 → σ bond → Head on Overlapping

 → π bond → Lateral Overlapping

Unit → 1 Chemical Bonding.

* Covalent Bonds →

→ Covalent compounds show directional behaviour because of overlapping of orbital in a particular direction whereas ionic compounds are non-directional in nature.

→ Due to directional behaviour, covalent compounds show isomerism.

* Valence Bond Theory →

→ Only e^-s of outermost shell participate in this.

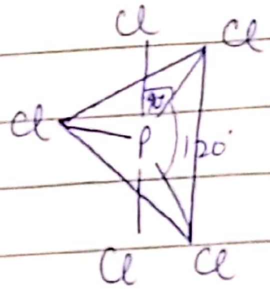
→ Individual properties of the participating elements are not lost.

* Hybridisation →

1. sp → C_2H_2 → 180° → Linear
2. sp^2 → C_2H_4 → 120° → Trigonal Planar ▽ [0 lone pair]
   → Bent shape ⌄ [1 lone pair]
3. sp^3 → CH_4 → 109° 28′ → Tetrahedral [0 lone pair]
   NH_3 → Pyramidal ^ [1 lone pair]
   H_2O → Bent/Angular ^ [2 lone pair]
   HF → Linear [3 lone pair]

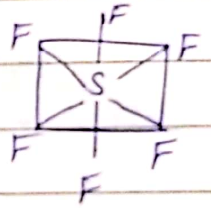
Ionic Bonds are non-directional because it is the electrostatic force b/w 2 opp. charges. Hence bonding direction does not matter.

4 sp^3d → Trigonal Bipyramidal → PCl_5 → 120°, 90°
[0 lone pair]

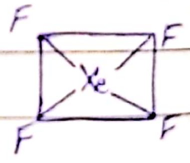


→ see-saw shape → SF_4 [1 lone pair]
→ T-shape → $XeOF_2$ [2 lone pair]
→ Linear → XeF_2 [3 lone pair]

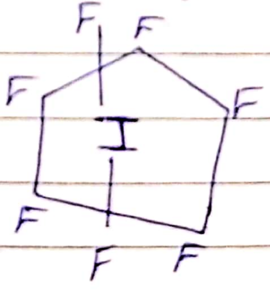
5 sp^3d^2 → Square Bipyramidal/Octahedral → SF_6 → 90°
[0 lone pair]



→ Square Pyramidal [1 lone pair]
→ Square Planar [2 lone pair] → XeF_4



6 sp^3d^3 → Pentagonal Bipyramidal → 90°, 72° → IF_7
[0 lone pair]



→ Distorted Pentagonal [1 lone pair] → XeF_6

7. dsp^2 } Complex Compounds
8. d^2sp^3 }

V.Imp ✗ Limitations of VBT →

→ It does not explain Mag. behaviour of elements
→ Unable to explain the colours of compounds
→ Unable to explain formation of complex compounds.

① Acc. to VBT, Oxygen is Diamagnetic in nature but experimental studies show that it is Paramagnetic in nature [Para. molecule]

② It does not explain formation of certain molecules like H_2^+, He_2^+, B_2H_6.

③ It does not give proper explanation regarding the colour of the compounds.

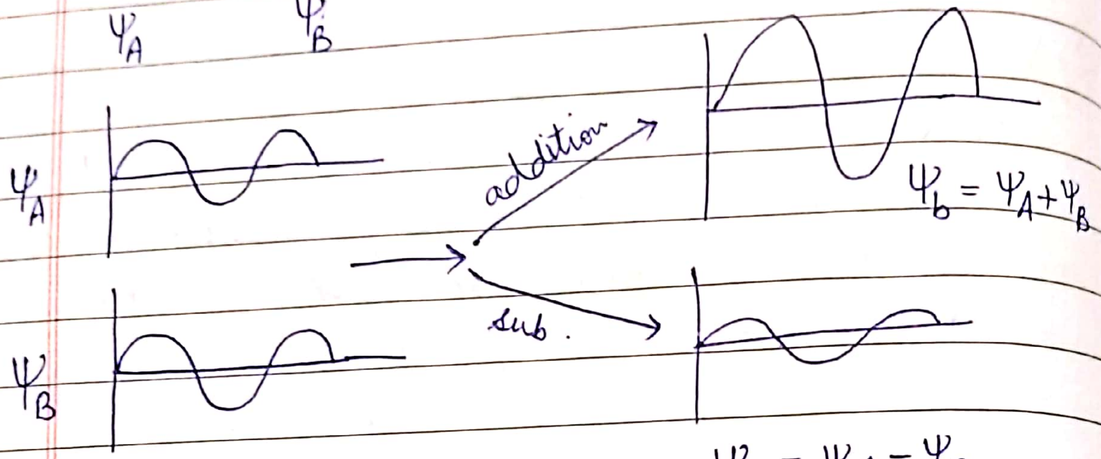
④ It does not explain the formation of Coord. complexes.

✗ Molecular Orbital Theory → It is given by Hunds and Mullikin and further developed/modified by Joule and Coulson.

$\psi_b \rightarrow$ Bonding Molecular Orbital
$\psi_a \rightarrow$ Antibonding M. Orbital

* Linear Combination of Atomic Orbital →

$$\underset{\psi_A}{\overset{\downarrow}{A}} + \underset{\psi_B}{\overset{\downarrow}{B}} \longrightarrow AB$$



$$\psi_a = \psi_A - \psi_B$$

$$(\psi_b)^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 \underline{+ 2\psi_A \psi_B}$$

$$(\psi_a)^2 = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 \underline{- 2\psi_A \psi_B}$$

→ Bonding M.O.s are more stable than Antibonding M.Orbitals

→ In MOT, e^- is considered as a particle or as a wave.

→ The valence e^-s are considered to be associated with all the nuclei in the molecule. Thus, the atomic orbital from different atom must be combined to produce molecular orbital.

Date __/__/____ Page No.: ______

→ Atomic orbitals having same energy and same symmetry combine to produce molecular orbital by LCAO principle.

→ Molecular orbitals formed by the addition of two atomic orbitals wave functions is known as bonding M.Orbital, and the probability of e^-s in bonding M.Orbital is greater in amount of $2\psi_A\psi_B$ as compared to probability of e^-s in individual Atomic orbital.

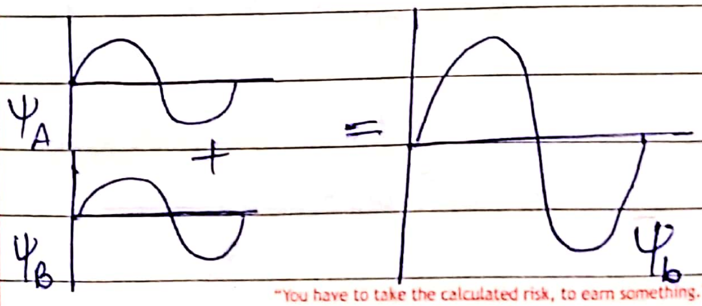
$$A + B \longrightarrow AB$$

$$\psi_b = \psi_A + \psi_B$$

ψ_A → Wave function of A.Orbital of atom A

ψ_B → Wave function of A.Orbital of atom B

ψ_b → Wave function of bonding M. Orbital



→ Prob of e^-'s in Bonding M. Orbitals,

$$\psi_b^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

→ Molecular Orbitals formed by the sub. of two atomic orbitals wave functions is known as antibonding M. Orbital, and the probability of e^-s in antibonding M. Orbitals is less in amount of $2\psi_A\psi_B$ as compared to probability of e^- in individual atomic orbital.

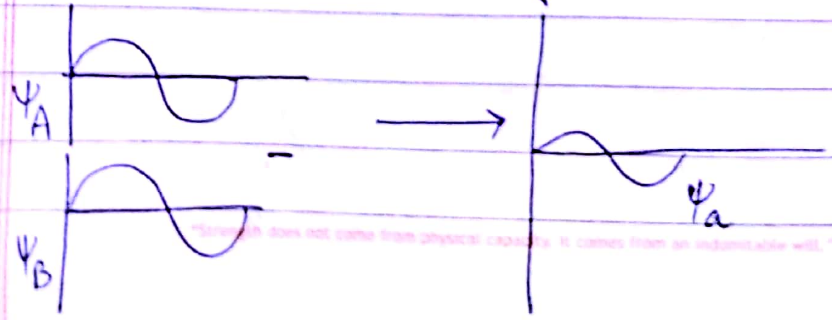
$$\underset{(\psi_A)}{A} + \underset{(\psi_B)}{B} \longrightarrow AB$$

$$\psi_a = \psi_A - \psi_B$$

ψ_A → Wave function of A. Orbital of atom A

ψ_B → Wave function of A. Orbital of atom B

ψ_a → Wave function of antibonding M. Orbital



→ Probability of e^-s in antibonding M.Orbitals,

$$\psi_a^2 = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

→ The atomic orbitals which do not take part in bonding are known as non-bonding M.Orbitals.

