

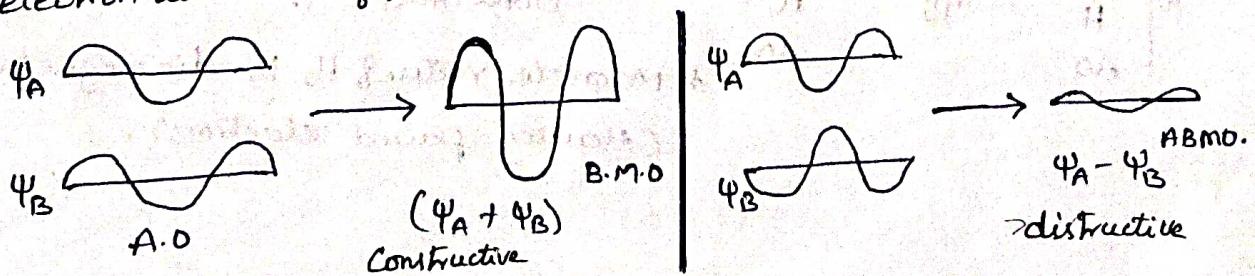
UNIT-I
STRUCTURE & BONDING MODELS

(1)

Molecular orbital theory: (MOT):

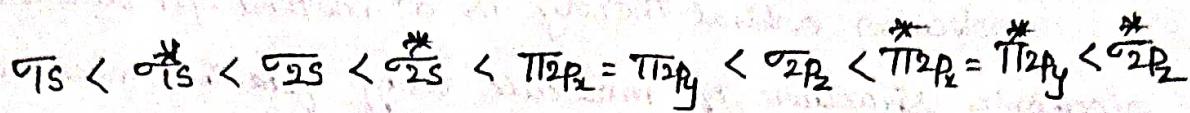
molecular orbital theory is a method for describing the electronic structure of molecule using quantum mechanics. It was proposed by Hund and Mulliken.

- Valence bond theory (VBT) fails to explain the formation of coordination covalent bonds. and this theory (VBT), fails to explain the magnetic properties of O_2 molecule.
- MOT provide to be more information then the VBT.
- The no. of atomic orbitals one combines to form exactly equal no. of molecular orbitals (They can represent as σ , π , δ etc..).
- When two atomic orbitals combine to form two molecular orbitals, one is Bonding molecular orbital (BMO) and another one is Anti bonding molecular orbital (ABMO). BMO is low energy, high stable. ABMO is high energy & less stable.
- The atomic orbitals are combined in linear manner. This is called Linear combination of atomic orbitals (LCAO).
- MOT also follows Pauli's, Hund's, and Aufbau principles.
- MOT depends on wave mechanics. An atomic orbital is an electric wave (ψ). The waves of the two atomic orbitals may be in phase or out of phase.
 - (i) Electron waves of two atomic orbitals are same side it means constructive electron wave (In phase). They can form Bonding mol. orbitals.
 - (ii) Electron waves of two atomic orbitals are opp. side it means destructive electron wave (Out of phase). They can form ABMO.

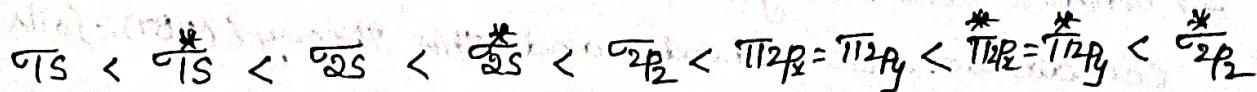


→ The electron occupying orbit in molecular orbitals.

Case-I: If no. of electrons present in a molecule having 14 or less than 14, the electronic configuration is.



