Teacher : Dr. Naorem Premjit Singh (Inorganic Chemistry)

Class – B. Sc. (H) IV semester, Section-B

Date : 18-03-2020

Molecular Orbital Theory (MOT)

- CFT consider that the bonding in metal complex is purely electrostatic interaction between the metal and ligand and it doesn't consider about covalent bonding in a complex. However some physical measurements suggest that there is some measure of covalent bonding also in complexes.
- This covalent bonding in a complex can be considered in terms of Molecular orbital.
- According to MOT theory, the bonding in between metal and ligand in a complex is formed by the overlapping of suitable atomic orbitals of metal and the ligand.
- In the formation of a molecular orbital, the two atomic orbitals which is going to be overlapped i.e., metal and ligand should be of same symmetry and same or nearly same energy, which means that an atomic orbital of metal can be overlapped with only that orbital of ligand having the same symmetry and same and nearly same energy.
- The number of molecular orbital produced is equal to the total number of atomic orbital overlapped.

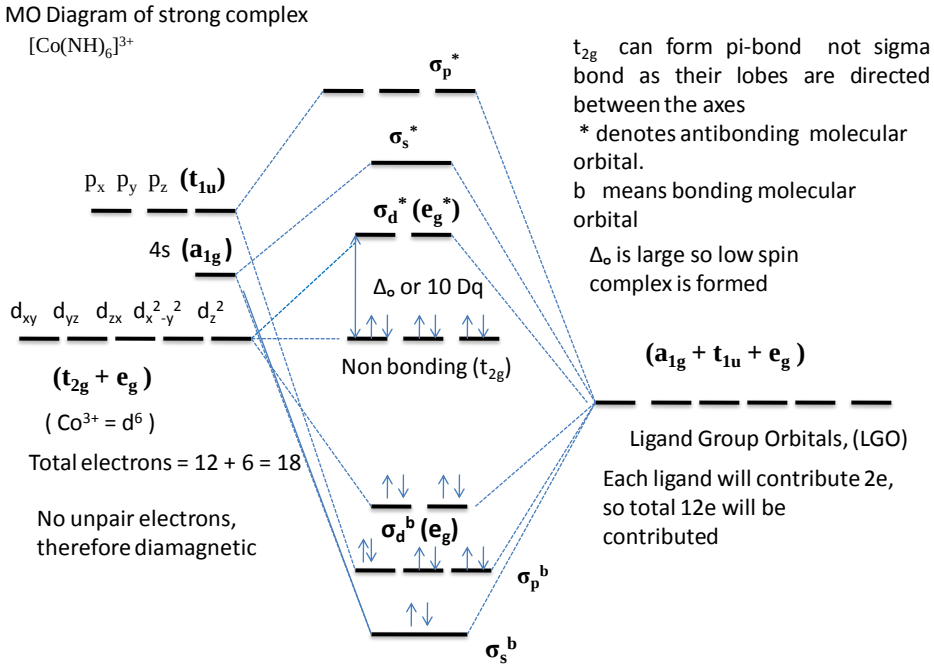
Consider for an Octahedral (Oh) complex: In an Oh complex there are six sigma (σ) bonds. The formation of this six (σ) bonds takes place as:

1) The central metal atom of transition elements contains 9 valence atomic orbitals say one ns, three np and five (n-1)d. They are ns, np_x, np_y, np_z, $(n-1)d_{xy}$, $(n-1)d_{yz}$, $(n-1)d_{zx}$, $(n-1)d_x^2$-$_y^2$ and$(n-1)$ d_z^2. Out of these 9 orbitals, only 6 orbitals should overlap with the ligand orbitals to form six σ bonds (because there are only six ligands in an octahedral complex)
2) According to the symmetry classes, the nine atomic orbitals of metal atom in an Oh complex can be transformed as
   S orbital as → a_{1g}
   p_x, p_y, p_z as → t_{1u}
   d_{xy}, d_{yz}, d_{zx} as →t_{2g}
   d_x^2-$_y^2$, d_z^2 → e_g
3) As ligands are approaching along the axes in an octahedral complex, the six atomic orbitals i.e, a_{1g}, t_{1u}, and e_g can form σ bond as their lobes are along the axes whereas the three atomic orbitals say t_{2g} remains as non bonding since their lobes are between

the axes. However they can form Π (pi) bond by sideways overlapping if there exist possibility of Π bonding.

