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Engineering Chemistry
Unit-I : Atomic & Molecular Structure

Lesson-3

Molecular orbital theory

Molecular orbital theory-Hund Mulliken theory

- Limitations of valence bond theory – could not explain

  bond order

  bond length

  magnetic behavior of molecules.
- Proposed by Friedrich Hund & Robert S.Mulliken.
- Describe the structure and properties of different molecules using quantum mechanics.
- Electrons are not assigned to individual bonds but under the influence of all the nuclei in the molecule.

Key features

- According to LCAO , molecular orbitals are formed by the combination of atomic orbitals and have similar characteristics.

  MO are associated with energy.

  they can accommodate two electrons with opposite spin.

- Each and every electron in the molecular orbital belongs to all the nuclei of the molecule.
- Molecular orbital is the region where an electron resides . Each MO is described by a wave function Ψ.
- MOs are associated with the entire molecule.
- Conditions for overlapping of atomic orbitals

➢ same energy

➢ same symmetry

➢ extent of overlapping between the atomic orbitals.

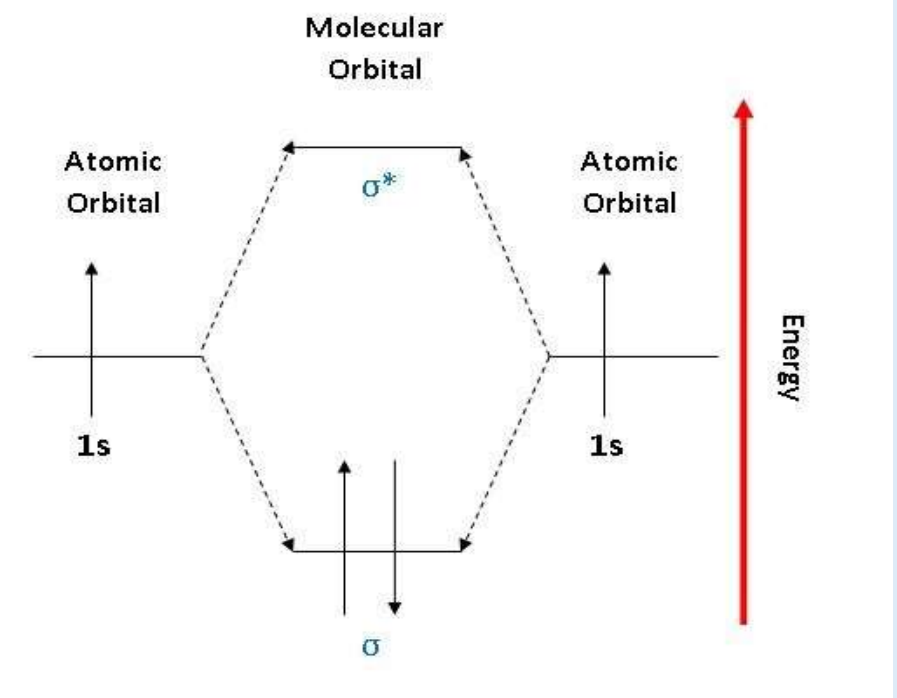
- The number of MOs formed is equal to number of overlapping Atomic orbitals
- The shapes of MOs depend on shape, size and orientation of AOs.
- MOs are arranged in the increasing order of their energy.

Types of MOs: According to LCAO , linear combination of AO take place by addition or subtraction of wave functions of atomic orbitals.

- Bonding MO
- Antibonding MO
- Non bonding orbitals

Order of energy:

BMO< NBO<ABMO



Bonding MO: σ, π, δ

Formed by the addition of wavefunctions of AO, constructive interference.