Case-II: If no. of electrons present in a molecule having above 14 electrons, the electronic configuration is



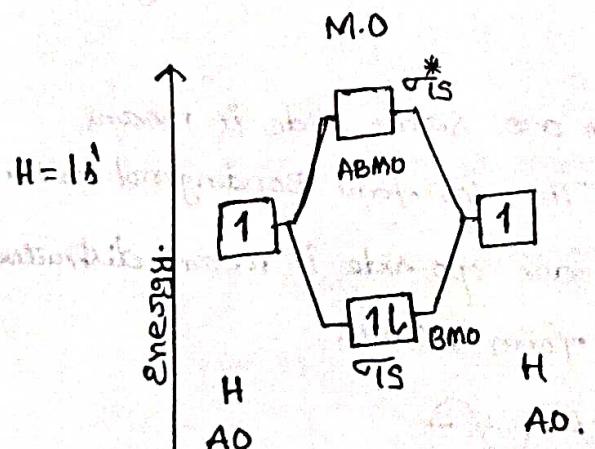
→ Electronic configuration in molecular orbitals explain stability of molecule, bond order, nature of bond, bond length, and magnetic properties.

→ If no. of electrons present in BMO is more than no. of e^- present in ABMO, then molecule is stable.

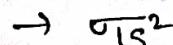
→ Bond order = $\frac{\text{No. of electrons in Bonding Orbital} - \text{No. of } e^- \text{ in ABMO}}{2}$

→ When the molecular orbitals contains unpaired electrons it is paramagnetic nature. And if it contains paired electrons it is diamagnetic nature.

Ex: Molecular orbital Diagram of H_2 Molecule



* Electron configuration of H_2 molecule is =



* Bond Order = $\frac{\text{No. of } e^- \text{ in BMO} - \text{No. of } e^- \text{ in ABMO}}{2}$

$$= \frac{2-0}{2} = 1$$

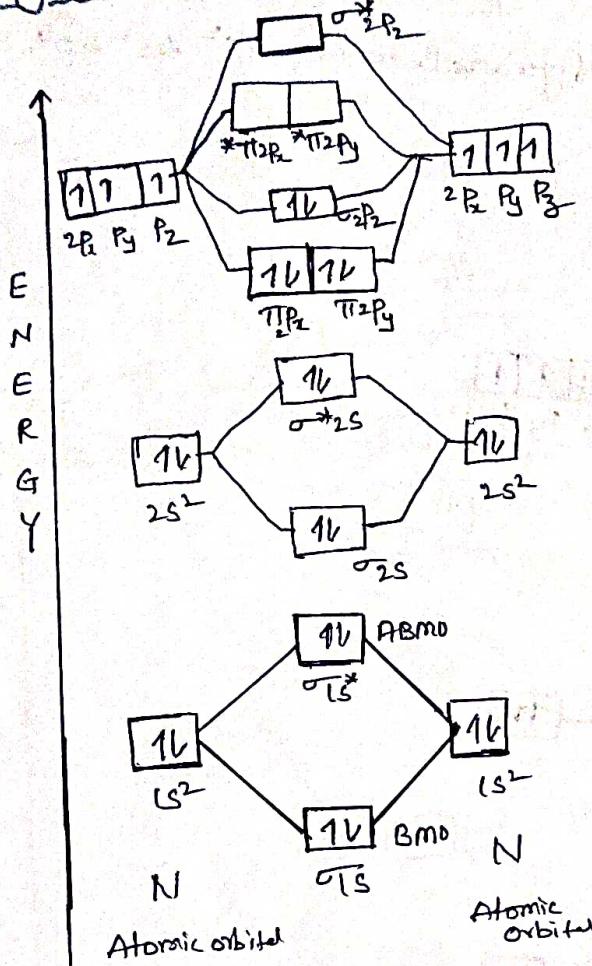
Bond order = 1.
* Magnetic nature of H_2 is diamagnetic nature (Having paired electrons).

MOT of Homo di atomic molecules:

(2)

Nitrogen (N_2) \rightarrow Nitrogen molecule having 14 e^- s.

$$N = 1S^2 2S^2 2P^3$$



\rightarrow Electronic configuration of N_2 molecule.

$$\sigma_{1s}^2 < \sigma_{1s}^* < \sigma_{2s}^2 < \sigma_{2s}^* < \pi_{2p_x}^2 = \pi_{2p_y}^2 < \sigma_{2p_z}^2$$