4) The orbitals of ligands are combined to overlap with the metal orbitals to form σ bonds, they are collectively called ligand group orbitals (LGO) and hence they should have the same symmetry as $a_{1g,}$ $t_{1u,}$ and e_g.
5) As ligands orbital contained electrons and donated to the central atom in the formation of σ bonds their atomic orbitals are lower in energy than the metal atomic orbitals.
6) As the overlap of 4s and 4p metal orbitals with the ligand orbitals is considerably better than that of 3d (e_g) orbital, the bonding $a_{1g,}$ and t_{1u} molecular orbitals are lowest in energy and the antibonding a_{1g}^{*}, and t_{1u}^{*} are highest in energy.

Molecular orbital diagrams of strong field ligands showing the σ bond formation: $[Co(NH_3)_6]^{3+}$

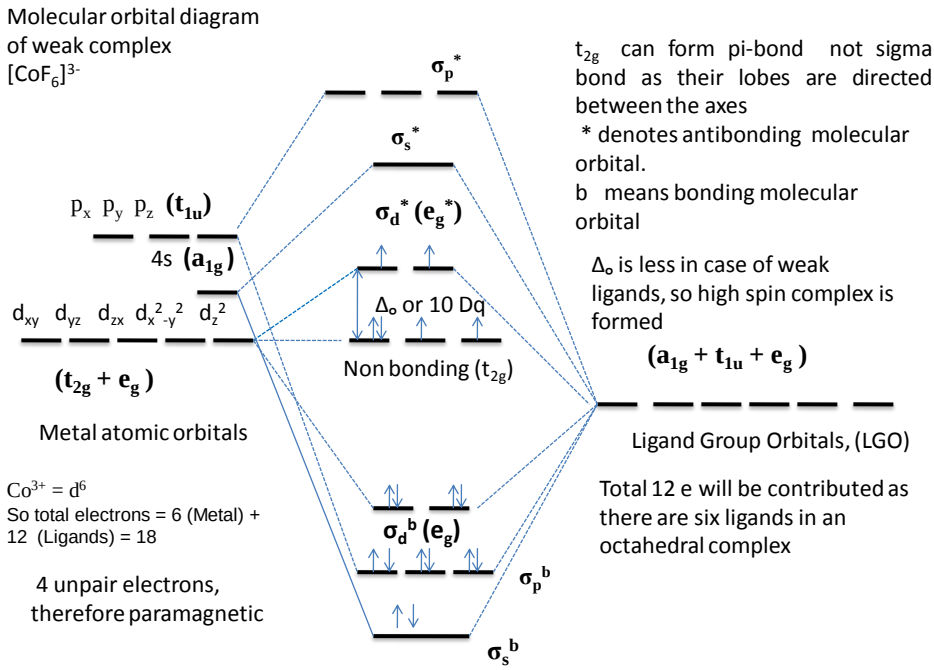


Atomic orbitals (Metal) (Molecular orbitals) Atomic orbitals (Ligands)

- Bonding molecular orbitals are more associated to the ligand group orbitals as the energy levels of ligand group orbitals is lower than of that of metal atomic orbitals.
- As the lobes of t_{2g} orbitals ($d_{xy,}$ $d_{yz,}$ d_{zx}) are directed between the axes, they cannot take part in σ bond formation since the ligand approaches along the axis in an oh (octahedral) complex. Therefore they are remaining as non-bonding orbital; hence their energy level is disturbed. However if there exist the possibility of Π bonding, their energy level can be disturbed due to the Π bond formation.

- Since bonding orbitals are more associated to ligand group orbitals, e_g^b (e_g bonding) is contributed from ligands. Therefore the d-splitting (Δ_o) is in between t_{2g} and e_g^* (e_g antibonding).
- As ligand is strong Δ_o is large, therefore the electrons in t_{2g} orbitals are pair up as $\Delta_o > p$ (pairing energy)
- Π bonding is not considered here

Molecular orbital diagrams of strong field ligands showing the σ bond formation: $[CoF_6]^{3-}$



Atomic orbital (Metal) (Molecular orbitals) Atomic orbital (Ligands)

- As ligand is weak, Δ_o is small, therefore the distribution of electrons takes place according to Hund's rule. Hence the t_{2g} orbitals are singly filled first and after all the orbitals are singly filled, pairing of electrons starts. Here $\Delta_o < p$ (pairing energy)
- Π bonding is not considered here