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CHEMISTRY
PAPER No. 7: Inorganic chemistry II
MODULE No. 5: Molecular Orbital Theory

TABLE OF CONTENTS

1. Learning Outcomes
2. Introduction to Ligand Field Theory
3. Delocalized approach To Bonding: Molecular Orbital Theory

3.1 Introduction to Molecular Orbital Theory

3.1.1 Homonuclear Diatomic Molecule

3.2 Principles of Ligand Field Theory

4. Molecular Orbital Theory of Octahedral Complexes-[ML₆]ⁿ⁺

4.1 Ligand Consideration

4.2 Sigma(σ) bonding

4.3 MO Diagrams of various octahedral complexes

5. Summary

1. Learning Outcomes (Times New Roman , size 14)

After studying this module, you shall be able to

- Know the basic principles of Molecular Orbital Theory
- Learn the rules of drawing a molecular orbital diagram
- Identify the ligands as strong or weak sigma donors
- Evaluate the ligand field splitting parameter in terms of ligand strength

2. Introduction to Ligand Field Theory

Crystal Field Theory describes the bonding between the ligands and the central metal ion orbitals purely on an electrostatic basis, however, the interactions between them is generally stronger than as expected. This is because in reality electrons are shared between the orbitals, or transfer between metal and ligand so the interactions should be treated in terms of the bonding interactions instead. Hence we can say that, the most severe limitation of CFT is its inability to account for the chemical bonding since complexes may also be formed between neutral metal atoms and neutral or cationic ligands.

The Ligand Field Theory explains the covalent bonding of metal and ligands with the help of molecular orbital (MO) diagram.

3. Delocalized approach To Bonding: Molecular Orbital Theory

3.1 Introduction to Molecular Orbital Theory

The localized models for bonding such as Lewis and Valence Bond Theory assume that all electrons are constrained in bonds between atoms or lone pairs. In most cases, MO theory provides with a more precise picture of the electronic arrangement of molecules and it gives more relevant information about their chemistry and reactivity. Molecular orbitals are constructed from the available atomic orbitals in a molecule in such a way that the number of molecular orbitals formed and Linear Combinations of Atomic Orbitals (LCAO) are same. In MO diagram of a molecule, electrons are fill in molecular orbital according to the Aufbau principle. Some basic rules for making MO's using the LCAO method are as follows:

- 1) n atomic orbitals must produce n molecular orbitals (e.g. 6 AO's must produce 6 MO's).
- 2) The atomic orbitals with the appropriate symmetry combine.
- 3) The atomic orbitals with similar energy combine.
- 4) Each MO must be normal and must be orthogonal to every other MO.
- 5) The more interaction between the atomic orbitals results in formation of more stable MO (Figure-1)

This means larger electronegativity difference between the two atoms, smaller is the stabilization provided by covalent bonding. If the energy difference in the orbitals is large, then the interaction of the atoms is not stabilizing by covalent bonding. Therefore, the more electronegative atom gain an electron from the less electronegative atom resulting formation of two ions. (Figure1)