→ Atomic Orbitals are Monocentric in nature whereas M.Orbitals are Polycentric in nature.

→ Filling of e^-s in M.Orbitals will follow Hund's Rule, Pauli's Rule and Aufbau's principle.

→ Stability of any bond is described by their bond order.

→ $\text{Bond order} = \frac{1}{2}\left[\text{No. of } e^-\text{s in Bonding M.O} - \text{No. of } e^-\text{s in Anti-bonding MO}\right]$

→ $\text{Bond order} \propto \text{Bond strength} \propto \frac{1}{\text{Bond length}}$

→ $\text{Bond Order} \propto \text{Stability}$

→ Energy sequence → (upto Nitrogen)

$$\sigma 1s < \sigma 1s^* < \sigma 2s < \sigma 2s^* < \pi 2px < \pi 2py < \sigma 2pz < \pi^* 2px \simeq \pi^* 2py < \sigma^* 2pz$$

Above N_2: ~~$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2px < \pi 2py <$~~

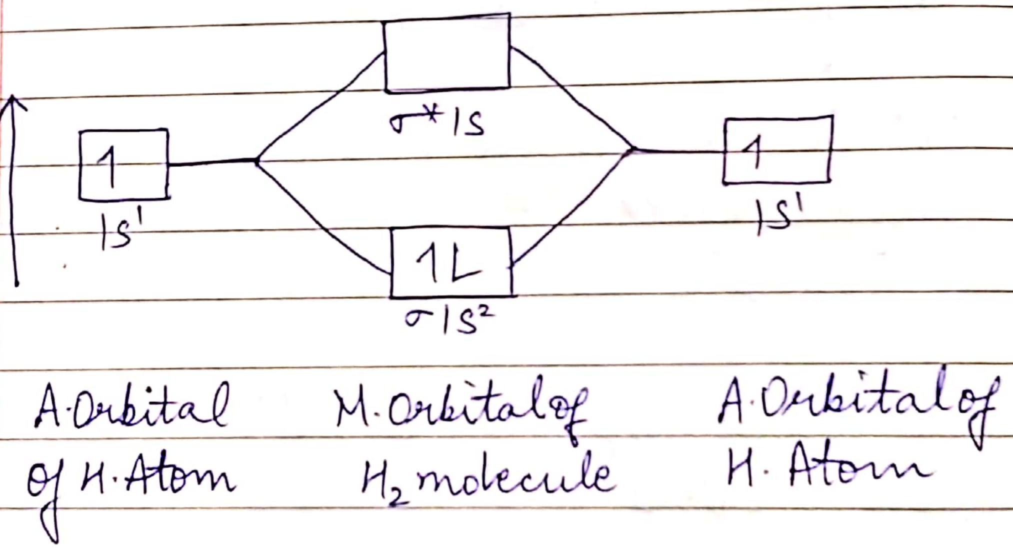
$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2pz < \pi 2px$

