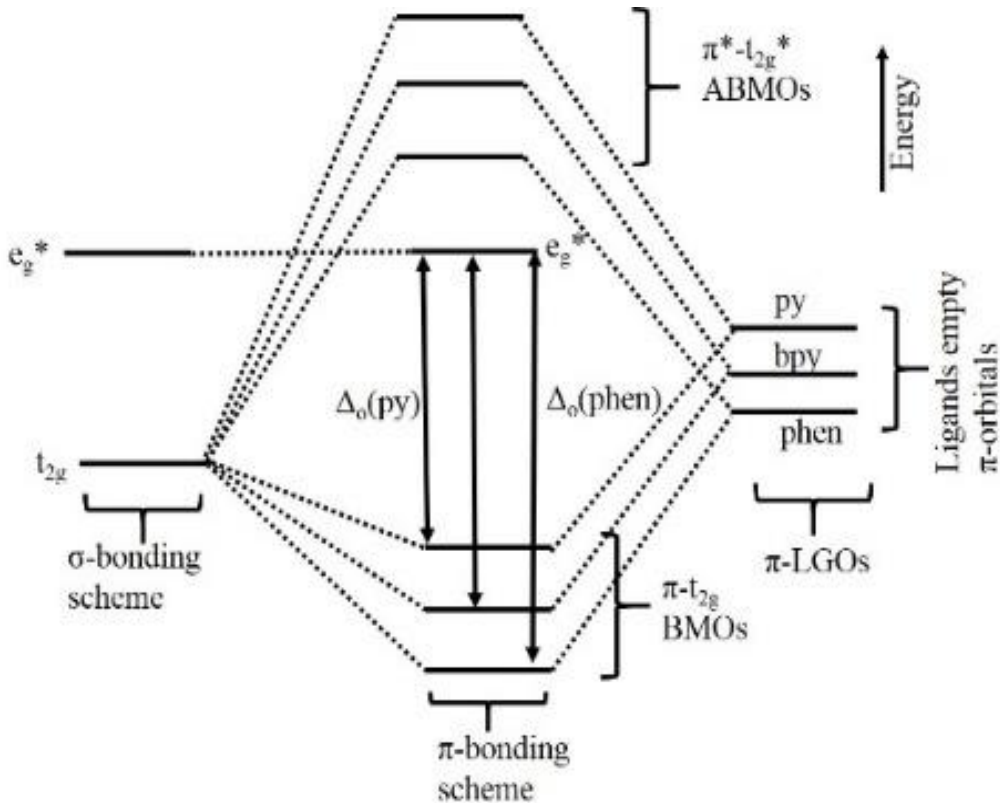
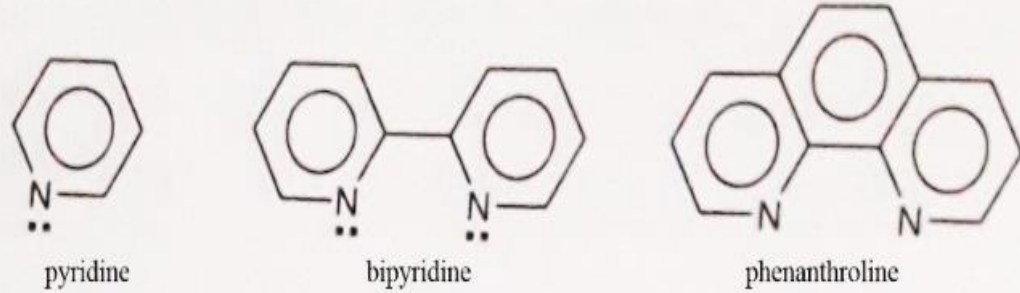


- Both  $\text{CO}$  and  $\text{CN}^-$  are  $\pi$ -acceptor ligands.
- Energy of lowest unoccupied  $\pi$ -orbital (LUMO) of  $\text{CO}$  is lower than that of  $\text{CN}^-$  (Energy of atomic orbitals of N is higher than that of O).
- Besides that,  $\text{CN}^-$  is a negatively charged ligand whereas  $\text{CO}$  is a neutral ligand. These facts make  $\text{CO}$  stronger  $\pi$ -acceptor ligand compare to  $\text{CN}^-$ .
- Energy of bonding  $t_{2g}$  MOs of metal- $\text{CN}^-$  complex is higher compare to that in metal- $\text{CO}$  complex. So the  $10 Dq$  value of  $\text{CO}$  is higher than that of  $\text{CN}^-$ .



# Effect of $\pi$ bonding

Compare field strengths of pyridine, bipyridine, phenanthroline.



- Pyridine (py), bipyridine (bpy) and phenanthroline (phen) are the  $\pi$ -acid ligands.
- In bpy and phen, the  $\pi$  electrons are delocalized over an extended carbon skeleton. HOMO and LUMO of bpy and phen have lower energy than that in py. Sequence of the energy of the empty  $\pi$ -orbitals (LUMO) is:  $py > bpy > phen$ .
- Lower energy  $\pi$ -LUMO makes bpy and phen better  $\pi$ -acceptor compare to py.
- Order of ligand field strength ( $10 Dq$ ) is:  $phen > bpy > py$ .