\rightarrow Bond order of $N_2 = \frac{\text{No. of Bonding electrons} - \text{No. of A.B. electrons}}{2}$

$$= \frac{10 - 4}{2} = 3.$$

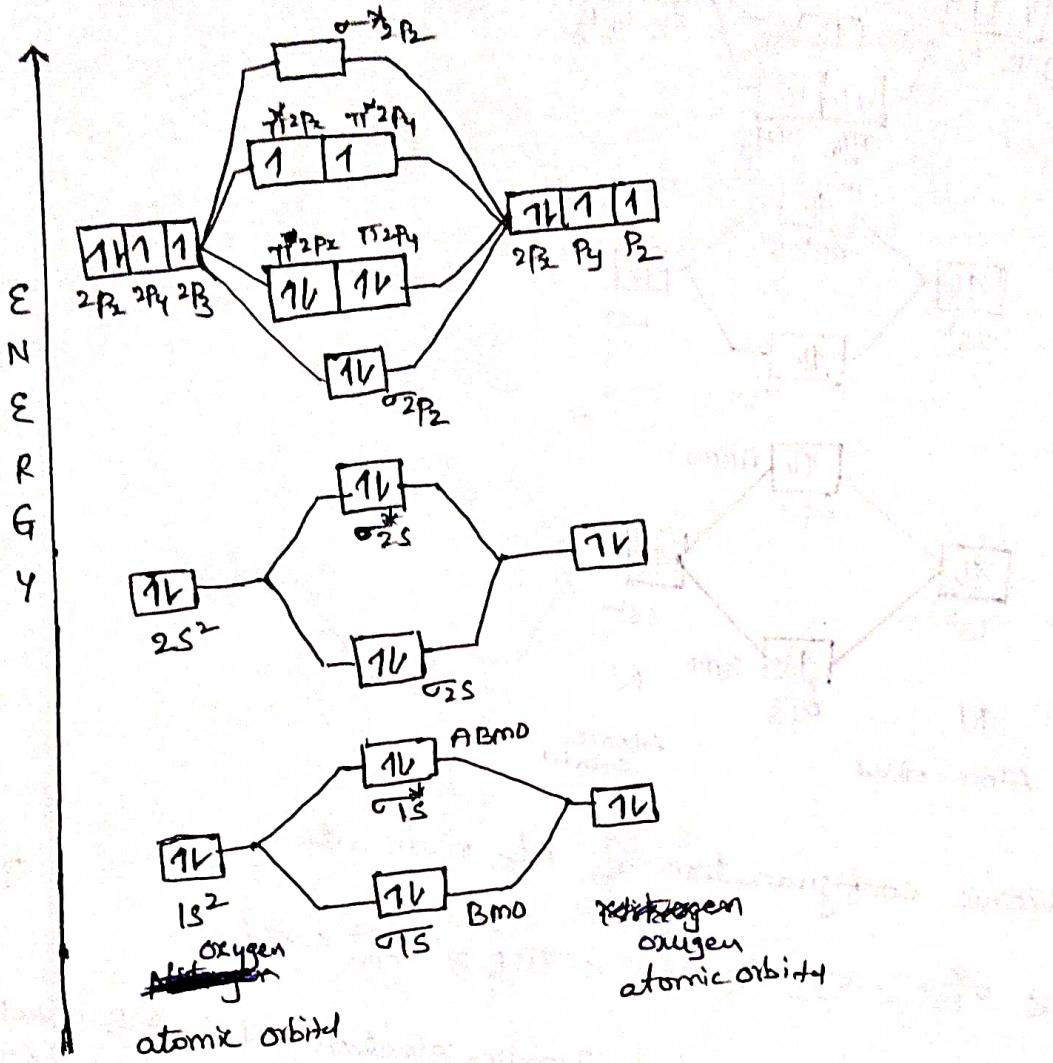
Bond order of Nitrogen molecule is '3'.

$\rightarrow N_2$ molecule having all paired electrons so N_2 is Diamagnetic property.

MOT of Oxygen (O_2) molecule:

→ Oxygen (O_2) molecule having 16 electrons.

→ Oxygen atom electron configuration is $1s^2 2s^2 2p^4$.