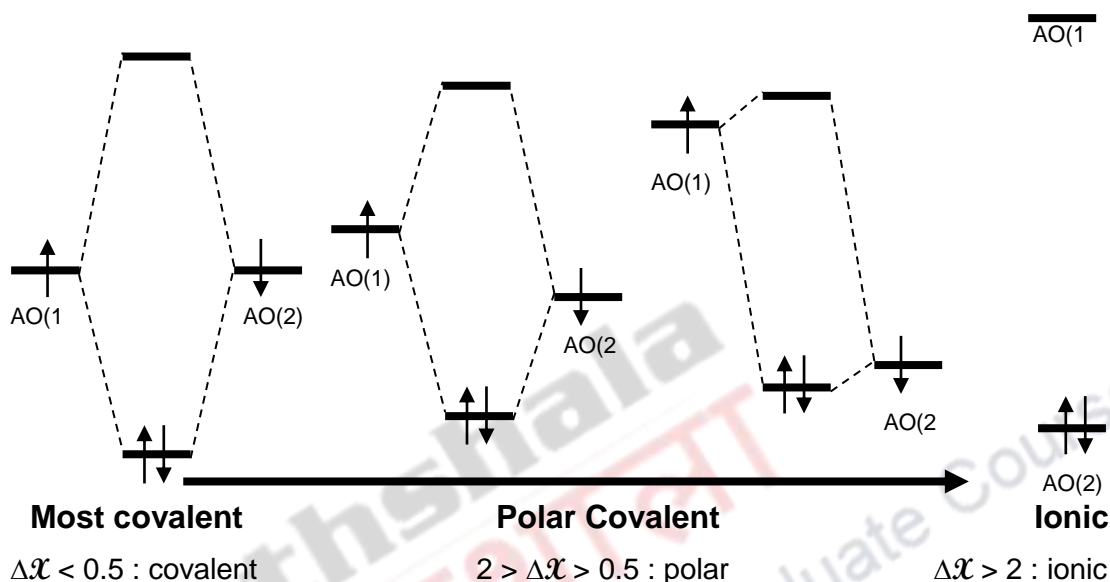


Figure1. Polarity of the bonds in terms of interaction between the atomic orbitals

3.1.1 Homonuclear Diatomic Molecule

For the homonuclear, linear and diatomic molecule H_2 , each H atom has only 1s orbital, so to obtain MO's for the H_2 molecule, we must make linear combinations of two 1s orbitals.

(A) Consider the addition of the two 1s functions (with the same phase):

This forms an MO for both H atoms having the same phase and symmetrical about the H-H axis. This is called as bonding MO and designated as σ because of its symmetry. The in-phase overlapping increases the amount of electron density between the two nuclei (Figure2)

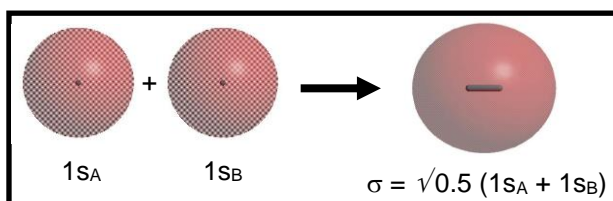


Figure2. In phase addition of two atomic orbitals

<http://mutuslab.cs.uwindsor.ca/macdonald/Teaching/651-class/651-IntroNotes4.ppt>

(B) Consider the addition of the two 1s functions (with opposite phase):

This produces an MO over the molecule with a node between the atoms (it is also symmetrical about the H-H axis). This is known as an antibonding MO and is given the label σ^* because of its symmetry. The

star indicates antibonding. The out of phase overlapping decreases the amount of electron density between the two nuclei(Figure3)

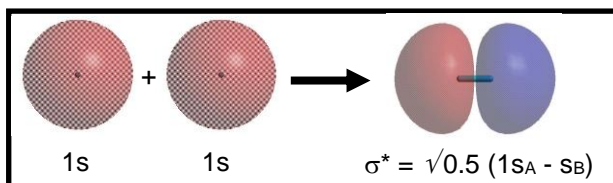


Figure3. Out of phase addition of two atomic orbitals
<http://mutuslab.cs.uwindsor.ca/macdonald/Teaching/651-class/651-IntroNotes4.ppt>

The increase of electron density between the nuclei from the in-phase overlap decreases the repulsion between positive charges. Therefore energy of MO is lower than the corresponding antibonding MO or two non-bonded H atoms. On this basis the molecular orbital diagram can now be constructed. To understand the symmetry of the different MO's, we label each MO with subscripts g and u. electrons are added in MO diagram following the Aufbau principle.

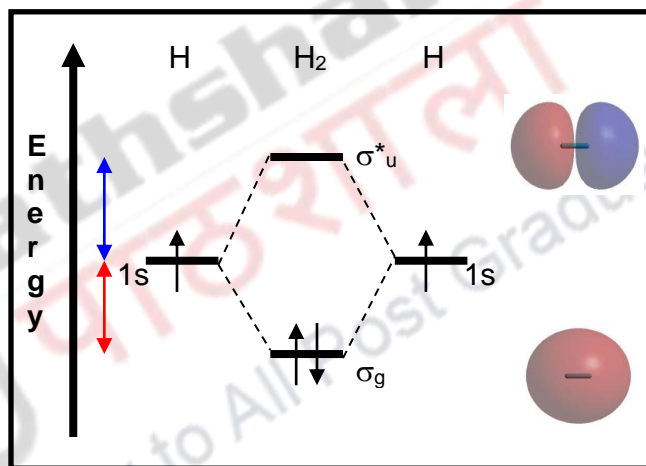


Figure4. Molecular Orbital Diagram of H₂ molecule
<http://mutuslab.cs.uwindsor.ca/macdonald/Teaching/651-class/651-IntroNotes4.ppt>

