

Molecular Orbital Theory:

In the molecular orbital theory, the valence electrons are considered to be associated with all the nuclei in the molecule. The atomic orbitals from different atom must be combined to produce molecular orbitals. The atomic orbital of the atom in a molecule completely loss their identity after the formation molecular orbitals. Electrons may be considered either as particle or waves. An electron in an atom may therefore be described as occupying an atomic orbital or by a wave function Ψ , which is a solution to the Schrodinger wave equation. Ψ is such that Ψ^2 represent the electron density. Each molecular orbital wave function (Ψ) is associated with a set of quantum number which ascertain the energy and the shape of the l=molecular orbital.

Ψ is associated with a definite energy value and the total energy of the molecule is the sum of the energies occupied molecular orbitals. Electrons tend to fill the molecular orbitals in the same way as they fill the atomic orbitals following the Aufbau principle, Pauli's exclusion principle and Hund's rule of multiplicity. Each electron in a molecular orbital belongs to all the nuclei present in the molecule. Each moving in a molecular orbital is having a spin of $+1/2$ or $-1/2$.

Basic difference between an atomic orbital and the molecular orbitalis that an electron in atomic orbital is influenced by one positive nucleus only while an electron in a molecular orbital is influenced by two or more nuclei depending upon the number of atom contained a molecule.

The wave function describing a molecular orbital may be obtained by one of two procedures:

- 1.Linear combination of atomic orbitals (LCAO) method
- 2.United atom method.

1.L.C.A.O. METHOD: Let two atom A and B which have two wave functions $\Psi_{(A)}$ and $\Psi_{(B)}$. If the electron cloud of these two atoms overlap then the wave function for the molecular orbital $\Psi_{(AB)}$ can be obtained by a linear combination of atomic orbitals $\Psi_{(A)}$ and $\Psi_{(B)}$:

$$\Psi_{(AB)} = N (C_1 \Psi_{(A)} + C_2 \Psi_{(B)})$$

Where N = normalizing constant,

C_1 and C_2 are constant chosen to a minimum energy for $\Psi_{(AB)}$.

If atom A and B are the same, then C_1 and C_2 are equal

In LCAO method two nuclei must approach one another along a line. When they come close to one another, two orbitals having comparable energies possessing large overlap combine to form two molecular orbitals. One of the new molecular orbitals has lower energy than the combining atomic orbitals and the other has higher energy than the combining atomic orbitals. The molecular orbital with higher energy than the atomic orbitals give rise to a repulsive state and is called antibonding orbital, while the molecular orbital with lower energy than atomic orbitals give rise to an attractive state and is called the bonding orbital.