* Electronic Configuration of O_2 is

$$\sigma_{1s}^2 < \sigma_{1s}^2 < \sigma_{2s}^2 < \sigma_{2s}^2 < \sigma_{1s}^{ABMO} < \sigma_{2s}^{ABMO} < \pi_{1s}^{ABMO} = \frac{1}{\pi_{1s}^{ABMO}} < \pi_{2s}^{ABMO} = \frac{1}{\pi_{2s}^{ABMO}} < \pi_{1s}^{ABMO} = \frac{1}{\pi_{1s}^{ABMO}}$$

$$\text{Bond order of } O_2 \text{ is } = \frac{\text{No. of Bonding } \Theta - \text{no. of A.B. } \Theta}{2}$$

$$= \frac{10 - 6}{2} = 4/2 = 2.$$

Bond order of O_2 is '2'

→ Oxygen (O_2) molecule having unpaired electrons. So O_2 is paramagnetic in nature.

(3)

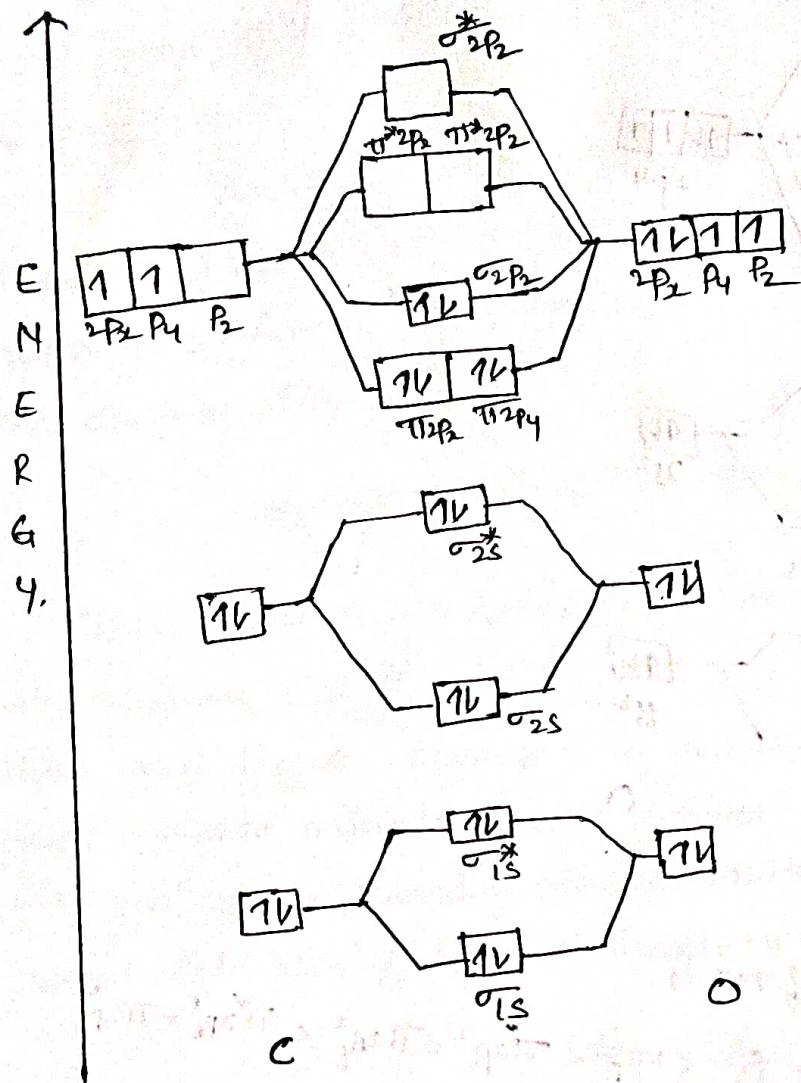
Molecular orbital theory of Hetero diatomic molecules.

Ex: CO

$${}^6C = 1s^2 2s^2 2p^2$$

$${}^8O = 1s^2 2s^2 2p^4$$

CO having 14 electrons.



→ In hetero diatomic molecule we can take carbon in one side and oxygen in another side.