3.2 Principles of Ligand Field Theory

In coordination chemistry, the ligand acts as a Lewis base because it is capable of donating a pair of electrons and metal is a Lewis acid that accept a pair of electrons resulting covalent bond between metal and the ligand. This is also called as a coordinate covalent bond or a dative covalent bond in order to show that both the bonds are formed from electron coming from the ligand. A more specified description of bonding in the coordination complexes is given by Ligand Field Theory. Essentially LFT is able to give an understanding of the true origins of Δ_o and the spectrochemical series by taking into account the roles of σ - and π - bonding in transition metal chemistry.

The Ligand Field Theory based on the same principle that of Molecular Orbital Theory.

- 1) One or more orbitals on the ligand overlap with one or more atomic orbitals on the metal.
- 2) If the metal and ligand-based orbitals have similar energies and compatible symmetries, a net interaction exists.
- 3) The net interaction produces a new set of orbitals, one bonding and the other antibonding in nature. (An * indicates an orbital is antibonding.)
- 4) Where no net interaction exists, the original atomic and molecular orbitals are unaffected and are nonbonding in nature as regards the metal-ligand interaction.
- 5) Bonding and antibonding orbitals are of sigma (σ) or pi (π) character, depending upon whether the bonding or antibonding interaction lies along the line connecting the metal and the ligand. (Delta (δ) bonding is also possible, but it is unusual and is relatively weak.)

The σ bonding interactions always involve the ligand acting as a Lewis base and the metal as a Lewis acid, the π bonding may involve donation of electrons from the ligand to the metal or donation of electrons from the metal to the ligand. (The latter interaction is known as π back-bonding.)

4. Molecular Orbital Theory of Octahedral Complexes- $[\text{ML}_6]^{n+}$

4.1 Ligand Consideration

In the formation of transition metal complexes, there is required central metal atom/ion and the surrounding ligands. The geometry and nature of the complex depends upon the type of the metal as well as ligands. The ligands in this context can be of various types:

- (a) σ donor
- (b) π donors
- (c) $\sigma+\pi$ donors
- (c) π acceptors

4.2 Sigma(σ) bonding

In an octahedral arrangement of ligands, in order to draw the Molecular Orbital diagram we must first generate the symmetry adapted linear combinations (SALC) for the ligand donor orbitals.

Table1. Character Table for the octahedral symmetry

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
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, xz, yz)
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		
Γ	6	0	0	2	2	0	0	0	4	2		$x^2 + y^2 + z^2$
A_{1g}	1	1	1	1	1	1	1	1	1	1		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$

Considering only the s-orbitals on the ligands, there are a total of six orbitals and in an octahedral symmetry environment, they transform as $A_{1g} + E_g + T_{1u}$. This can be seen from the character table shown below (Table1) The metal orbitals to be considered are the nd-orbitals, and the (n+1)s- and (n+1)p-orbitals. From the character table shown above and the figure shown below (figure5), it can be seen that the A_{1g} group of orbitals have the same symmetry as an s orbital on the central metal. The T_{1u} groups of orbitals have symmetry similar to the p orbitals on the central metal. The E_g groups of orbitals have the similar symmetry as the d_{z^2} and $d_{x^2-y^2}$ orbitals on the central metal. The d_{xy} , d_{yz} and d_{xz} orbitals on the metal will be non-bonding when considering σ bonding because the ligands don't have a combination with t_{2g} symmetry.