$$\Psi MO = (\psi A + \psi B)$$

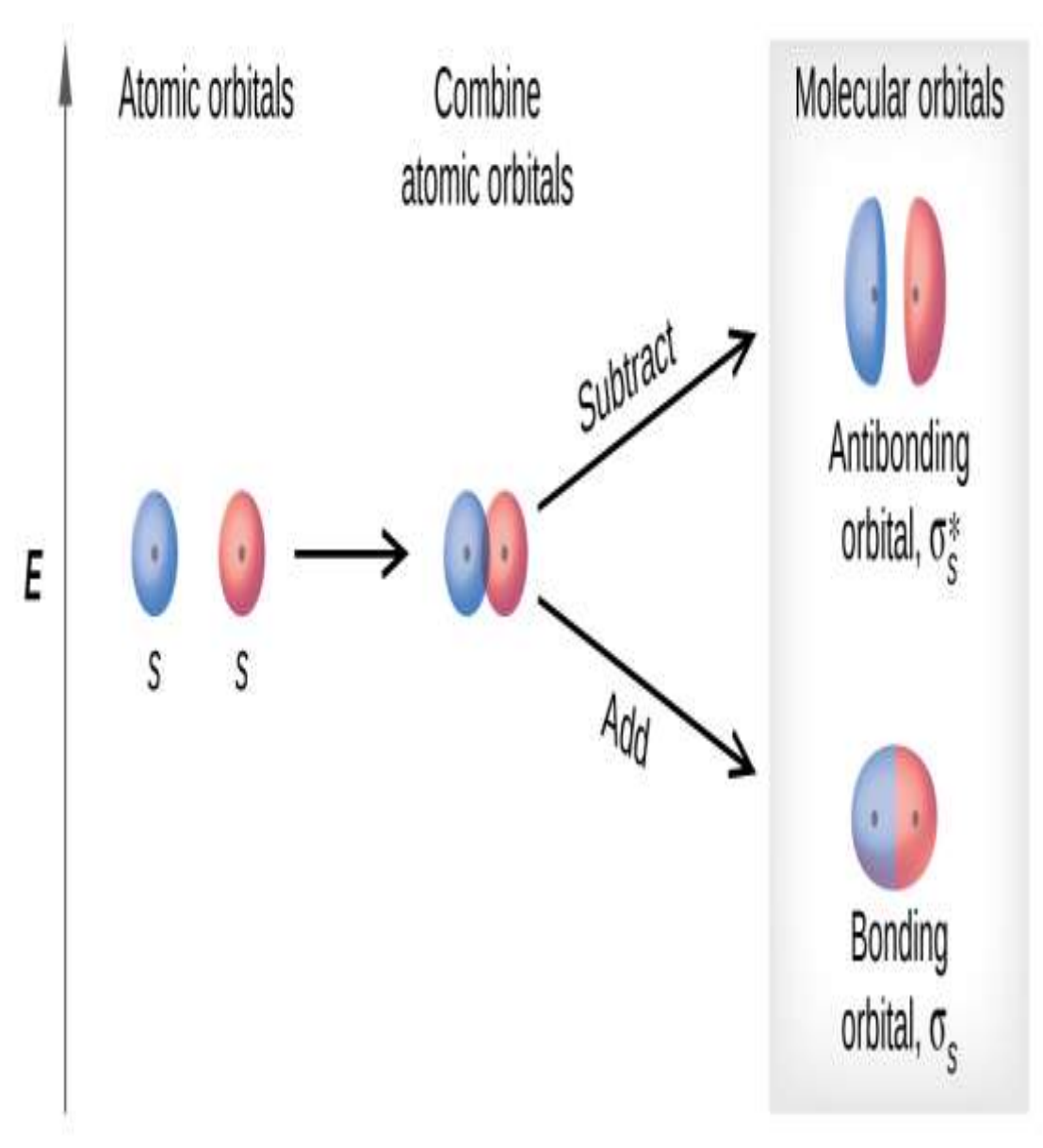
Posses high electron density between the nuclei and thus imparts stability to the molecule.

Anti Bonding MO: σ*, π*, δ*

Formed by the subtraction of wavefunctions of AO , destructive interference.

$$\Psi^* MO = (\psi A - \psi B)$$

Posses less electron density between the nuclei and thus imparts instability to the molecule.