→ Electron Configuration of CO is

$$\rightarrow \sigma_{1s}^2 < \sigma_{1s}^* < \sigma_{2s}^2 < \sigma_{2s}^* < \pi_{2p_z}^* = \pi_{2p_y}^* < \sigma_{2p_z}^2$$

$$\text{Bond order} = \frac{\text{Bonding } e^- - \text{A} \cdot \text{B} \cdot e^-}{2} = \frac{10 - 4}{2} = \frac{6}{2} = 3$$

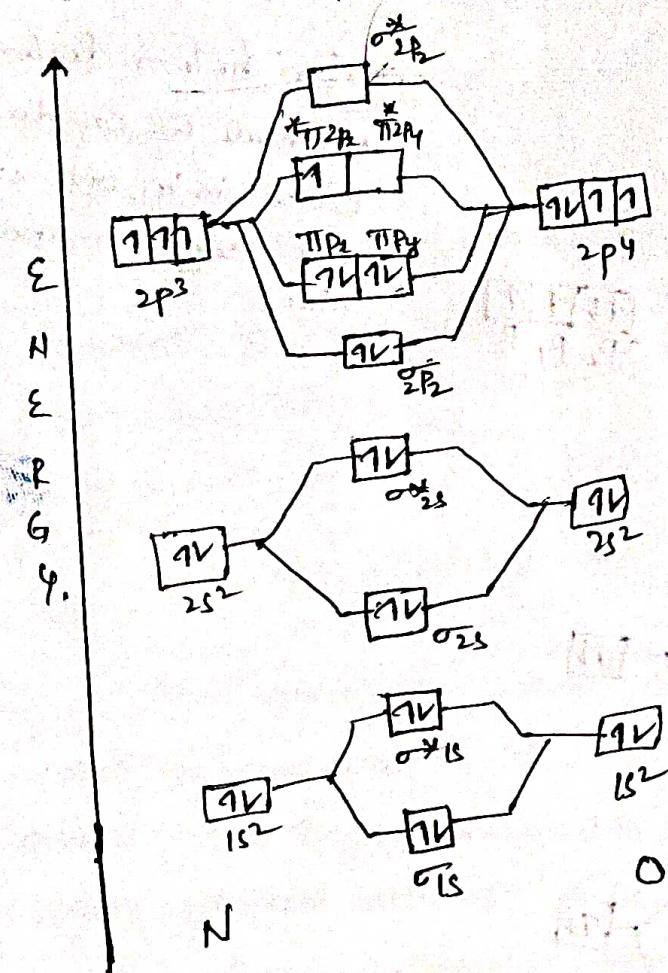
Bond order of CO is '3'

→ CO molecule having all paired electrons, so CO is diamagnetic in nature.

MOT of NO:

$${}^7N = 1S^2 2S^2 2P^3$$

$${}^8O = 1S^2 2S^2 2P^4.$$



Electronic Configuration of NO is

$$\sigma_{1s}^2 < \sigma_{1s}^* < \sigma_{2s}^2 < \sigma_{2s}^* < \sigma_{2p_2}^2 < \sigma\pi_{2p_x}^2 = \pi_{2p_y}^2 < \pi_{2p_z}^* = \pi_{2p_y}^*$$

$$\text{Bond order} = \frac{\text{Bonding e}^- - \text{AB.electrons}}{2} = \frac{10-5}{2} = 5/2 = 2.5.$$

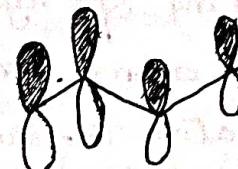
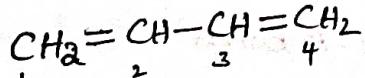
N₂ molecule having unpaired electrons so NO is paramagnetic in nature

π-molecular orbitals of Butadiene:-(1,3 butadiene)