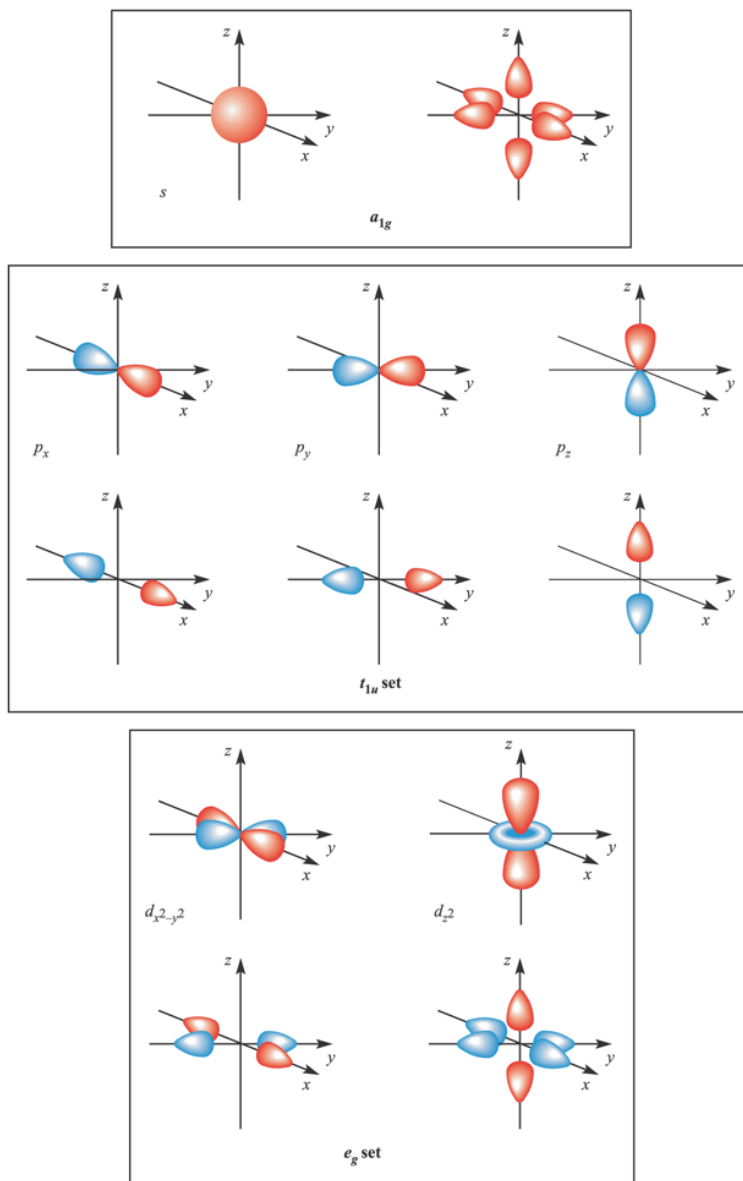


Figure 5. Metal atomic orbitals s , p_x , p_y , p_z , $d_{x^2-y^2}$, d_{z^2} matched by symmetry with ligand group orbitals for an octahedral complex with only σ bonding. (taken from Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition)

Considering an octahedral complex having all the six ligands with single valence orbital of σ symmetry focused toward the central metal atom. Such ligands are called “sigma donor ligands” and can be neutral (eg. NH_3), or charged (eg. F^-). In an octahedral environment, the metal orbitals are divided into four sets according to symmetry given in the labels that describe their symmetry and multiplicity (Table 2). These symmetry labels (also called Mulliken Symbols) are important to explain the sets of orbitals in a complex, which can only relate with a ligand set of orbitals that is described by the same label.

Table2. Symmetry sets of the Metal Orbitals

Metal Orbital	Symmetry Label	Degeneracy
s	A_{1g}	1
px, py, pz	T_{1u}	3
dxy, dyx, dxz	T_{2g}	3
dx^2-y^2, dz^2	E_g	2

Molecular orbitals for the given complex can be formed by combination of SALCs and metal orbitals with similar symmetry. Six metal orbitals can be divided into three groups according to their symmetry (A_{1g} , T_{1u} and E_g) and six ligand SALCs, these combine to form 6 bonding and 6 antibonding MOs. The metal T_{2g} set remains non-bonding (Figure6)