- The probability of BMO formation (ψ^2) > ABMO formation (ψ^{*2})

Probability= square of amplitude

$\Psi^2 = (\psi A + \psi B)^2 = \psi^2 + \psi^2 + 2\psi A \psi B$

Shapes of Molecular orbitals

- When two atomic orbitals combine, they form molecular orbitals , which may be σ or π

  σ MO are formed by the overlap of two AO along internuclear axis

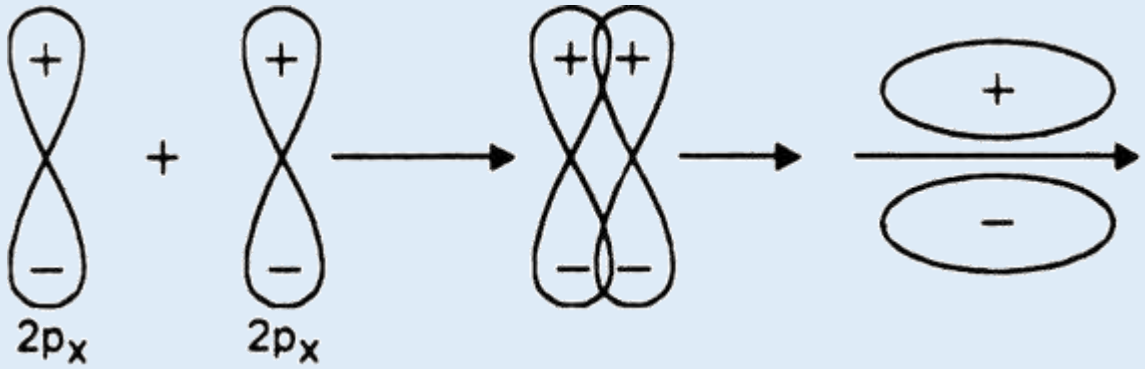
  π MO are formed by the sidewise overlap of two AO.

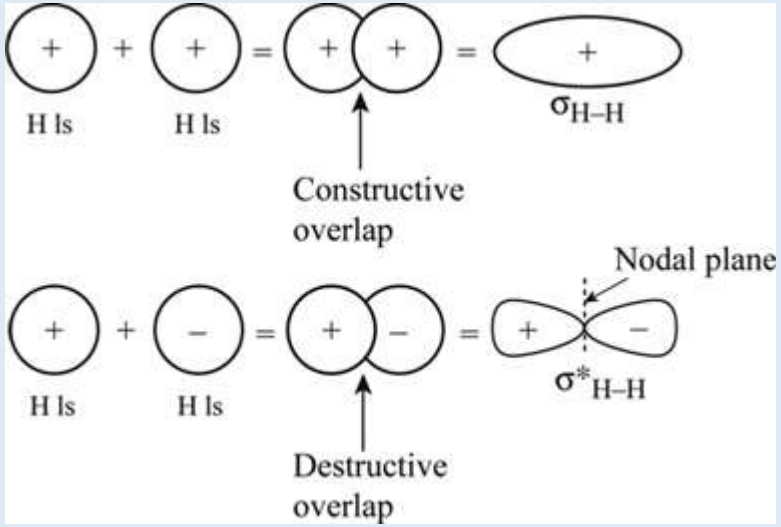
- The shape of MO depends on type of combining AO.

