

Chemical Bonding - II

2.2. VSEPR Theory :-

(Valence shell electron pair repulsion)

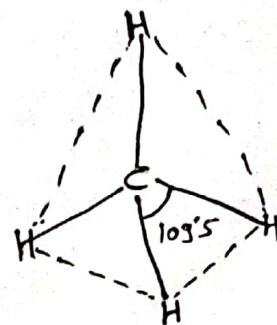
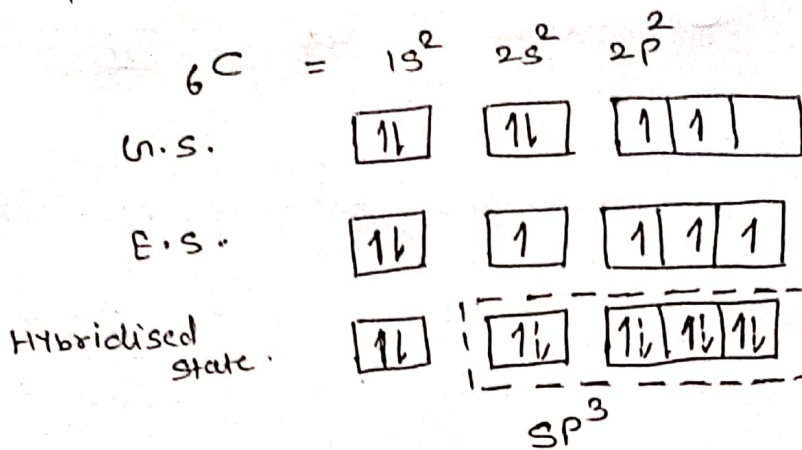
- VSEPR Theory is used to predict the shape of the molecules from the \bar{e} pairs that surround the central atoms of the molecule.
- The theory was first presented by Sidgwick & Powell in 1940. This theory is based on the assumption that the molecule will take a shape such that electronic repulsion in the valence shell of that atom is minimized.

Postulates of VSEPR Theory :-

- 1) In polyatomic molecules one of the constituent atoms is identified as the central atom to which all other atoms belonging to the molecule are linked.
- 2) The total number of valence shell \bar{e} pairs decides the shape of the molecule.
- 3) The \bar{e} pairs have a tendency to orient themselves in a way that minimizes the $e-e$ repulsion betⁿ them & maximizes the distance betⁿ them.
- 4) If the central atom of a molecule is surrounded by hybrid orbitals containing only shared pairs of \bar{e} i.e. bond pairs then the molecule has a regular geometry.
- 5) If the central atom is surrounded by one or more hybrid orbitals containing lone pairs of \bar{e} in the valence shell then the geometry of the molecule is distorted.

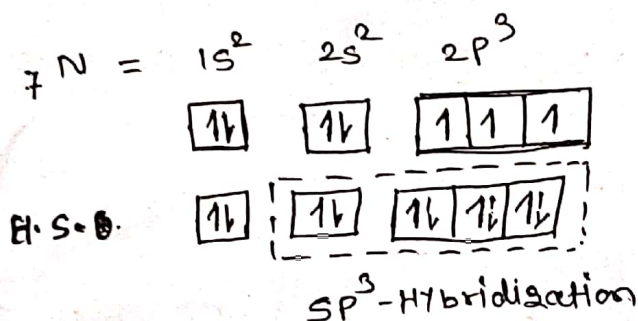
This is because $\{ \text{L.P.} - \text{L.P.} > \text{L.P.} - \text{B.P.} > \text{B.P.} - \text{B.P.} \}$
the repulsive interaction betⁿ L.P. & B.P.

① CH₄ molecule :-



Geometry - Tetrahedral.

② NH₃ molecule

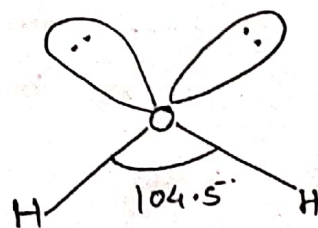
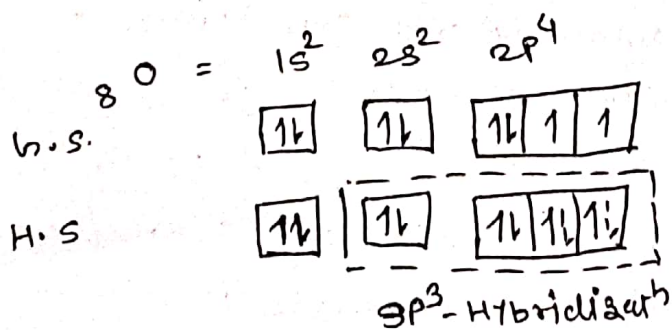


Geometry - Pyramidal.