$\simeq \pi 2py < \pi^* 2px \simeq \pi^* 2py < \sigma^* 2pz$

✗ Homoatomic Molecules →

- H_2

$H = 1s^1$

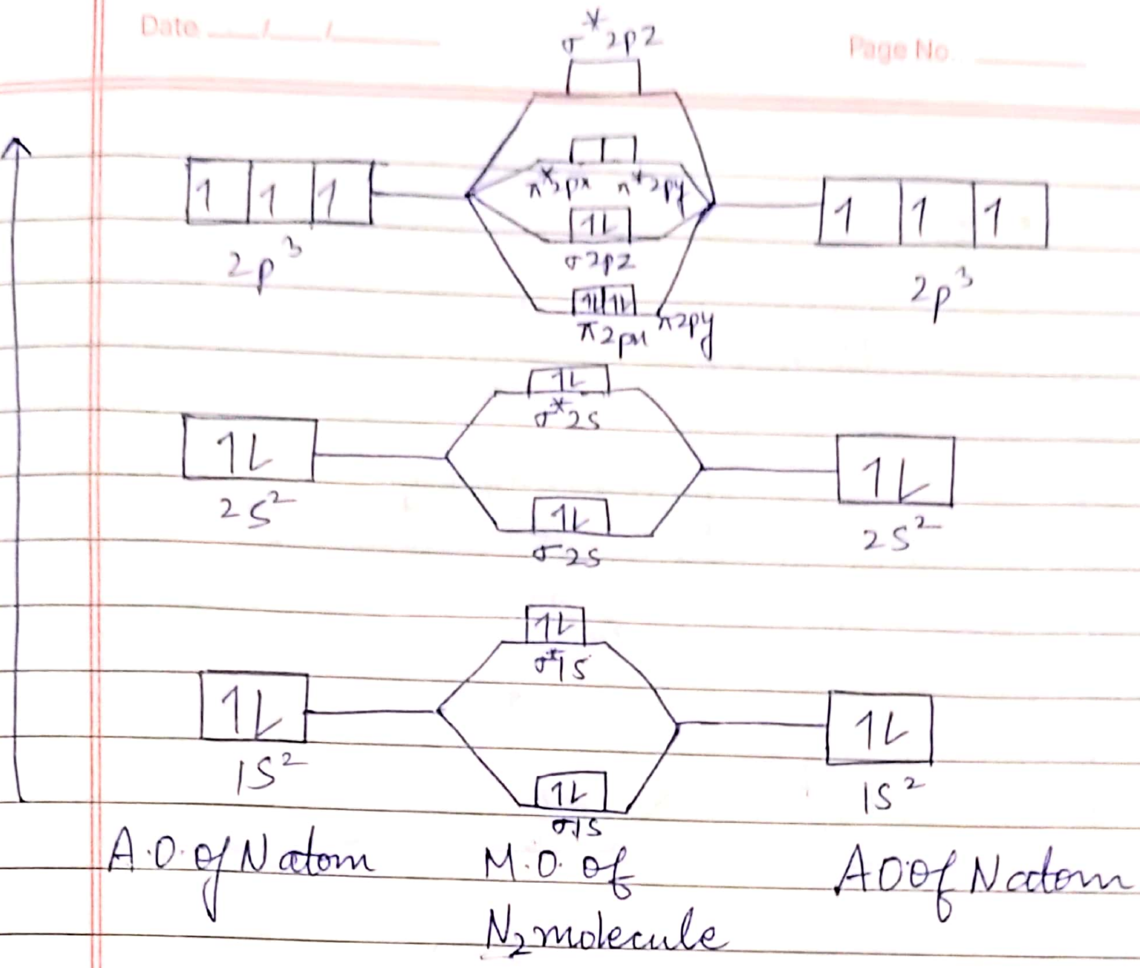


$B \cdot O = \frac{1}{2} [2 - 0] = 1$

Diamagnetic

- N_2

$N = 1s^2 \, 2s^2 \, 2p^3$

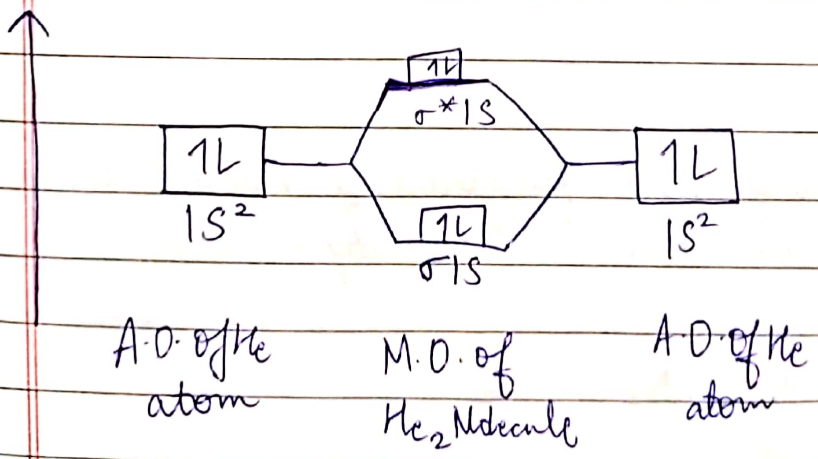


$$B.O = \frac{10-4}{2} = 3$$

Diamagnetic

- He_2

$He = 1s^2$

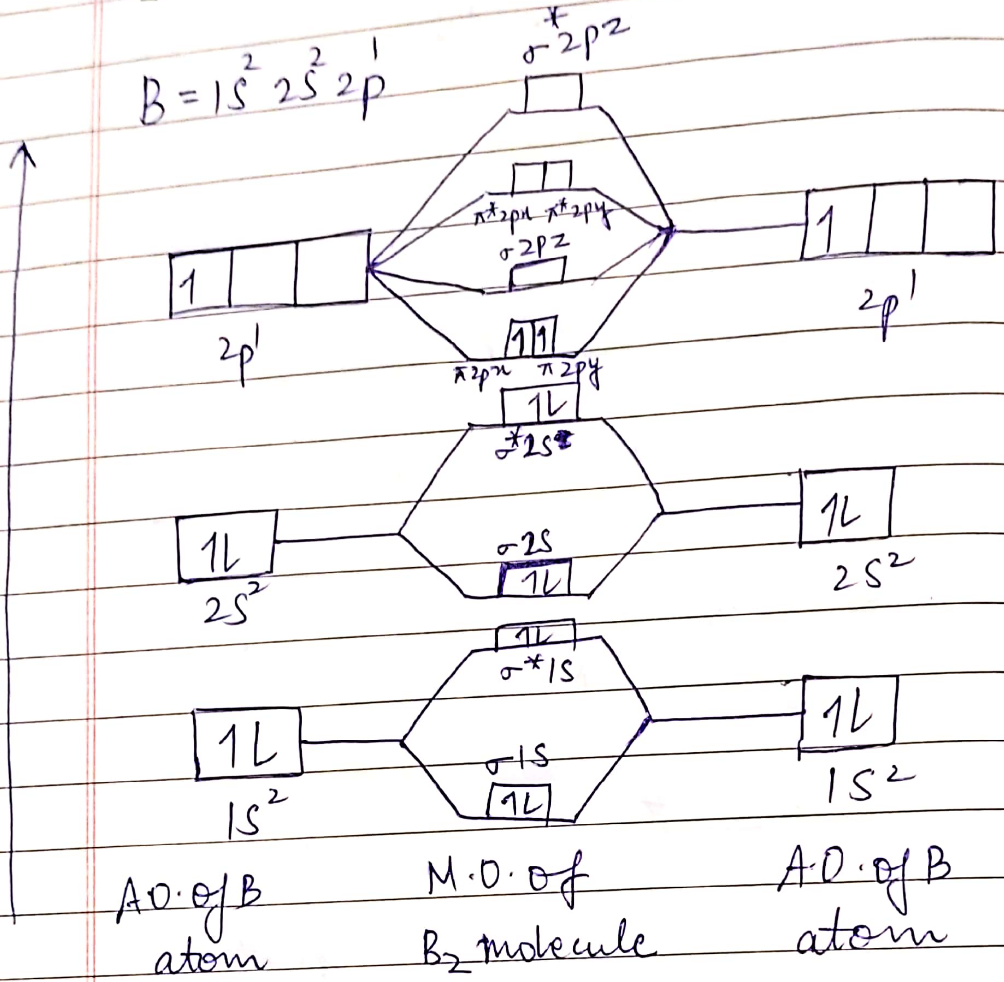


$$B.O = \frac{2-2}{2} = 0$$

∴ It does not exists

- B_2

$B = 1s^2 2s^2 2p^1$



$$B.O = \frac{6-4}{2} = 1$$

Paramagnetic.

Imp Q. Arrange the following molecules in order of their stability:

N_2^+, N_2^-, N_2^{--}, N_2

Ans. $N_2 \rightarrow$

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x^0, \pi^* 2p_y^0, \sigma^* 2p_z^0$

(Dia.)

$N_2^+ \rightarrow$

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2, \sigma 2p_z^1, \pi^* 2p_x^0, \pi^* 2p_y^0, \sigma^* 2p_z^0$

(Para)

$N_2^- \rightarrow$

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

$\pi^* 2p_y^0\ \sigma^* 2p_z^0$ (Para)

N_2^{--}

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x^1, \pi^* 2p_y^1\ \sigma^* 2p_z^0$

(Para)

B.O of $N_2 = 3$
BO of $N_2^+ = 2.5$
B.O of $N_2^- = 2.5$
B.O of $N_2^{--} = 2$

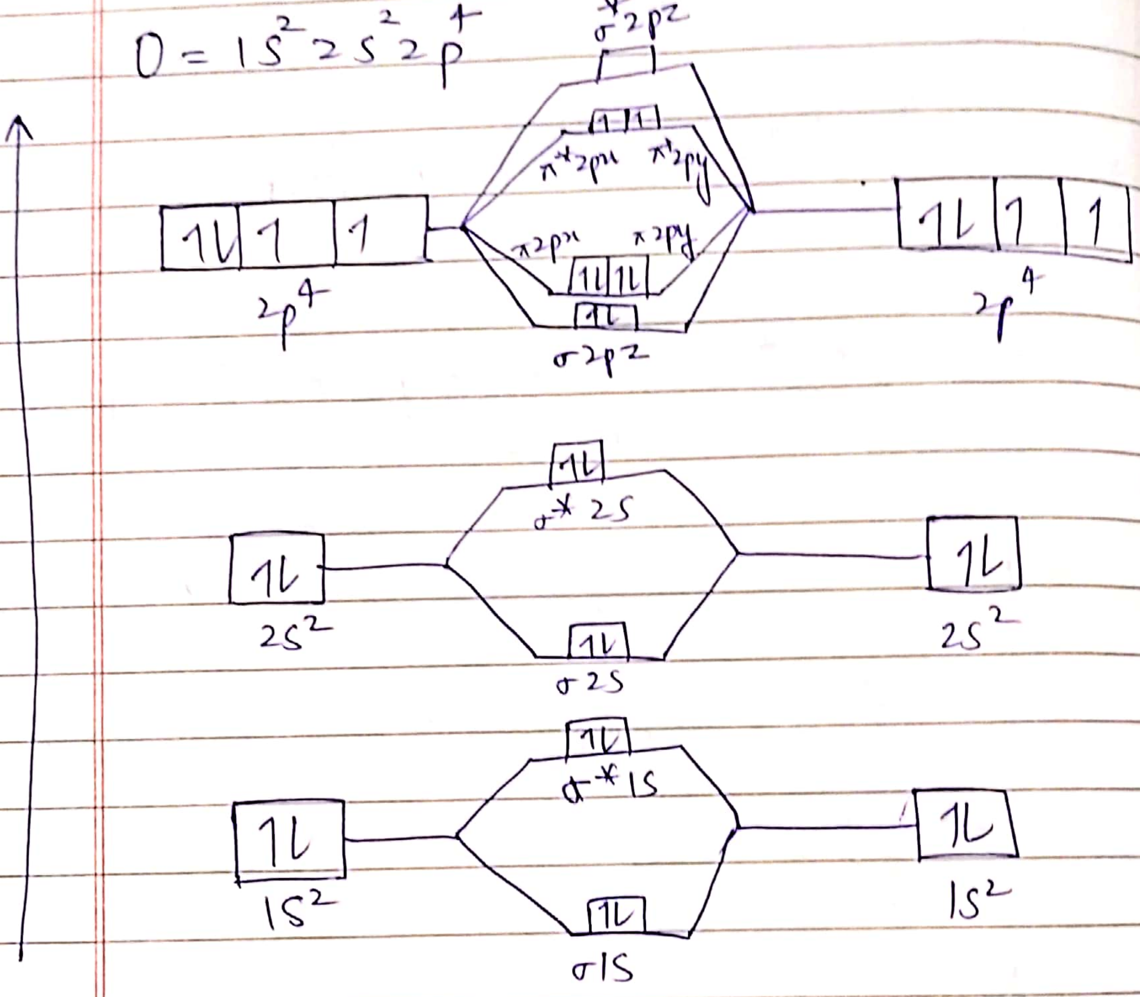
B.O ∝ stability.