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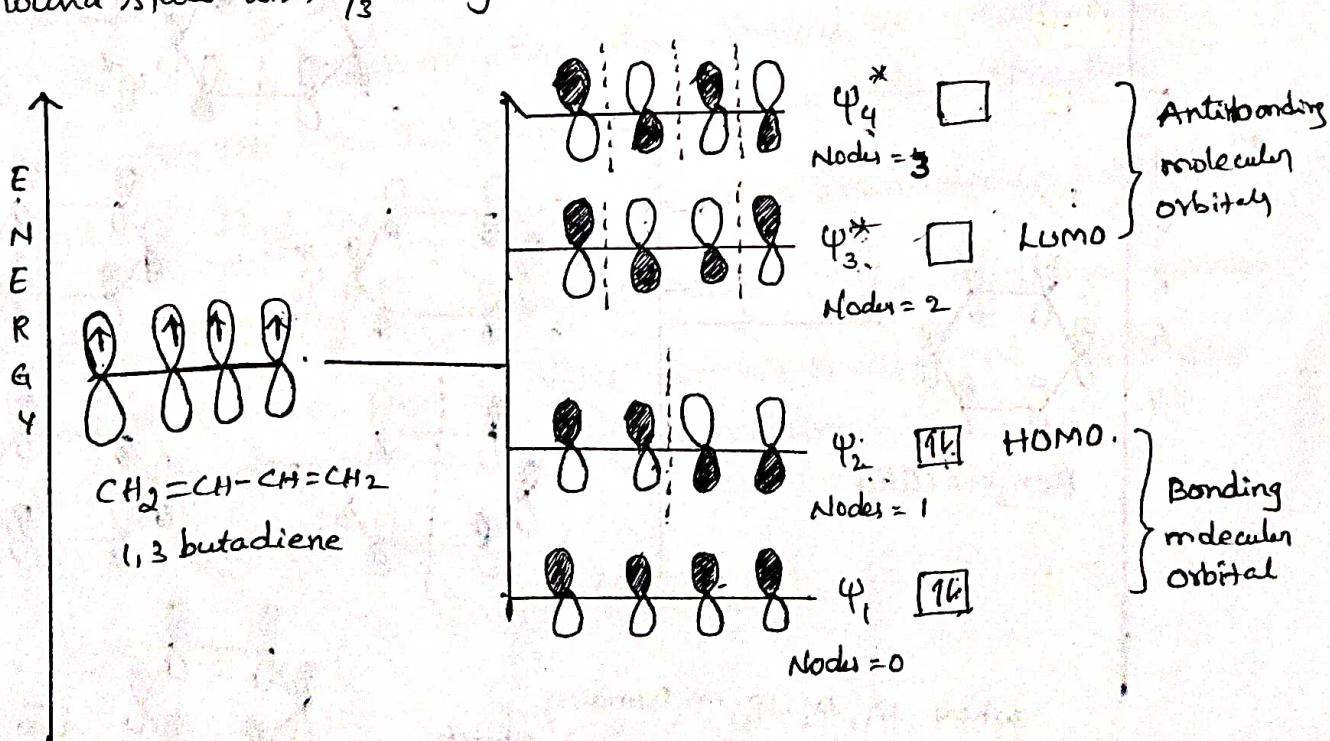
1,3 Butadiene contains two double bonds and They are conjugated. Every carbon atom undergoes sp^2 hybridisation and forms strong σ -bonding with hydrogens and adjacent carbon atom.

The unhybridized fourth P_z orbital containing one electron of each carbon atom undergo molecular bonding by overlapping, forming molecular orbital above and below the carbon atom.



Then result four π molecular Orbitals formed $\psi_1, \psi_2, \psi_3^*, \psi_4^*$ (also referred to as $\pi_1, \pi_2, \pi_3^*, \pi_4^*$): ψ_1 & ψ_2 are bonding molecular orbitals and They are occupied in ground state, with ψ_2 being highest occupied molecular orbital (HOMO).

$\rightarrow \psi_3^*$ & ψ_4^* are antibonding molecular orbitals are unoccupied in ground state with ψ_3^* being the lowest unoccupied orbital (LUMO).