Bond angle $\text{H}-\text{N}-\text{H} = 107^\circ$

According to VSEPR theory, the force of repulsion betⁿ a l.p. & b.p. is greater than the force of repulsion betⁿ b.p. \bar{e} s. Therefore NH₃ molecule gets a little distorted & the bond angle decrease from tetrahedral angle of 109.5° to 107°. & thus shape is pyramidal.

③ H₂O molecule :-



Geometry - Bent.

-V-shaped

molecular orbital Theory :-

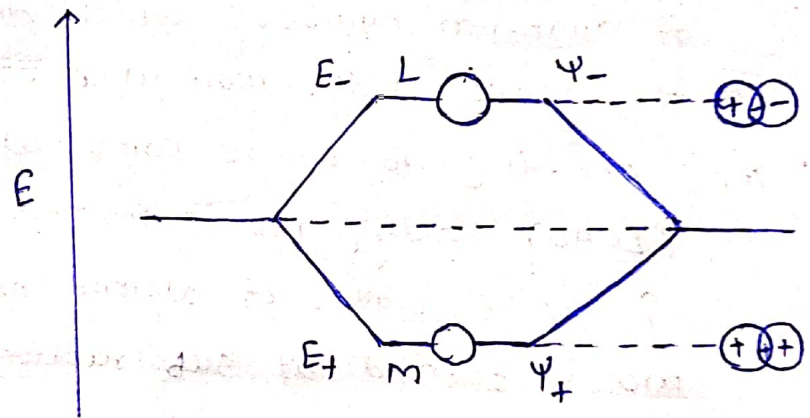
molecular orbital theory was put forwarded by Hunds & Mulliken.

The main points of this theory are as follows (Basic Principles)

- 1) When two atomic orbitals (AOs) combine, they lose their identity & form two new orbitals called molecular orbital. one of which is bonding molecular orbital (BMO) while the other is antibonding molecular orbital (ABMO)
- 2) Each MO is described by a wave function ψ , known as MO wave function.
- 3) Each MO wave function (ψ) is associated with a set of quantum numbers which determine the energy & the shape of the molecular orbital.
- 4) According to Linear combination of atomic orbitals (LCAO) bonding MO is formed by addition of wave functions of the \bar{e} waves of atomic orbitals, while antibonding MO is formed by subtraction of the wave functions of AO.
- 5) The \bar{e} present in BMO result in attraction betⁿ the atoms & hence contribute towards stability of the molecule. In contrast, \bar{e} present in ABMO contribute to the repulsion betⁿ two atoms. i.e. the energy of the bonding MO is less than those of the combining AOs while the energy of the antibonding MO is more than those of combining AOs.
- 6) Only AOs of comparable energies & proper orientation combine to form MOs. e.g. 1s combine with 1s & not with 2s.
- 7) \bar{e} fill the MOs in the same way as they fill the AO following aufbau principle, Pauli's exclusion principle & Hund's rule of maximum multiplicity.

Linear combination of Atomic orbital (LCAO)

- 1) A LCAO ψ_A & ψ_B leads to the formation of two molecular orbitals ψ_+ & ψ_-
- 2) The energy E_+ of MO ψ_+ is lower than either E_A & E_B . It is therefore designated as BMO
- 3) The energy E_- of MO ψ_- is higher than either E_A & E_B . It is therefore designated as ABMO.
- 4) The extent of lowering of energy of the BMO is equal to the extent of increase of energy of the ABMO