$\therefore$ Order of stability $\rightarrow N_2 > N_2^+ \underset{>}{[illegible]} N_2^- > N_2^{--}$

$\longleftarrow$ stability (due to the presence of last e^- in BMO)

- O_2

$O = 1s^2 2s^2 2p^4$



A.O. of O atom M.O. of O_2 molecule A.O. of O. atom

$$B.O = \frac{10-6}{2} = 2$$

(Paramagnetic)

$\sigma 1s^2 \ \sigma^* 1s^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ {}_{\wedge}\sigma 2pz^2 \ \pi 2px^2 \ \pi 2py^2 \ \pi^* 2pz^1$

$\pi^* 2py^1 \ \sigma^* 2pz^0$

Q. Explain and arrange the stability of O_2, O_2^+, O_2^-, O_2^{--}, O_2^{++}

Sol^n. $O_2 \rightarrow$

$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2pz^2 \pi 2px^2 \pi 2py^2$

$\pi^* 2px^1 \pi^* 2py^1 \sigma^* 2pz^0$ (Para)

$O_2^+ \rightarrow$

$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2pz^2 \pi 2px^2 \pi 2py^2$

$\pi^* 2px^1 \pi^* 2py^0 \sigma^* 2pz^0$

(Para)

$O_2^- \rightarrow$

$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2pz^2 \pi 2px^2 \pi 2py^2$

$\pi^* 2px^2 \pi^* 2py^1 \sigma^* 2pz^0$

(Para)

$O_2^{--} \rightarrow$

$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2pz^2 \pi 2px^2 \pi 2py^2$

$\pi^* 2px^2 \pi^* 2py^2 \sigma^* 2pz^0$ (Dia)

$O_2^{++} \rightarrow$

$\sigma 1s^2 \; \sigma^* 1s^2 \; \sigma 2s^2 \; \sigma^* 2s^2 \; \sigma 2pz^2 \; \pi 2px^2 \; \pi 2py^2$

$\pi^* 2px^0 \; \pi^* 2py^0 \; \sigma^* 2pz^0$ (Dia)

B.O of $O_2 \rightarrow 2$
B.O of $O_2^+ \rightarrow 2.5$
B.O of $O_2^- \rightarrow 1.5$
B.O of $O_2^{--} \rightarrow 1$
B.O of $O_2^{++} \rightarrow 3$

B.O $\propto$ stability

$\therefore$ Order of stability $\Rightarrow O_2^{++} > O_2^+ > O_2 > O_2^- > O_2^{--}$

* Heterodiatomic Molecules →

(14e^-) (13e^-) (15e^-)
CO , CN , NO , $\boxed{HF}$

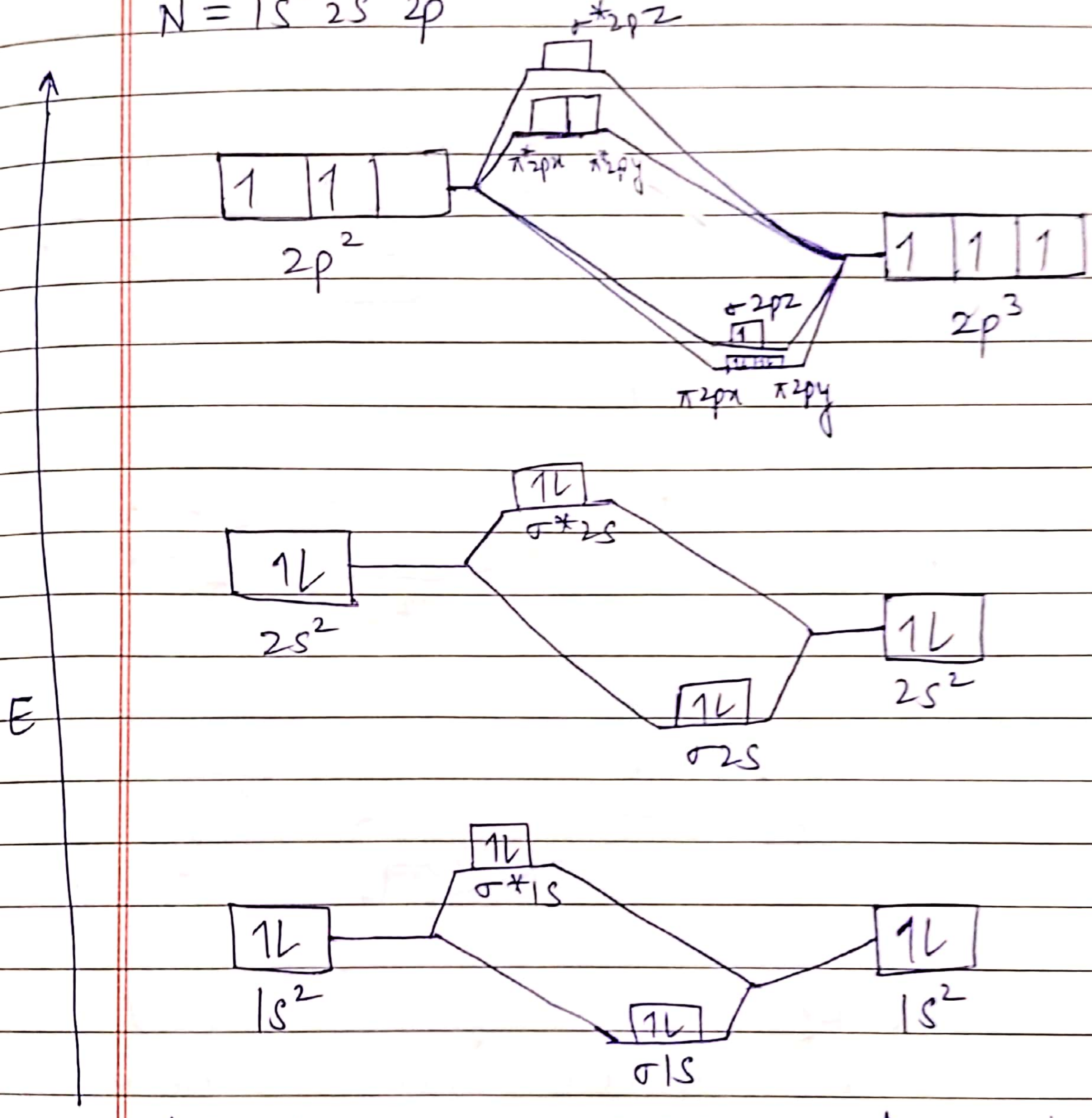
CO, CN → (upto N_2) follow N_2
NO → (above N_2) follow O_2

$O > N > C$
$\xleftarrow{\text{electronegativity}}$

$CO \rightarrow \overline{CO}$ $\overset{+}{C}O$
$CN \rightarrow \overline{CN}$ $\overset{+}{C}N$
$NO \rightarrow N\overline{O}$ $N\overset{+}{O}$
[(−ve) → electronegativity]
[(+ve) → $N > O > C$
$\xleftarrow{\text{Ionisation}}$
$\xrightarrow{\text{+ve charge}}$]