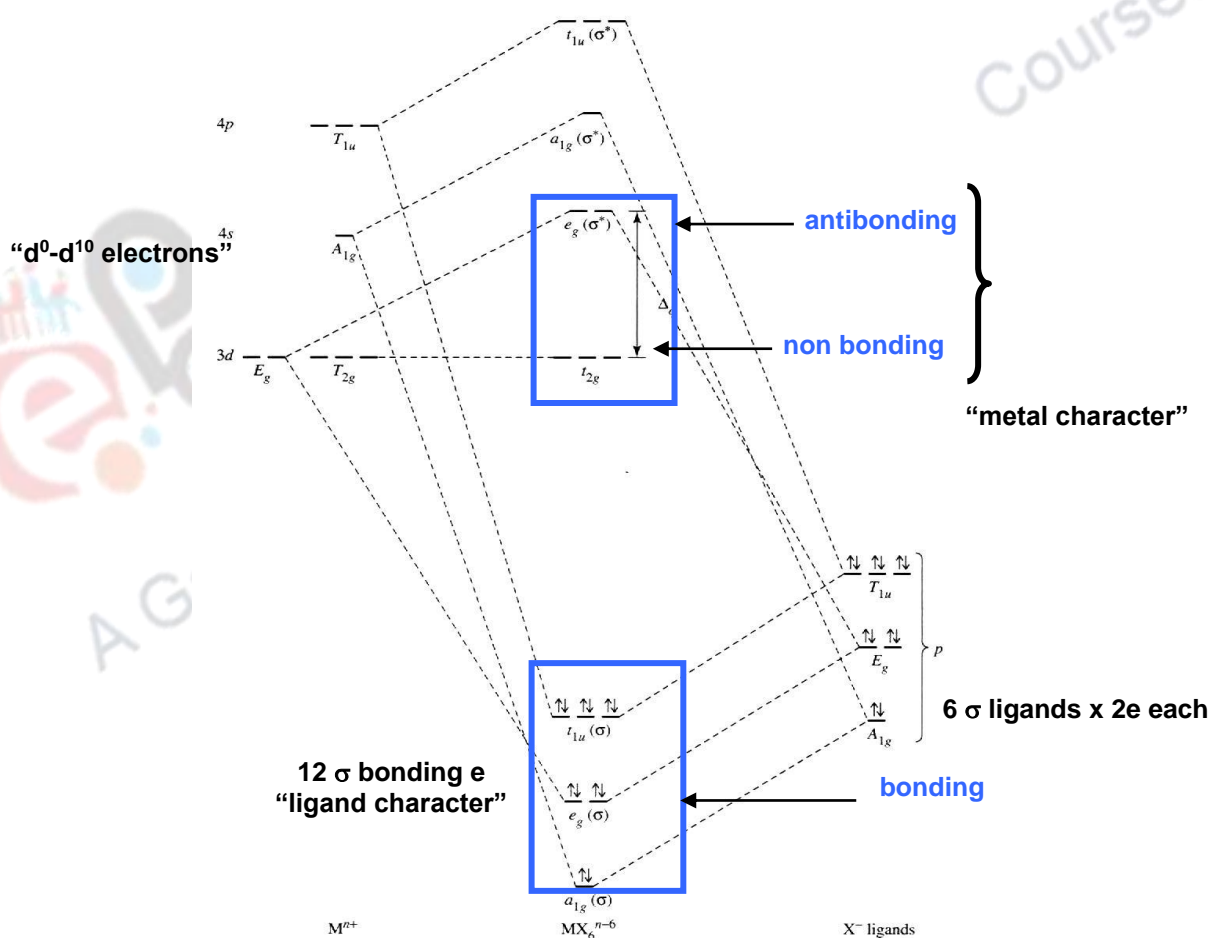


Figure6. MO diagram for the formation of $[ML_6]^{n+}$ complex using ligand group orbital approach. The bonding involves only M-L σ interactions. (taken from Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition)

The MO diagram formed can now be filled with the electrons according to the Aufbau, Pauli's and Hund's rule. The maximum contribution to the molecular orbitals of lowest energy is from atomic orbitals of lowest energy which in most of the cases (particularly those of period 2 and 3) in the main group) is from the ligand σ orbitals, with lower energy than the metal d-orbitals. Thus, the six bonding molecular orbitals of the complex formed are mainly ligand based in character.

These six bonding orbitals can accommodate the 12 electrons provided by the six ligand lone pairs. Therefore, the electrons provided by the ligands are largely confined to the ligands in the complex. The d electrons of the metal centre occupy the lower energy, non-bonding t_{2g} set and the higher energy, antibonding e_g set. Therefore, the metal based d electrons tend to reside largely on the metal atom. The octahedral ligand field splitting parameter, Δ_o , in this approach is called the HOMO-LUMO separation, or HOMO-LUMO gap (figure 6).

It is approximately the splitting of the metal d orbitals caused by the ligands, whereas in CFT Δ_o is purely a metal d orbital separation. Good σ -donor ligands (eg. CH_3^- and H^-) result in strong metal-ligand overlap resulting in higher value of Δ_o .