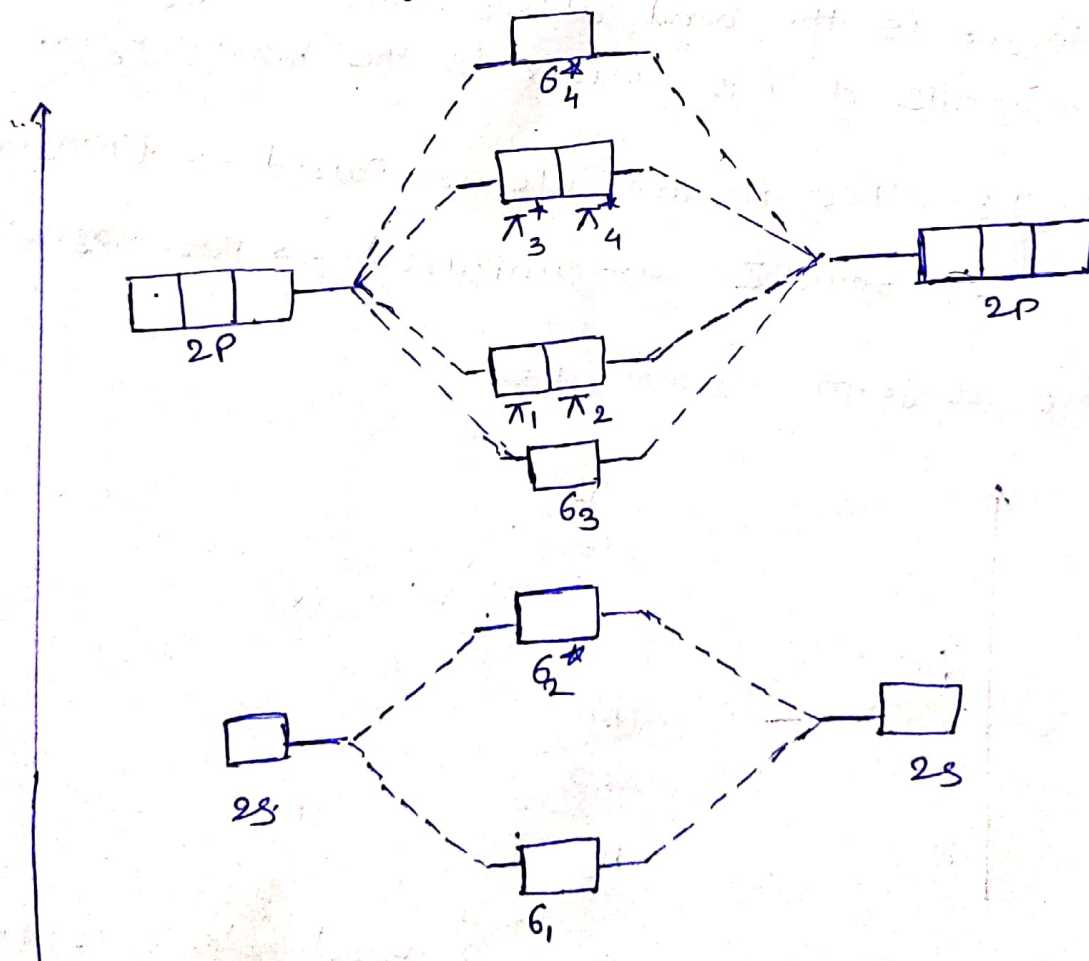
Energies of Bonding & ABMO.

- 5) LCAO calculation show that the greater the overlap of the two combining atomic orbitals ψ_A & ψ_B the lower would be the energy of the BMO (ψ_+) formed.

* Difference betⁿ BMO & ABMO

BMO	ABMO
1) It is formed by the add ⁿ overlap of atomic orbital	1) Formed by the subtraction of AO
2) It has lower energy than AOs from which is formed	2) It has higher energy than the AOs from which it is formed.
3) \bar{e} density of charge in bet ⁿ the nuclei is high	3) \bar{e} charge density in bet ⁿ the nuclei is low.
4) Repulsion bet ⁿ the nuclei is very low.	4) Repulsion bet ⁿ nuclei is high
5) \bar{e} in the BMO favour stable bond form ⁿ	5) \bar{e} in ABMO oppose bond form ⁿ .