- CN →

$C = 1s^2 2s^2 2p^2$
$N = 1s^2 2s^2 2p^3$



A.O. of C. atom

M.O. of CN molecule

A.O. of N atom

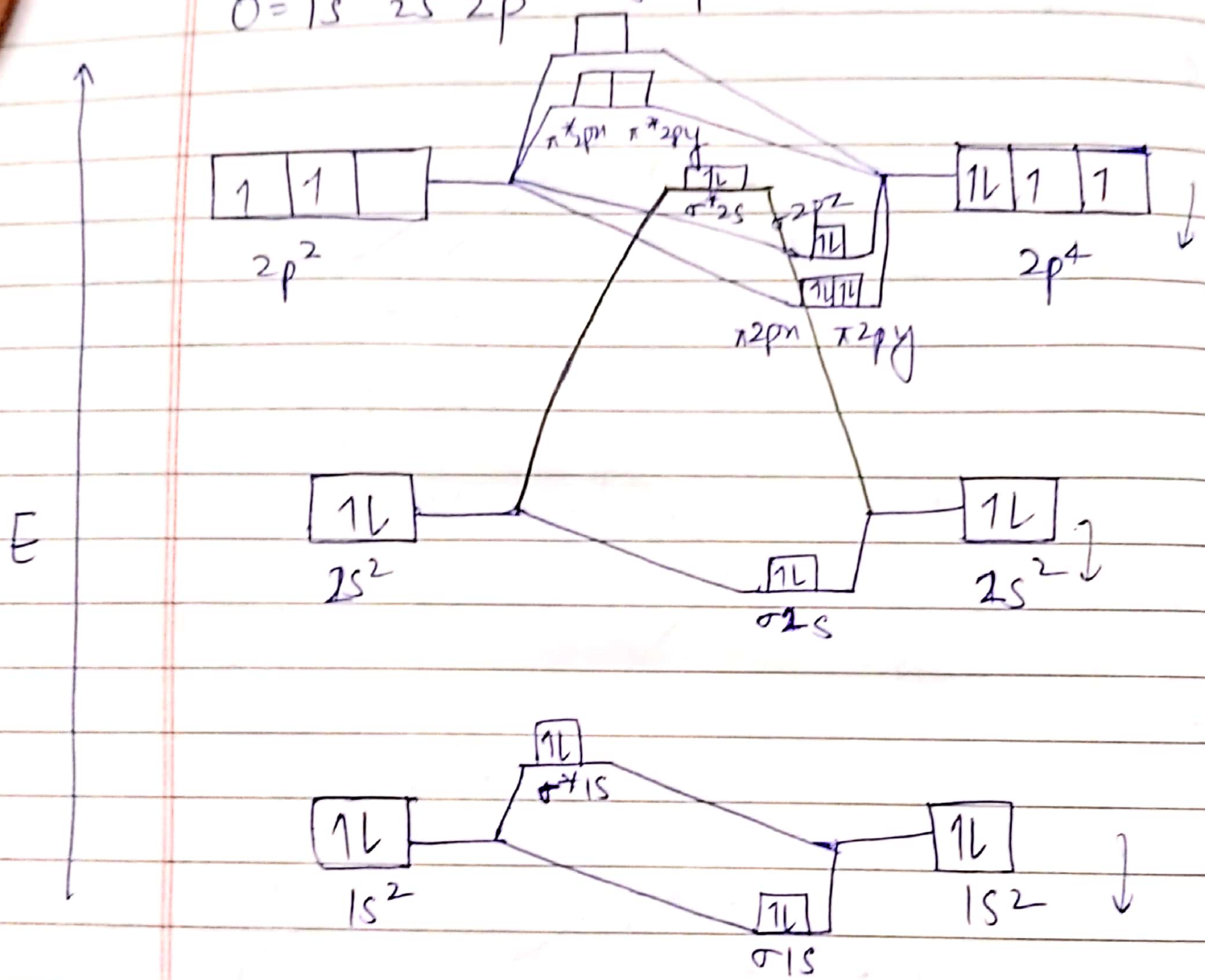
$$B.O = \frac{9-4}{2} = 2.5$$

(Paramagnetic)

- CO →

Coulson Diagram

$C = 1s^2 2s^2 2p^2$
$O = 1s^2 2s^2 2p^4$



A.O. of C atom   M.O. of CO molecule   A.O. of O atom

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

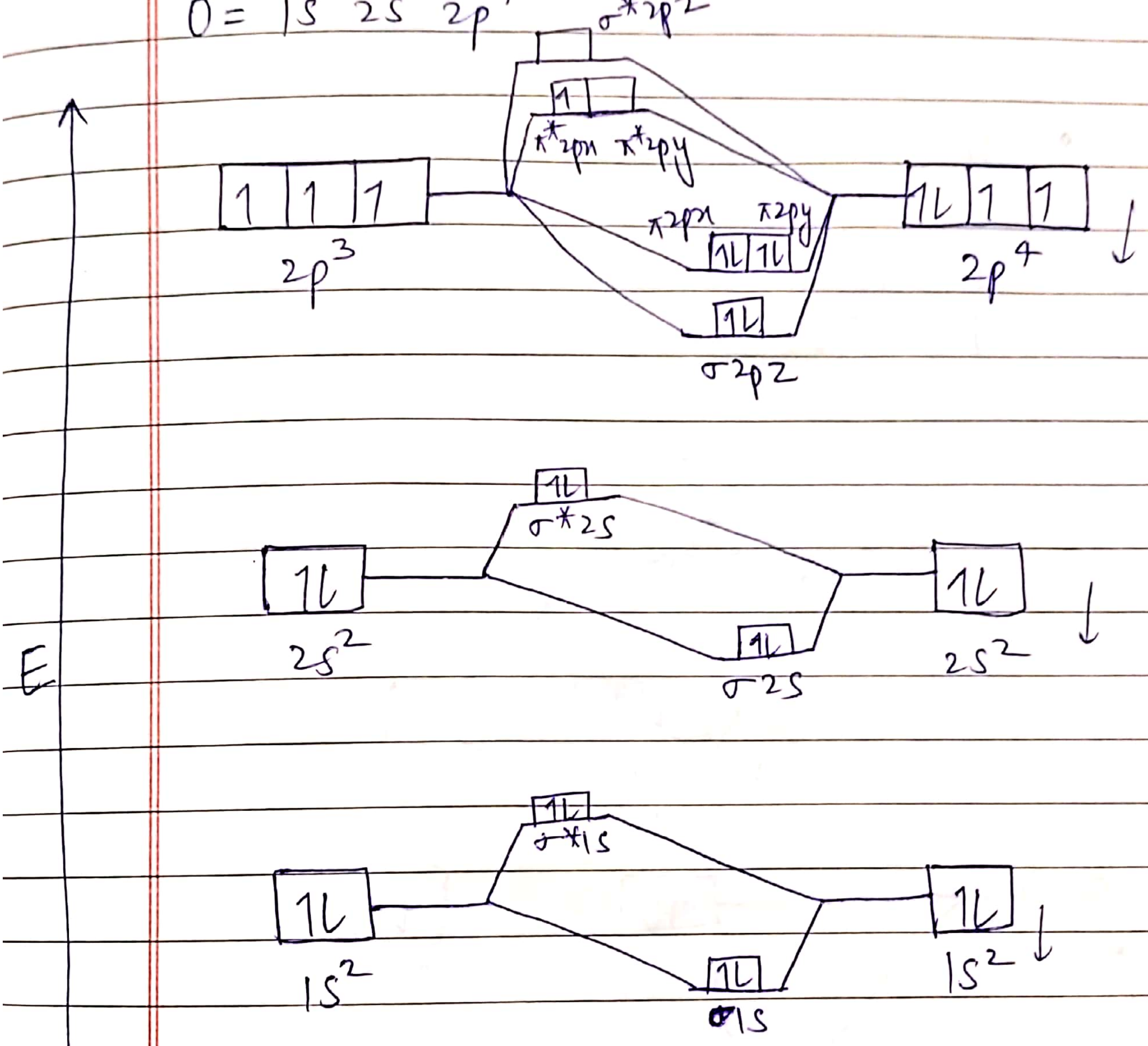
Diamagnetic

CO^+ → $B.O = 3.5 \left[\frac{10-3}{2}\right]$ $\left\{\sigma^* 2s^1\right\}$

- NO →

$N = 1s^2\, 2s^2\, 2p^3$

$O = 1s^2\, 2s^2\, 2p^4$



A.O. of N atom

M.O. of NO molecule

A.O. of O atom

$$B.O = \frac{10-5}{2} = 2.5$$

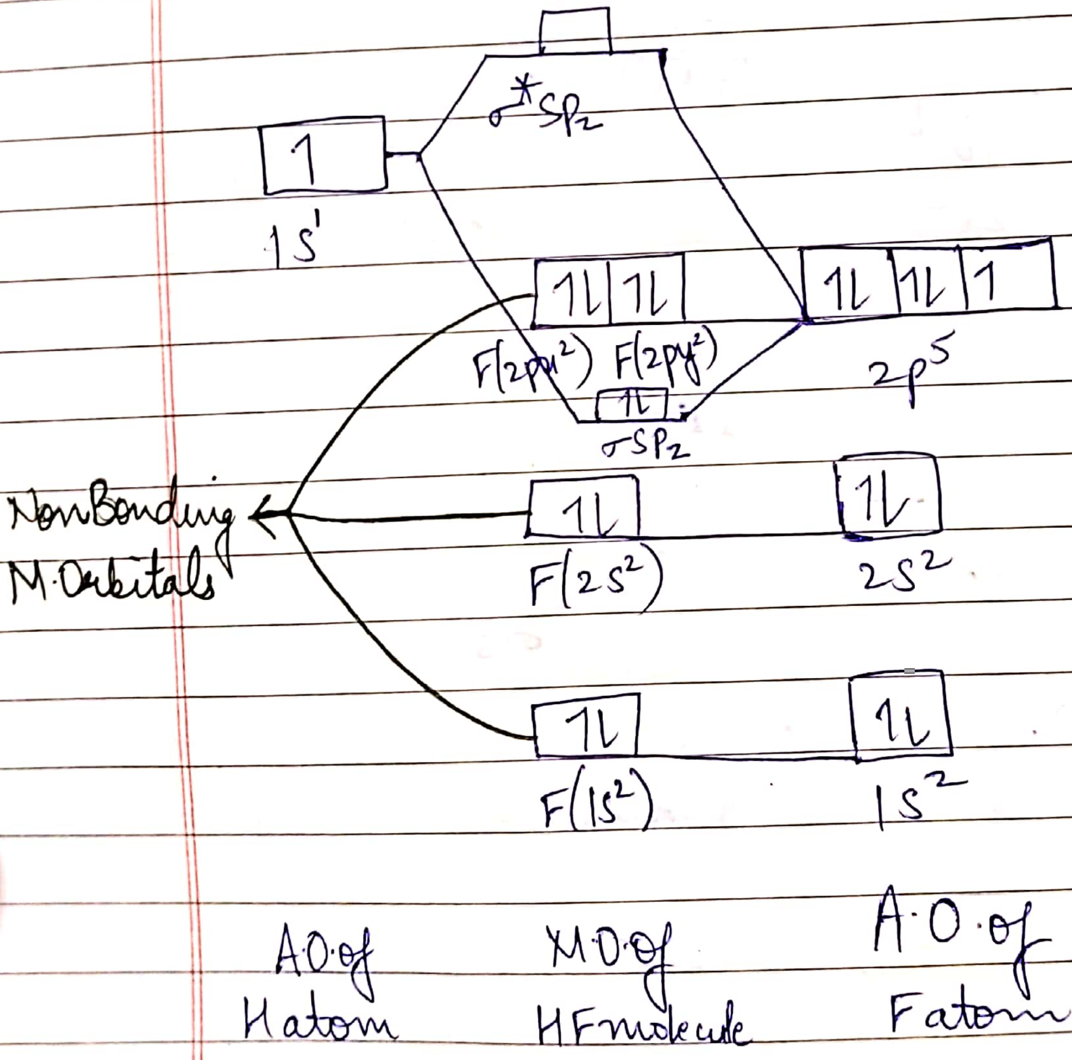
(Paramagnetic)

