Molecular Orbital Theory

or Ligand field theory

The molecular orbital theory is more complicated than the valence bond and Crystal field theory. M.O theory explains more satisfactorily the nature of bonding involved in Co-ordination Complexes.

To understand M.O theory of Metal - Ligand bond we use group theory terminology and symbols

where a refers Non degenerated

e refers Doubly degenerated

Doubly or Tritly degenrated orbitals imply two orbital of same energy, and three Orbitals of the same energy respectively.

The Symmetry Symbol for a particular orbital of a metal may be different in different environments.

Thus a p orbitals of a metal has t_{1u} Symmetry in Octahedra complexes, whereas it has t_2 Symmetry in terahedral environment.

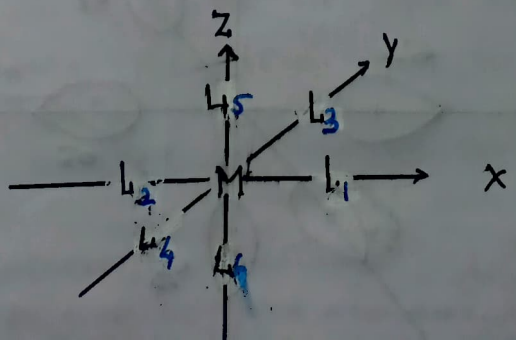
For an effective combination of atomic orbitals to form molecular orbitals the following requirments are needed.

1. The Symmetry of the combining atomic orbitals must be the same so that the additive combination of atomic orbitals permits the maximum overlap of orbitals.

2. The difference in the energies of the combining orbitals is not large.

3. If the two atomic orbitals orbitals are unequal energies, then the bonding molecular orbital would have more characteristics of the lower energy atomic orbital and the antibonding molecular orbital would have more chaharacteristics of the higher energy atomic orbitals, the greater would be the incorporation of the Character of the lower energy atomic orbital in the binding molecular orbital and the greater would be the incorporation of the character of the higher energy atomic orbital in the antibonding molecular orbital.

Now we shall discuss the molecular orbital theory to explain the nature of bonding in Co-ordination Complex-



The MO's we shall be using here ... and we shall consider the formation of MO's specifically in Octahedral Complexes only.

MOT as applied to Octahedral Complexes.

According to MOT the metal ligand σ bonding in Octahedral Complexes results from the Overlap of Suitable atomic Orbitals of the Central metallic Cation with Ligand σ orbitals.

The formation of Six metal - Ligand σ bonds (or MO's) in an Octahedral Complex takes place through the following steps: -

(i) The Central metal Cation of 3d Series elements Contains in all Nine Valence-shell atomic orbitals, which are 4s, $4p_x$, $4p_y$, $4p_z$, $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, & $3d_{x^2-y^2}$, $3d_{z^2}$

All the nine atomic orbitas have been grouped in to four Symmetry Classes, which are given below: -

$4s \longrightarrow A_{1g}$ or a_{1g}

$4p_x, 4p_y, 4p_z \longrightarrow T_{1u}$ or t_{1u}

$3d_{x^2-y^2}, 3d_{z^2} \longrightarrow E_g$ or e_g

$3d_{xy}, 3d_{yz}, 3d_{xz} \longrightarrow T_{2g}$ or t_{2g}

In Case of Octahedral Complex, Six σ - Orbitals of the Six ligands are approaching along the axes represented below.