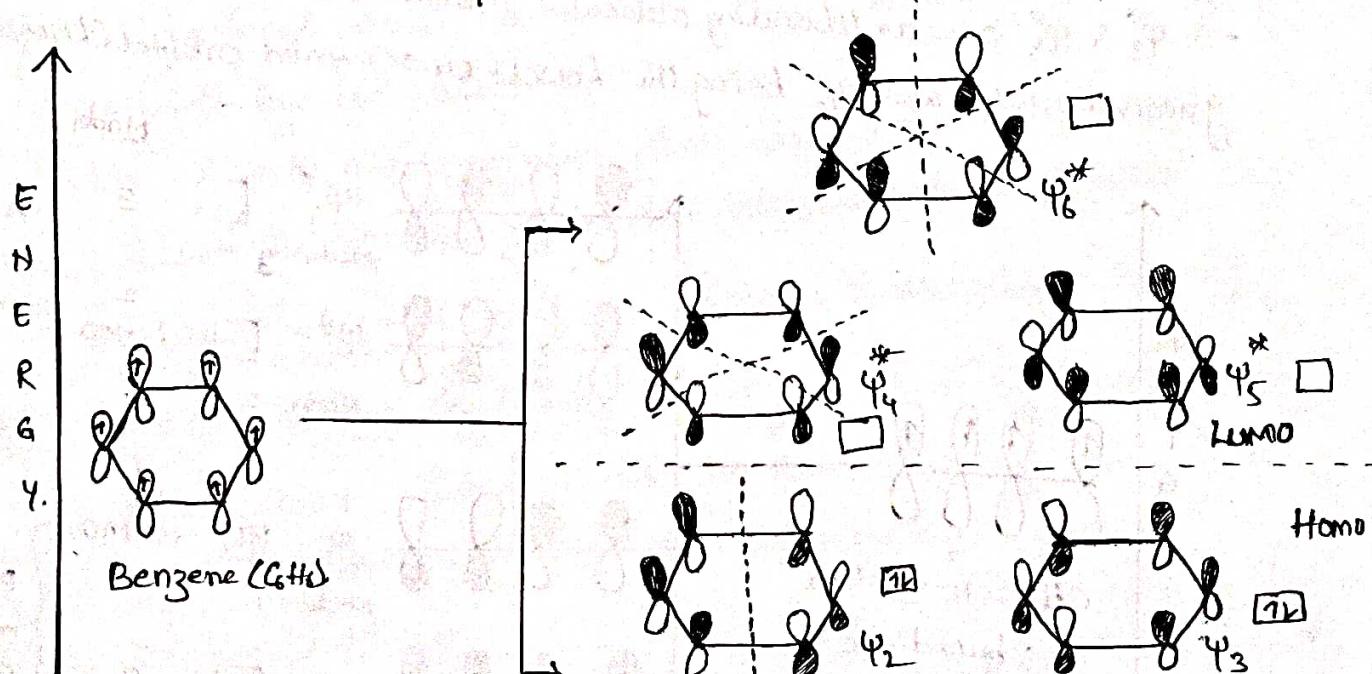
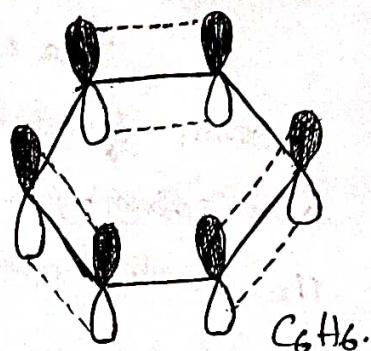
π-molecular orbital of Benzene:

→ The structure of Benzene is best described by modern molecular orbital theory. All six carbons in benzene are sp^2 hybridized.

→ Two sp^2 hybrid orbital of each carbon atom overlap with sp^2 hybrid orbital of adjacent carbon atom to form six C-C (sigma) bonds which are in hexagonal plane.

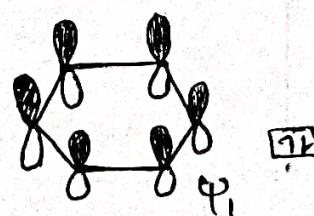
→ The remaining sp^2 hybrid orbital of each carbon atom overlap with $1s$ orbital of hydrogen atom to form six C-H bonds.

* Each carbon atom now left with one unhybridized p orbital perpendicular to the plane of the sigma bond. The overlap of these p-orbital produces a π -molecular orbital containing 6 electrons, one half of this π -molecular orbital lies above and other half lies below the plane of the sigma bonds.

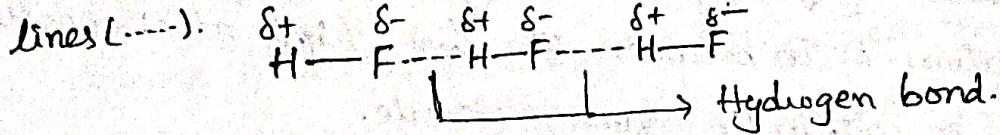


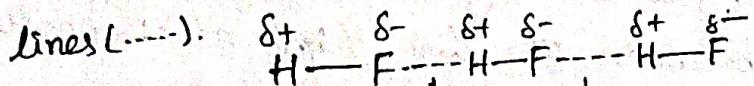
where ψ_1, ψ_2, ψ_3 — Bonding molecular orbitals

$^*\psi_4^*, \psi_5^*, \psi_6^*, \psi_7^*$ — A.B.M.O.