Q. Why the B.O. of CO^+ is greater than CO?

Sol^n. Explain it with the help of diag.

- HF

$H - 1s^1$
$F - 1s^2 2s^2 2p^5$



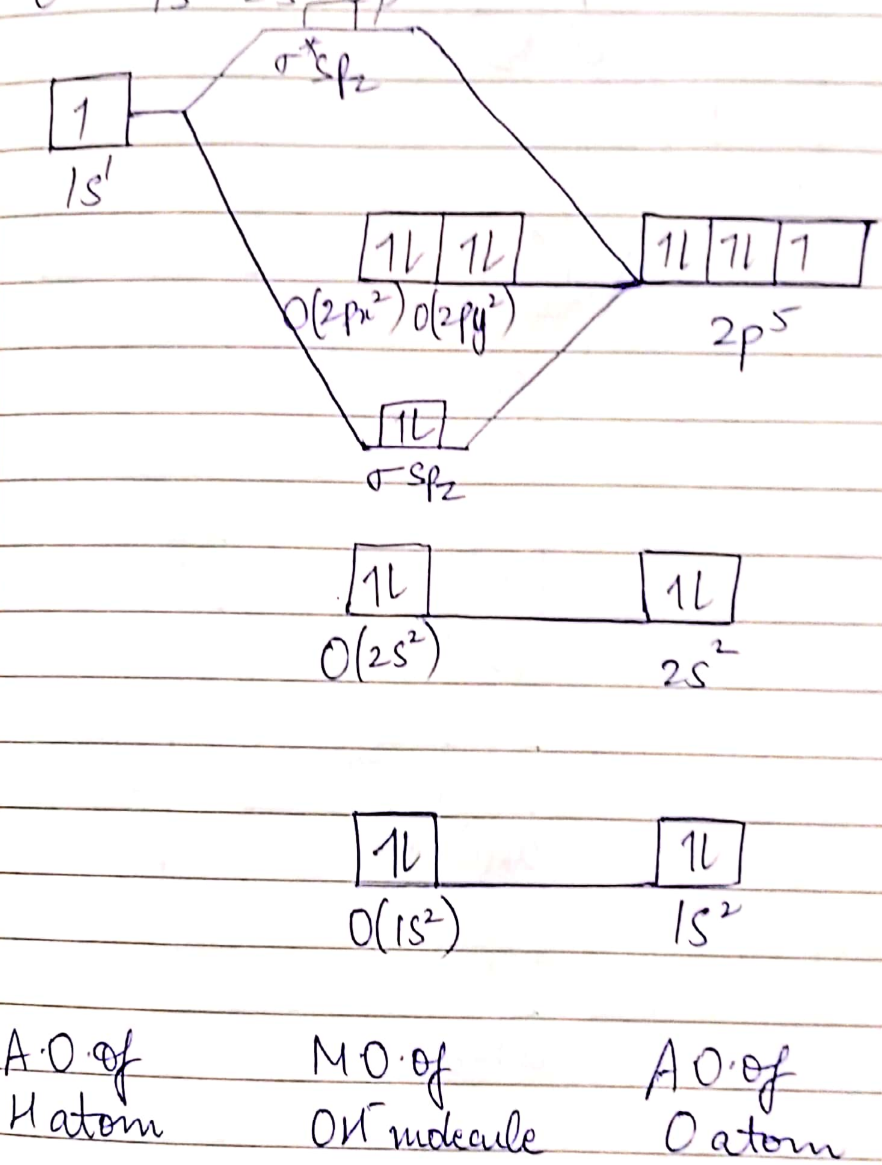
$B.O = \frac{2-0}{2} = 1$ (Diamagnetic)

- OH^-

$H \to 1s^1$

$O \to 1s^2\ 2s^2\ 2p^4$

$O^- \to 1s^2\ 2s^2\ 2p^5$



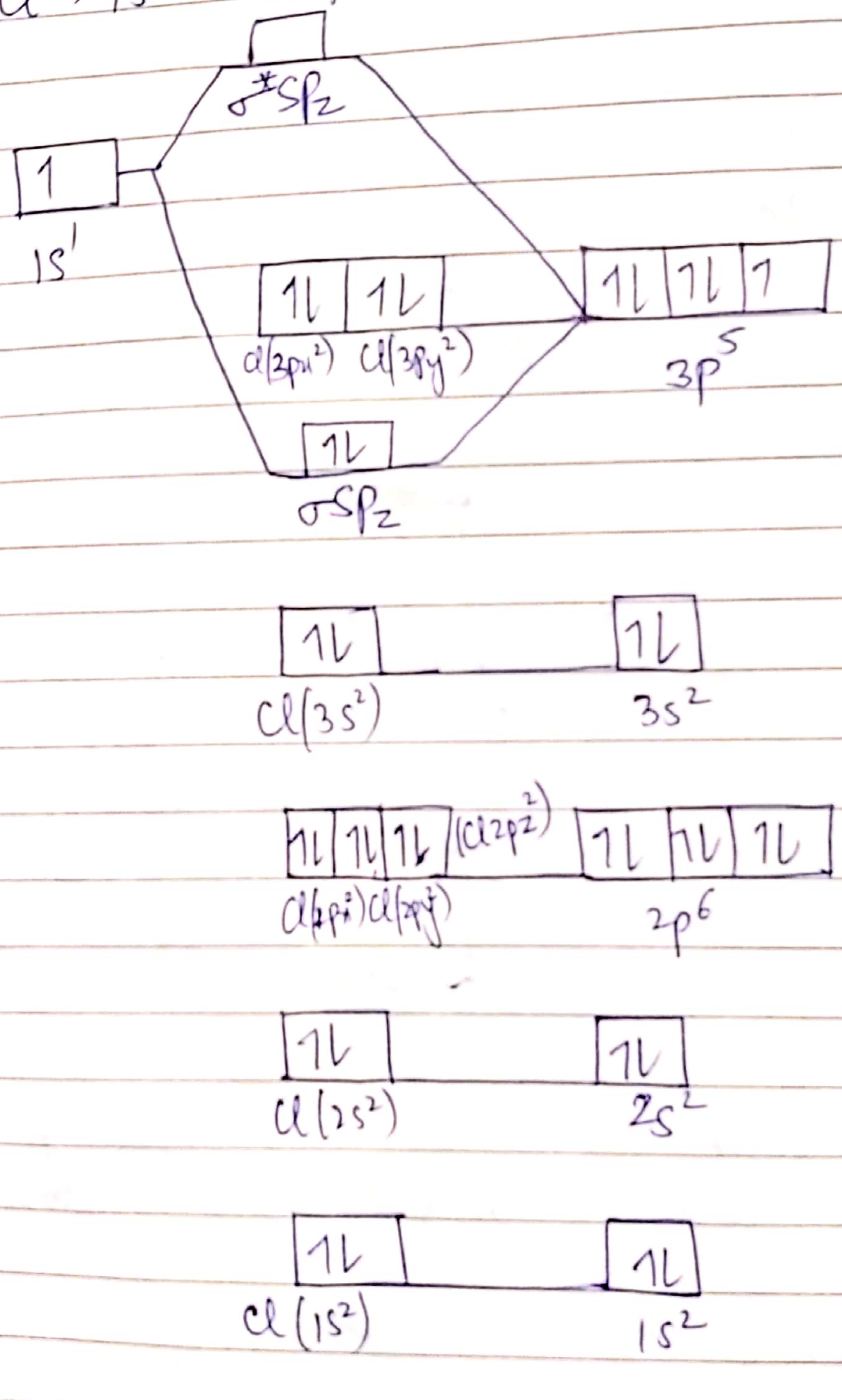
$\boxed{B.O = 1}$

(Diamagnetic)

