Molecular Orbital Theory (MOT)

- The crystal field theory fails to explain many physical properties of the transition metal complexes because it does not consider the interaction between the metal and ligand orbitals.
- The molecular orbital theory can be very well applied to transition metal complexes to rationalize the covalent as well as the ionic character in the metal-ligand bond.

- A transition metal ion has nine valence atomic orbitals which are consisted of five *nd*, three (*n*+1)*p*, and one (*n*+1)*s* orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands.
- The molecular orbital theory is highly dependent on the geometry of the complex and can successfully be used for describing octahedral complexes, tetrahedral and square-planar complexes. The main features of molecular orbital theory for metal complexes are as follows:

Postulates of MOT

- The atomic orbital of the metal center and of surrounding ligands combine to form new orbitals, known as molecular orbitals.
- The number of molecular orbitals formed is the same as that of the number of atomic orbitals combined.

- The additive overlap results in the bonding molecular orbital while the subtractive overlap results in the anti-bonding overlap.
- The energy of bonding molecular orbitals is lower than their nonbonding counterparts while the energy of anti-bonding molecular orbitals is higher than that of nonbonding orbitals.

- The energy of nonbonding orbitals remains the same.
- The ionic character of the covalent bond arises from the difference in the energy of combining orbitals.
- If the energy of a molecular orbital is comparable to an atomic orbital, it will not be very much different in nature from atomic orbital.

Polarity Explanation of Molecular orbitals

- The polarity of the bond can be explained by considering the overlap of two atomic orbitals of different energies.
- Suppose φA and φB are two atomic orbitals of atoms A and B, respectively. These two atomic orbitals have one electron in each of them and combine to form one bonding (σ) and one anti-bonding (σ^*) molecular orbital. After the formation of molecular orbitals, both electrons occupy σ-orbital.

- Now, if the energy of σ-orbital is closer to φA, it will have more φA character and hence the electron density of both of the electrons will be concentrated more on atom A than B.
- Similarly, if the energy of σ-orbital is closer to φB, it will have more φB character and the electron density of both of the electrons will be concentrated more on atom B than A. This same explanation holds for the ionic character in metal-ligand bond.