4.3 MO Diagrams of various octahedral complexes

In this section we will discuss the molecular orbital diagrams of various octahedral complexes having ligands which are sigma (σ) donors. Depending on the strength of sigma donation, ligands can be differentiated into strong or weak field ligands. The ligands which have strong sigma donation such as NH_3 , CH_3^- , H^- etc lead to increase in the value of Δ_o by increasing the gap between T_{2g} and E_g levels (Figure 7). Thus these ligand leads to the formation of low spin complexes. Otherwise the weak field ligands such as Cl^- , Br^- , S^{2-} etc which have small sigma donation leads to the formation of high spin complexes (Figure 8). It is to be worth noting that the ligands having weak sigma donation can have π donation as well. Order of coulomb energies for metal and ligand orbitals is in the order,

$$\sigma(\text{L}) < nd < (n+1)s < (n+1)p$$

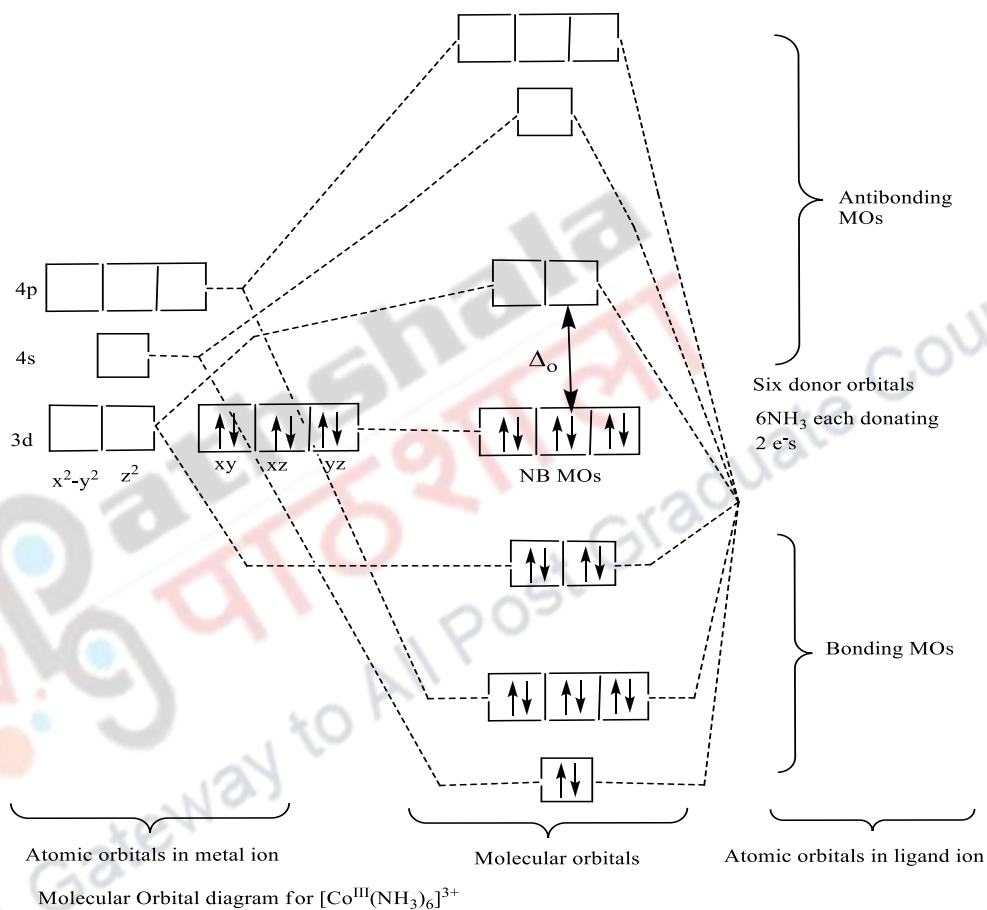


Figure 7. MO diagram for the formation of $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex using ligand group orbital approach. The bonding involves only M-L σ interactions.