- HCl

$H \rightarrow 1s^1$

$Cl \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

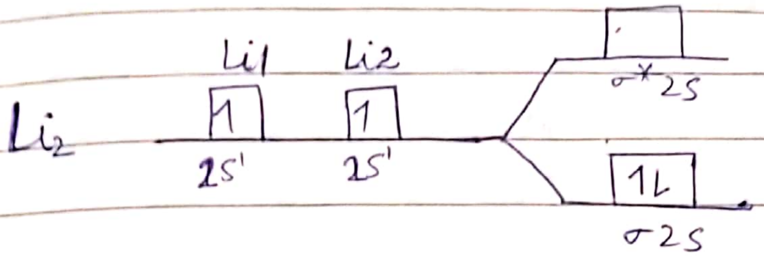


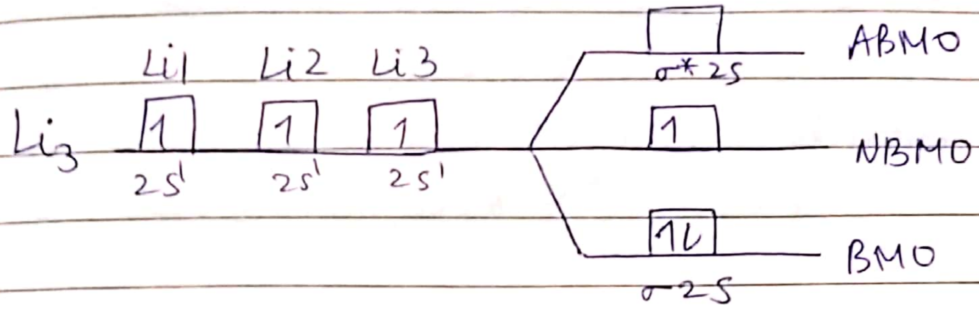
$B.O = \frac{2-0}{2}$

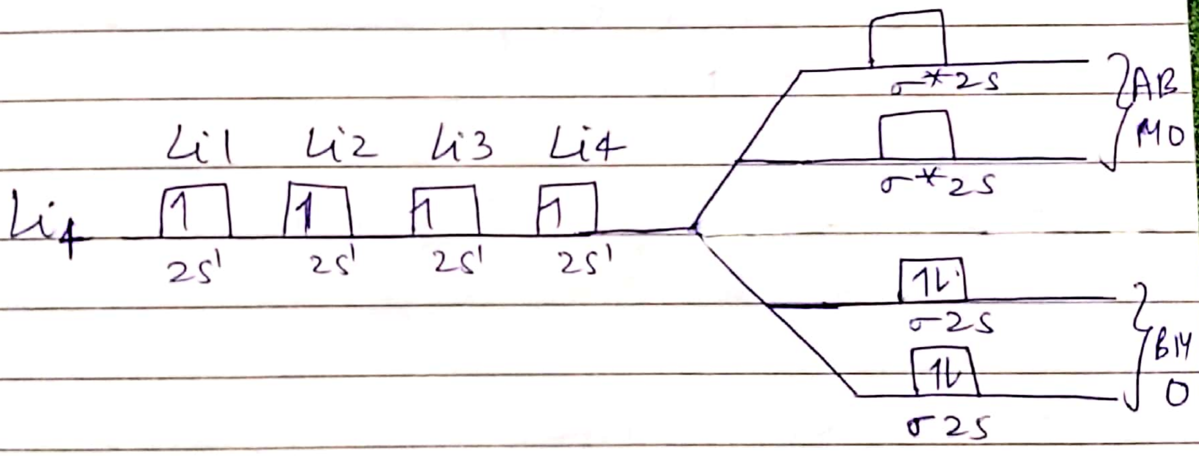
$\boxed{B.O = 1}$

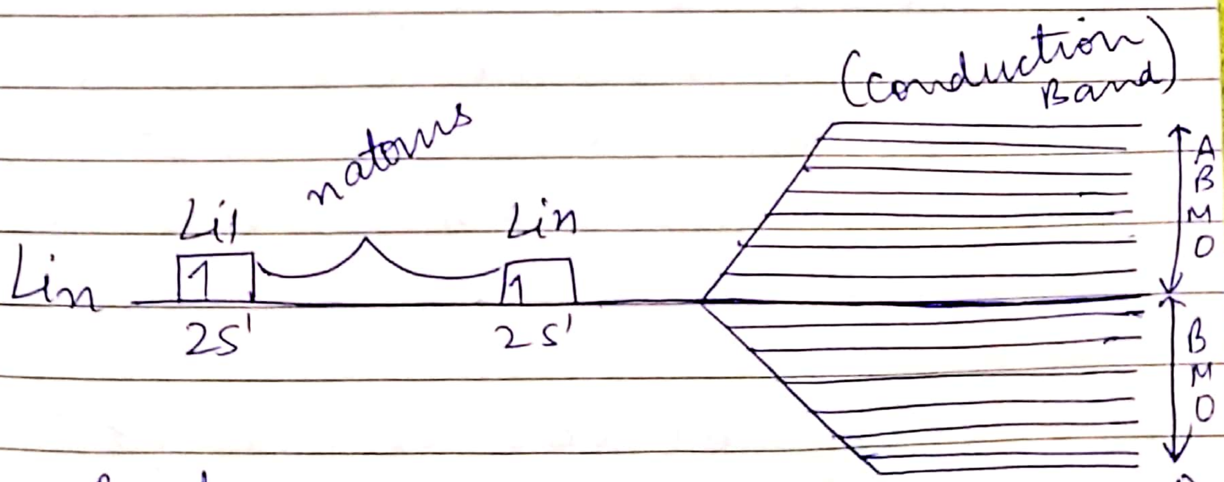
(Dia)

✗ Band Theory of solids / MOT of solids →









Band gap = 0

→ Acc. to this theory, e⁻s in the metal are considered to cover the whole crystal lattice & metallic bond is formed by the delocalisation of all orbitals containing free e⁻s.

→ When diatomic molecule is formed, one of the 2 atomic orbital of equal energy combine together and give 2 A.O, one Bonding & one Antibonding.

→ When Li_3 is formed, three M.O. will be generated, one is BMO, one ABMO & one NBMO.

→ In case of metal, BMO is completely filled & ABMO is completely vaccant

→ The outermost energy band that is completely filled is known as Valence band while the band above the valence band is empty at room temperature & known as Conduction band.

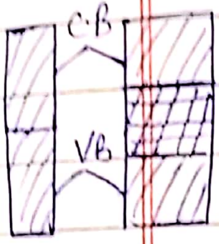
→ The gap b/w VB to CB is almost negligible in case of metals & known as Band gap.

→ In metals, e^- can easily jump from VB to CB, so metals are good electrical & thermal conductors.

