Molecular Orbital Theory : Octahedral Complexes

- In octahedral complexes, the molecular orbitals created by the coordination of metal center can be seen as resulting from the donation of two electrons by each of six σ-donor ligands to the *d*-orbitals on the metal.
- The metal orbitals taking part in this type of bonding are *nd*, (*n*+1)*p* and (*n*+1)*s*.
- It should be noted down that not all *nd*-orbitals but only d_z^2 *and* $d_{x^2-y^2}$ orbitals are capable of participating in the σ-overlap.
- The d_{xy}, d_{xz} and d_{yz} orbitals remain non-bonding orbitals.

- The ligands approach the metal center along the *x*, *y* and *z*-axes in such a way that their σ-symmetry orbitals form bonding and anti-bonding combinations with metal's *s*, p_x, p_y, p_z, d_z^2 *and* $d_{x^2-y^2}$ orbitals.
- For a first row transition metal series,the metal orbitals are :-
- i. 3s & 3p; filled low energy ; hence ineffective for overlap with ligand orbitals.

  ii.five 3d orbitals;partially filled and may be involved in bonding.

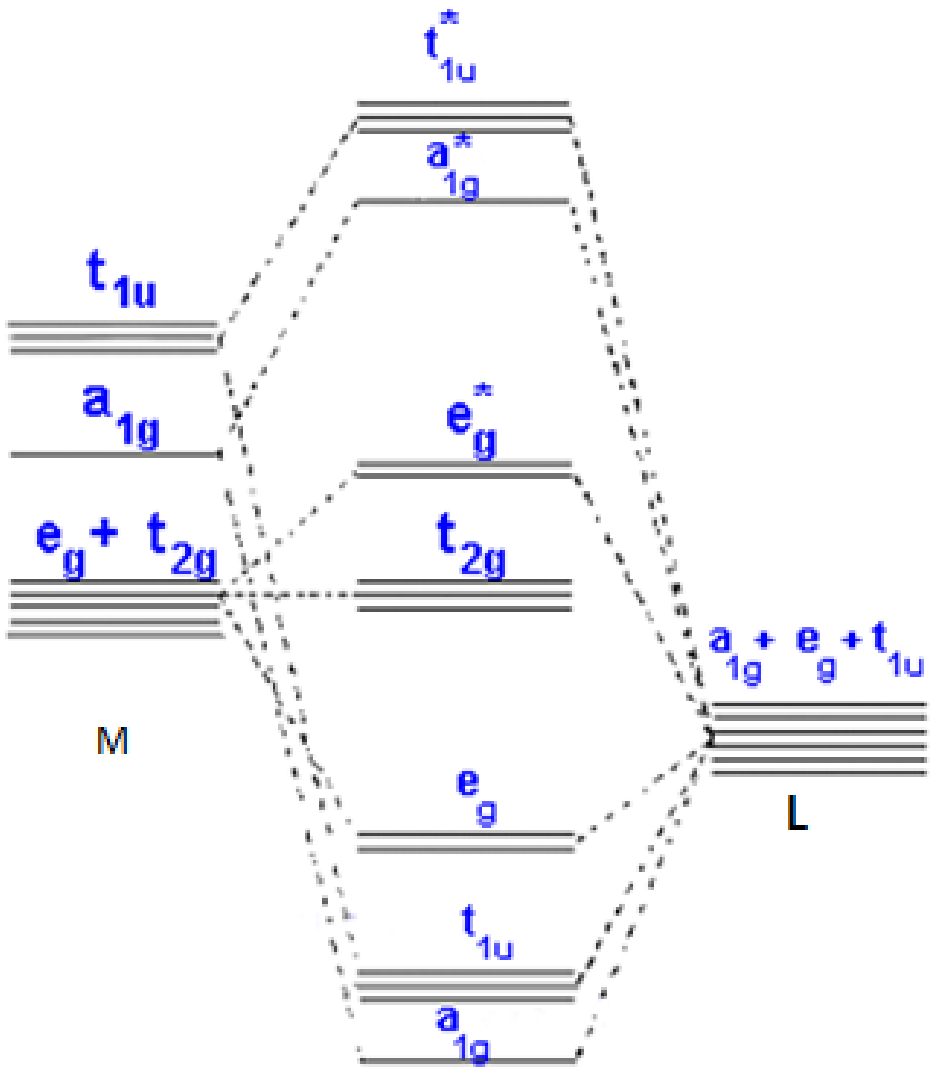
  iii.One 4s and Three 4p ;empty and somewhat higher energy than the 3d,May be involve in bonding.

- Out of nine metal orbitals six ($3d_{x^2-y^2}$,$3d_{z^2}$,4s,4p_x,4p_y,4p_z) have their lobes projected along the corners of the octahedron.
- A total of six bonding and six anti-bonding molecular orbitals formed. The symmetry designations of different metal orbitals taking part in octahedral overlap are:

Symmetry of Oh Complexes

$dz^2, dx2\text{-}y2$	–	eg
s	–	$a1g$
px, py, pz	–	$t1u$
dxy, dxz, dyz	–	$t2g$

MO Diagram of Octahedral Complex



Molecular Orbital Theory : Tetrahedral Complexes

- For a tetrahedral complex the nine metal orbitals may be classified according to their symmetry as follows.

s	–	$a1$
px, py, pz	–	$t2$
dxy, dxz, dyz	–	$t2$
$dz^2, dx^2{}_y{}^2$	–	e

- note that the subscribe g has been adopted since the system becomes non-centrosymmetric.
- . The ligand orbitals may be combined to form a set of three ligand group orbitals (t_2) and one orbital of a_1 symmetry.
- The ‘e’ orbitals of the metal can not entired sigma interaction with the ligand group of orbitals .
- Remaining non- bonding metal t_2 orbitals (both p and d) can be combined with the t_2 ligand group of orbitals to give three sets of σ-molecular orbitals, three bonding (t_2),three strongly antibonding(t_2*) and three slightly antibonding(t_2*).

- The a1 metal orbital and the a1 ligand group of orbitals similarly give rise to one bondning and one antibonding molecular orbitals.
- Δ_t corresponds to the separation between the e(nb) and the t_2* orbitals.

  The central portion of the molecular orbital diagram, thus resembles the description in crystal field theory.
- The MO energy level diagram in tetrahedral complex is shown in below.

MO Diagram of Tetrahedral Complex