② Energy Level diagram for molecular orbitals



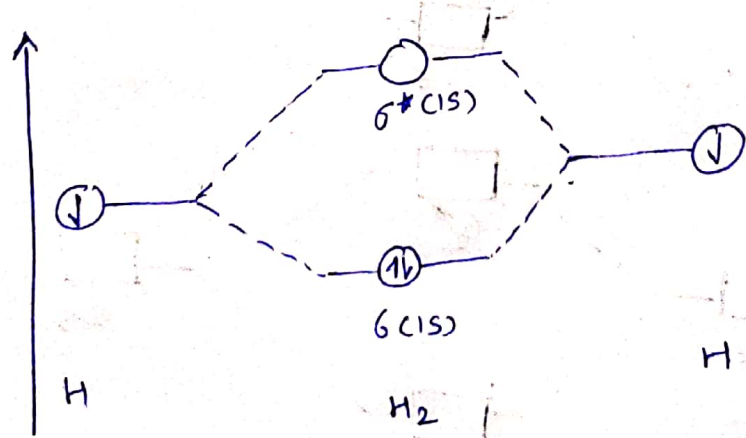
① Rules for adding \bar{e} in mos :-

- 1) The molecular orbital with lowest is filled first.
- 2) The maximum number of \bar{e} in a molecular orbital cannot exceed two & the two \bar{e} must be of opposite spin.
- 3) If there are two or more mo at the same energy level, pairing of \bar{e} will occur only after each orbital of the same energy has one \bar{e} .

$$\text{Bond order} = \frac{1}{2} [\text{no. of } \bar{e} \text{ in } \text{BMOs} - \text{no. of } \bar{e} \text{ ABMO}]$$

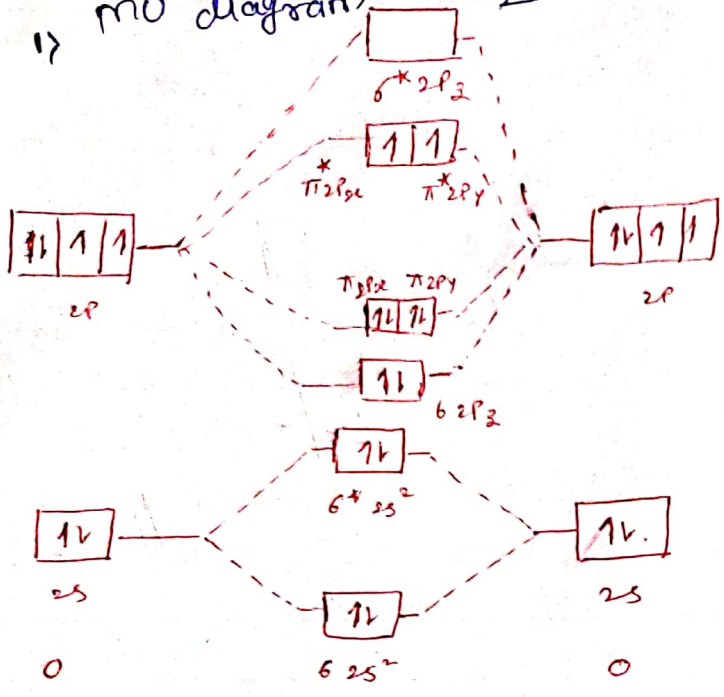
- The bond order of a molecule is directly proportional to its bond ~~order~~ dissociation energy & inversely proportional to its bond length.
- It means that the higher the bond order, the larger is the bond dissociation energy of the molecule & the smaller is the bond length.
- If all \bar{e} in molecule are paired \rightarrow diamagnetic
If some \bar{e} are unpaired \rightarrow paramagnetic.