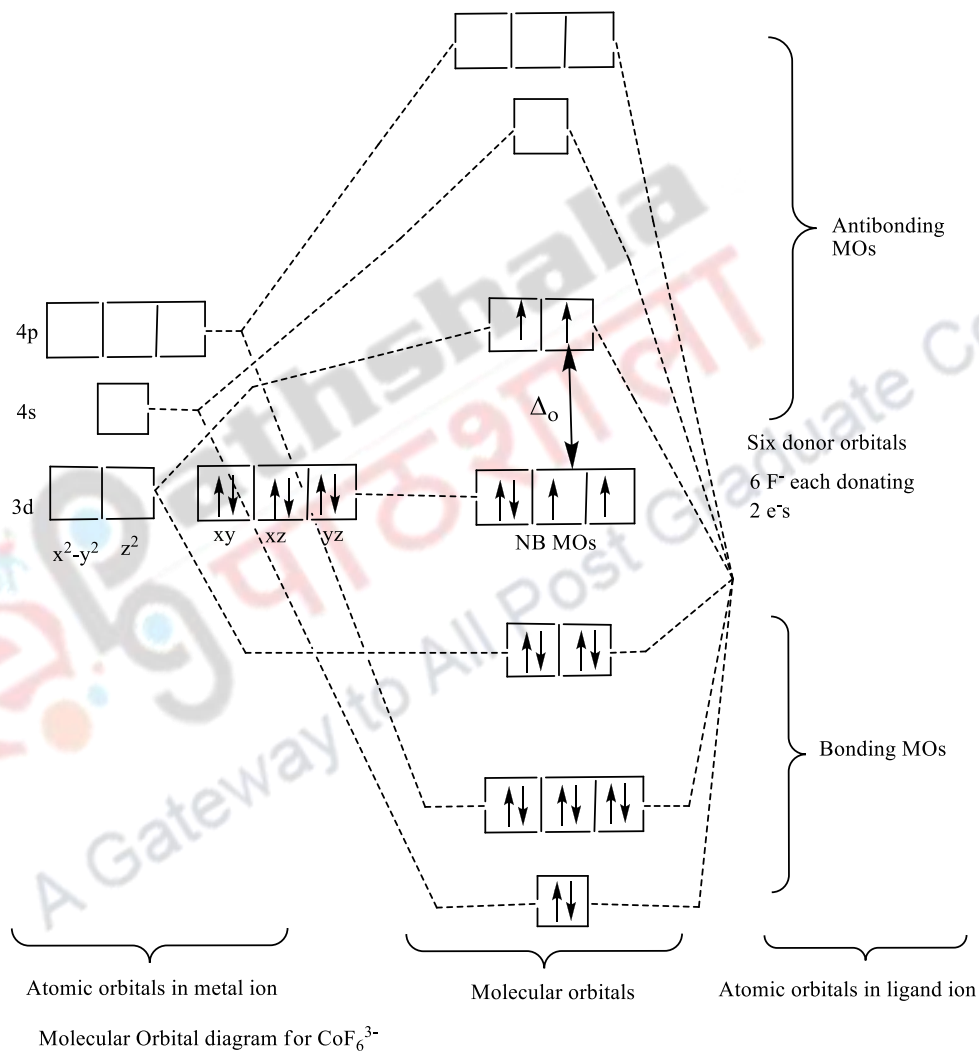


Figure 8. MO diagram for the formation of $[\text{CoF}_6]^{3-}$ complex using ligand group orbital approach. The bonding involves only M-L σ interactions.

5. Summary

- The shortcomings of the Crystal field Theory gave rise to the evolution of Ligand Field Theory
- The Ligand Field Theory incorporates Crystal Field Theory with the Molecular Orbital Theory can better explain the coordination complexes.
- The main postulates of the Molecular Orbital Theory are well compatible with that of Ligand Field Theory.
- Ligands can be of various types such as
 - (a) σ donor
 - (b) π donors
 - (c) $\sigma+\pi$ donors
 - (c) π acceptors
- Symmetry adapted linear combinations of the various atomic orbitals for the ligand molecule is done which forms the specified molecular orbitals with overlapment with metal orbitals of matching symmetry.
- Molecular orbitals for the given complex can be formed by combination of SALCs and metal orbitals with similar symmetry. Six metal orbitals can be divided into three groups according to their symmetry (A_{1g} , T_{1u} and E_g) and six ligand SALCs, these combine to form 6 bonding and 6 antibonding MOs. The metal T_{2g} set remains non-bonding
- Good σ -donor ligands (eg. CH_3^- and H^-) result in strong metal-ligand overlap resulting in higher value of Δ_o .