Hydrogen bonding:-

When a hydrogen atom linked to highly electronegative atom (like F, O, N, etc.) comes under the influence of another strong electronegative atom, then the weak bond is developed between them, which is called "hydrogen bond". It is represented by dotted lines (----). 



→ As a result of hydrogen bonding, the hydrogen atom links the two electro negative atoms simultaneously, one by a covalent bond another by a hydrogen bond.

→ It is only a strong electrostatic force of attraction and not a normal chemical bond. It is very weak. (Strength about $2-10 \text{ kJ/mol}$).

Ex: H_2O , NH_3 , HF , alcohols, carboxylic acids, etc...

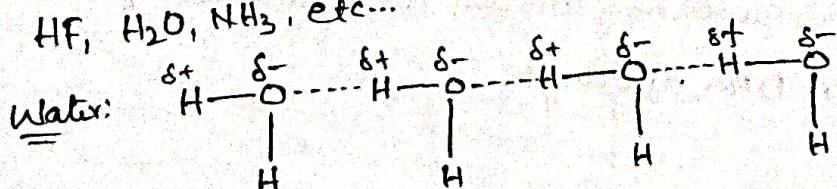
Conditions for Hydrogen bonding:-

- The molecule must contain a highly electronegative atom linked to hydrogen atom.
- The size of electronegative atom should be small. The smaller the size, the greater is the electrostatic attraction.

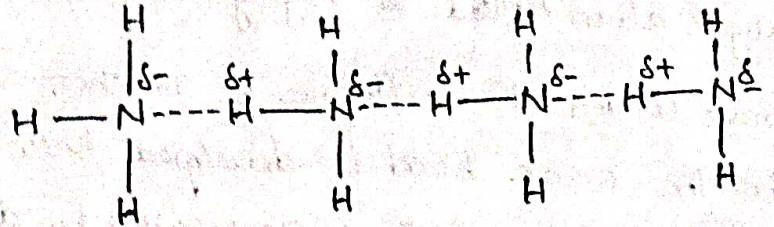
Types of Hydrogen bond:- [Inter & Intramolecular H-bonds]

A. Intermolecular hydrogen bonding: The hydrogen bonding is done between two or more similar or different molecules is called intermolecular hydrogen bonding.

Ex: HF , H_2O , NH_3 , etc...

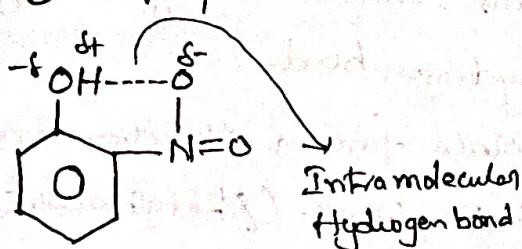


Ex-2: NH_3^+

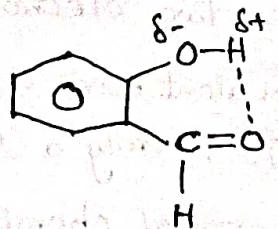


B. Intramolecular Hydrogen bonding: It is formed when a hydrogen atom is in between the two highly electronegative atoms present within the same molecule.

Ex-3: O₂-nitro phenol.

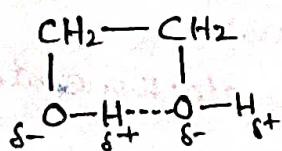


Ex-2: Salicilaldehyde



(O-hydroxy benzaldehyde).

Ex-3: Ethylene glycol:



Properties:

- * It is a weak force of attraction between molecules.
- * It is changes the melting point and boiling points of a substance.
- * It is comparatively weaker than covalent bond, and ionic bond.
- * Hydrogen bond is stronger than the weak Van der waals bonds.
- * It is stronger than the weak Van der waals bonds.

Applications:

- Study in hydrogen bonds in plants (cohesion & adhesion)
- To study hydrogen bonding proteins - explains primary, sec, tertiary and quaternary proteins and structure of nucleic acids.
- To study in DNA structures.