② mo diagram H_2 molecule



E.c. $H_2 = \sigma(1s)$ & Bond order = $\frac{1}{2}(2-0) = 1$

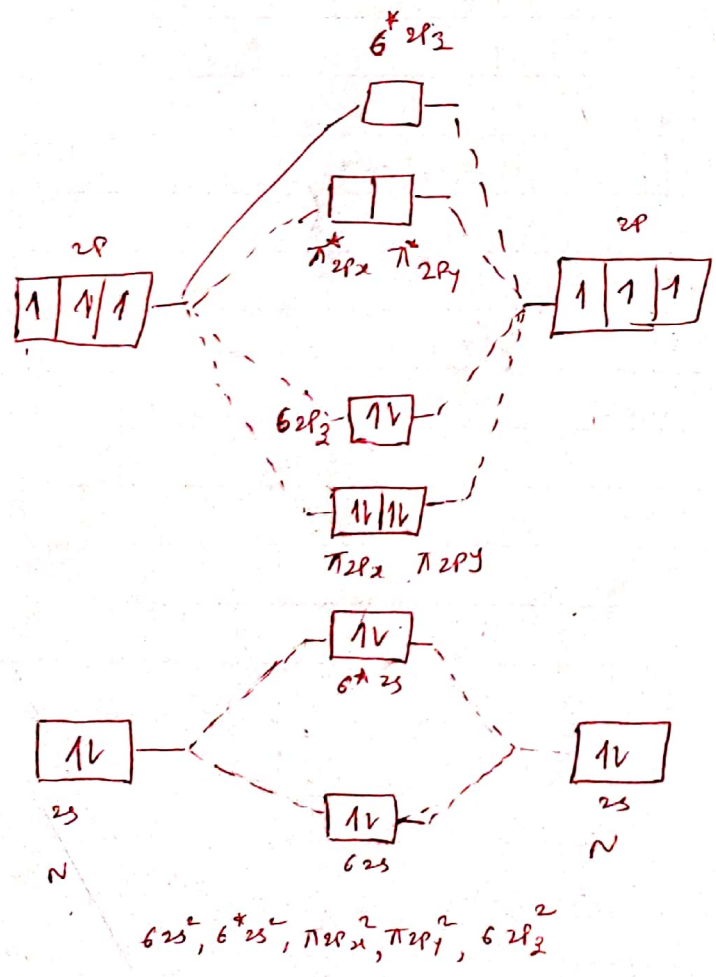
1) MO diagram of O₂



There is negligible mixing of $\sigma 2s$ and $\sigma 2p$

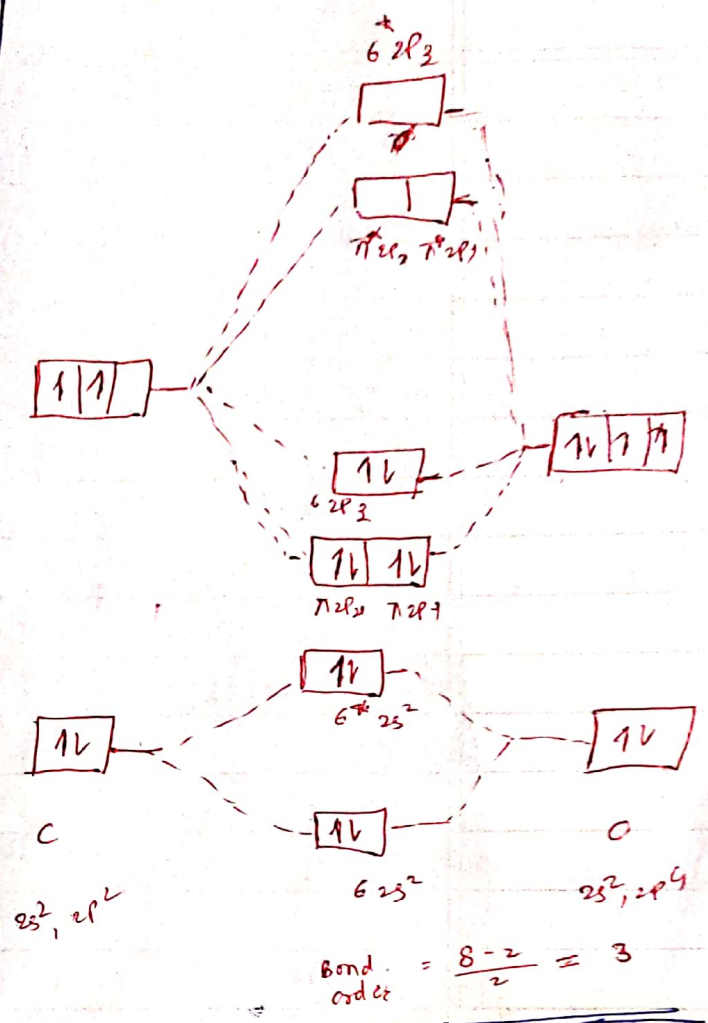
E.g. $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^1, \pi^* 2p_y^1$

2) MO diagram of N₂



$\sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2, \sigma 2p^2$

3) For CO



Bond order = $\frac{8-2}{2} = 3$

Assignment 1

1) Draw the MO diagram for Ne₂.