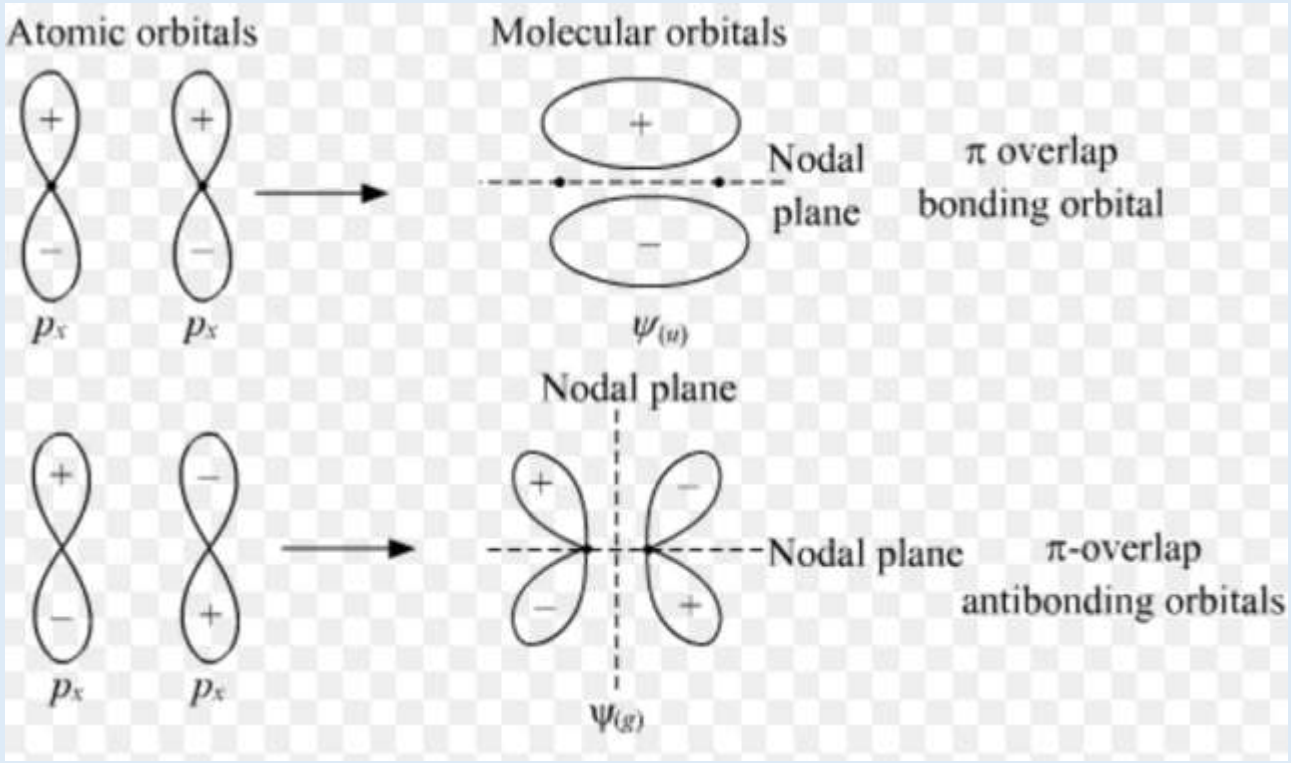
- BMO are designated as σ, π, δ and ABMO as σ*, π*, δ* .

- If the signs of the wave functions are the same i.e.,in-phase, a lower-energy (more stable) **bonding orbital** is produced.

- If the signs are different i.e., out-of phase, a higher-energy (less stable) **antibonding orbital** is produced.


2p$_x$
2p$_x$


H ls
H ls
σ_{H-H}
Constructive overlap
Nodal plane
H ls
H ls
σ^*_{H-H}
Destructive overlap


Atomic orbitals
Molecular orbitals
Nodal plane
π overlap
bonding orbital
p_x
p_x
$\psi_{(u)}$
Nodal plane
Nodal plane
π-overlap
antibonding orbitals
p_x
p_x
$\psi_{(g)}$

Filling of electrons in molecular orbitals

MO are arranged in the increasing order of their energy.

$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$

Electrons are filled in the same order based on

- Aufbau principle
- Pauli's exclusion principle
- Hund's rule of maximum multiplicity

Magnetic behavior of molecules:

- If all the electrons are paired, there is a slight repulsion and it is classified as diamagnetic.
- If unpaired electrons are present, it is attracted to a magnetic field, and therefore paramagnetic.

Bond order :

- B.O is the measure of strength of the bond between two atoms.

$$Bondorder = \frac{1}{2}[N_b - N_a]$$

Where,

Nb is the number of bonding electrons

Na is the number of antibonding electrons

- With increasing bond order , the bond length decreases .
- Higher the bond order, higher is the dissociation energy.

Bond order & stability of molecule

The bond order of a molecule is directly proportional to the stability of that molecule.

- Negative or zero value --- molecule is unstable & does not exist
- Positive value --- molecule is stable & exist