✗ Classification Of Solids

Conductors | Semi-Conductors | Insulators

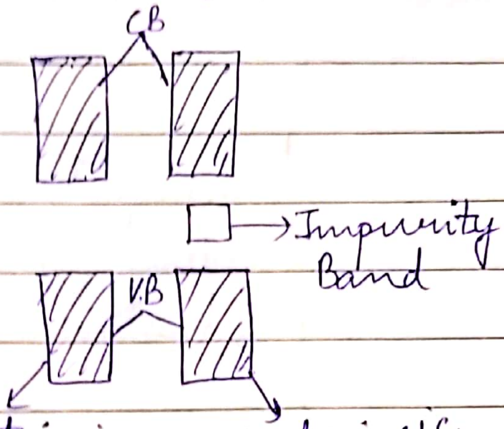
Conductors



{Banggap = negligible}

{Ex→ Metals}

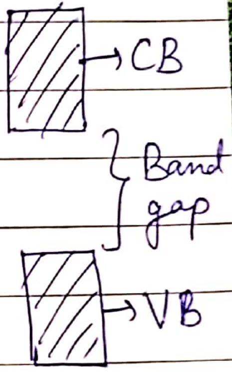
Semi-Conductors



{Bandgap = 0 to 3eV}

{Ex→ Silicon ≃ 3eV}

Insulators

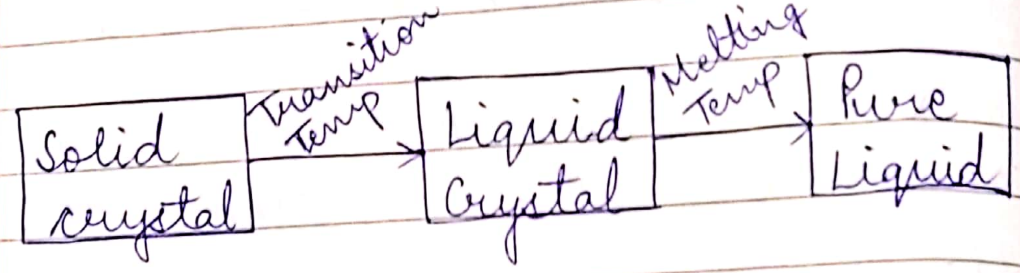


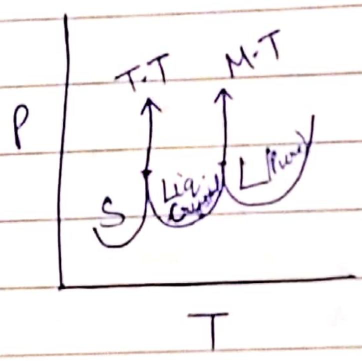
{Ex→ Diamond ≃ 5.1eV}

{Bandgap is more than 3eV}

✗ Liquid Crystal OR Mesophase OR Anisotropic Liquid OR Mesomorphic State →

→ A state of matter that is intermediate between the solid crystalline & ordinary liquid is known as mesamorphic state. The intermediate phase that shows an anisotropic behaviour is known as liquid crystal.





Properties	Solid	Liq. Crystal	Liquid
1. Orientational Order	✓	✓	✗
2. Positional Order	✓	✗	✗
3.	Anisotropic	Anisotropic	Isotropic
4	Immobile	Mobile	Mobile

$-\overset{O}{\overset{\|}{C}}-O-$ ester group

$-N=N-$ azo group

$-N=\underset{O}{\underset{\downarrow}{N}}-$ azoxy group

* Classification of Liquid Crystal

Thermotropic Liquid Crystal {Formed by change in temp}

Lyotropic Liquid Crystal {Formed by using critical conc of solvent}

Solid crystal → (critical conc. of solvent) → liquid crystal → (excess solvent) → Lyotropic Liq. Crystal

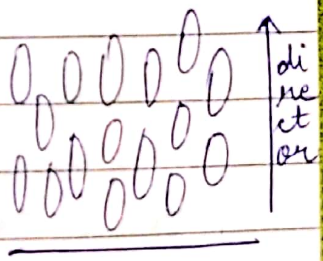
* Thermotropic Liquid crystal →

Nematic Mesophase

Cholesteric Mesophase

Smectic Mesophase

* Nematic Mesophase → Nematic means thread-like.



→ This phase is characterized by total loss of positional order & it ~~flows~~ behaves like a normal liquid.

→ The molecules are less ordered

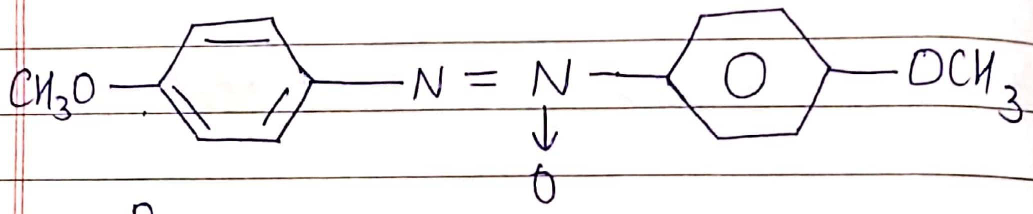
→ They point in the same dirⁿ but they start & stop at different positions within the liquid.

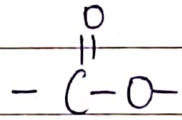
→ The molecules in Nematic liquid crystal appear to have thread-like appearance when observed in polarised light.

→ They are oriented || to the director.

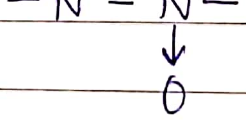
→ The molecules in this phase are optically inactive or racemic mixture.

→ Ex→ p-azoxy anisole



→  $-\overset{\overset{O}{\|}}{C}-O-$ ester group

→ −N=N− azo group

→  $-N=\underset{\underset{O}{\downarrow}}{N}-$ azoxy group

{Optically Inactive & Achiral}

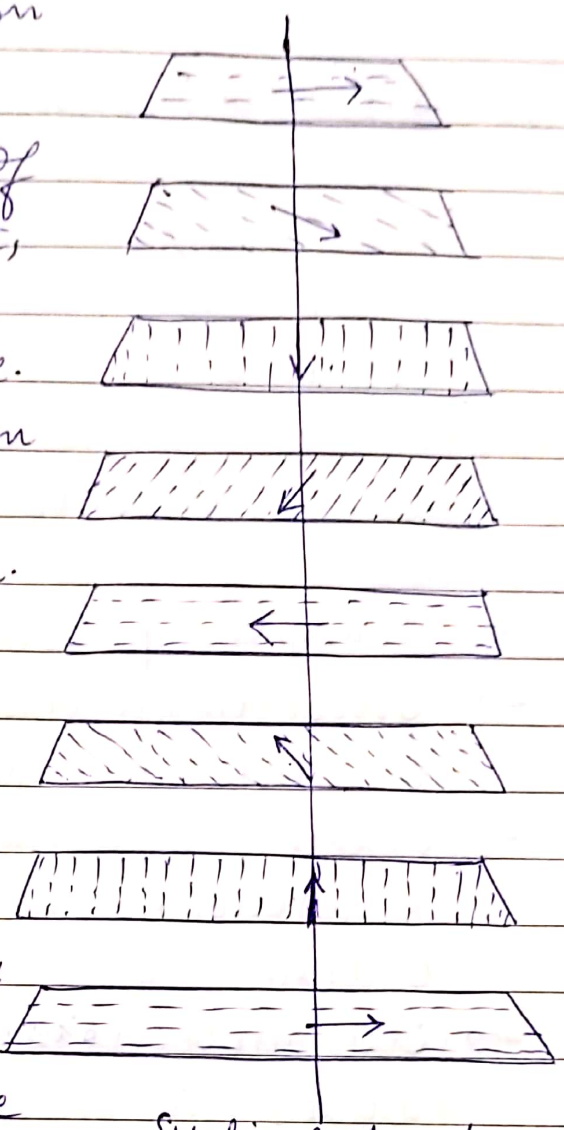
✗ Cholesteric Mesophase → [Cholesterol Derivative] [OR Chiral Nematic phase]

→ Many derivatives of cholestrol form this type of liquid crystal.

→ A necessary condition for the formation of this phase is that, molecules are chiral in nature.

→ This is also known as twisted Nematic phase.

→ They have str^{r} similar to Nematic phase but each plane of molecules is twisted slightly in relation to the plane above or below.



{Helical structure}

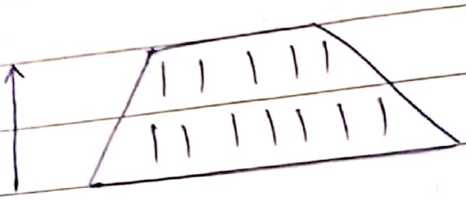
→ The molecules are aligned || to the Director.

→ The slight twisting makes these Liq. crystals as a color indicator.

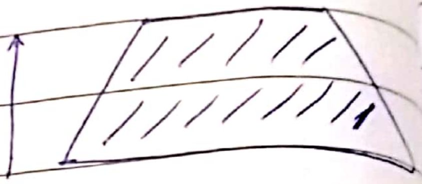
→ Example → ~~tota~~ Cholesteric Chloride.

* Pitch → It is defined as the distance it takes for the director to rotate one full turn in the helix.

* Smectic Mesophase → [Soapy/Slippery]



Smectic A



Smectic C [Tilted]

→ Example → p-azoxybenzoate

→ Smectic means soap b/c these liquid crystals are slippery in nature.

→ There is a small amount of orientation as well as positional order is present.

→ The molecules form plane ⊥ to the axes of the molecules & they point along the director.

→ <u>Smectic-A</u> → The long axis of the molecules are || to the director which may be normal to the planes or tilted by certain angle <u>[Smectic C]</u>

→ In Smectic B phase, the director is ⊥ to the smectic plane with the molecules arranging themselves into a network of hexagons.

✗ Applications of liquid crystal →

→ Cholesteric liquid crystal is used in:

1. Basic study of circulatory system.
2. Detection of cancer.
3. Detection of tumer.

→ ~~Chlore~~ Cholesteric liquid crystal is also used in solid state electronic devices to locate fault.

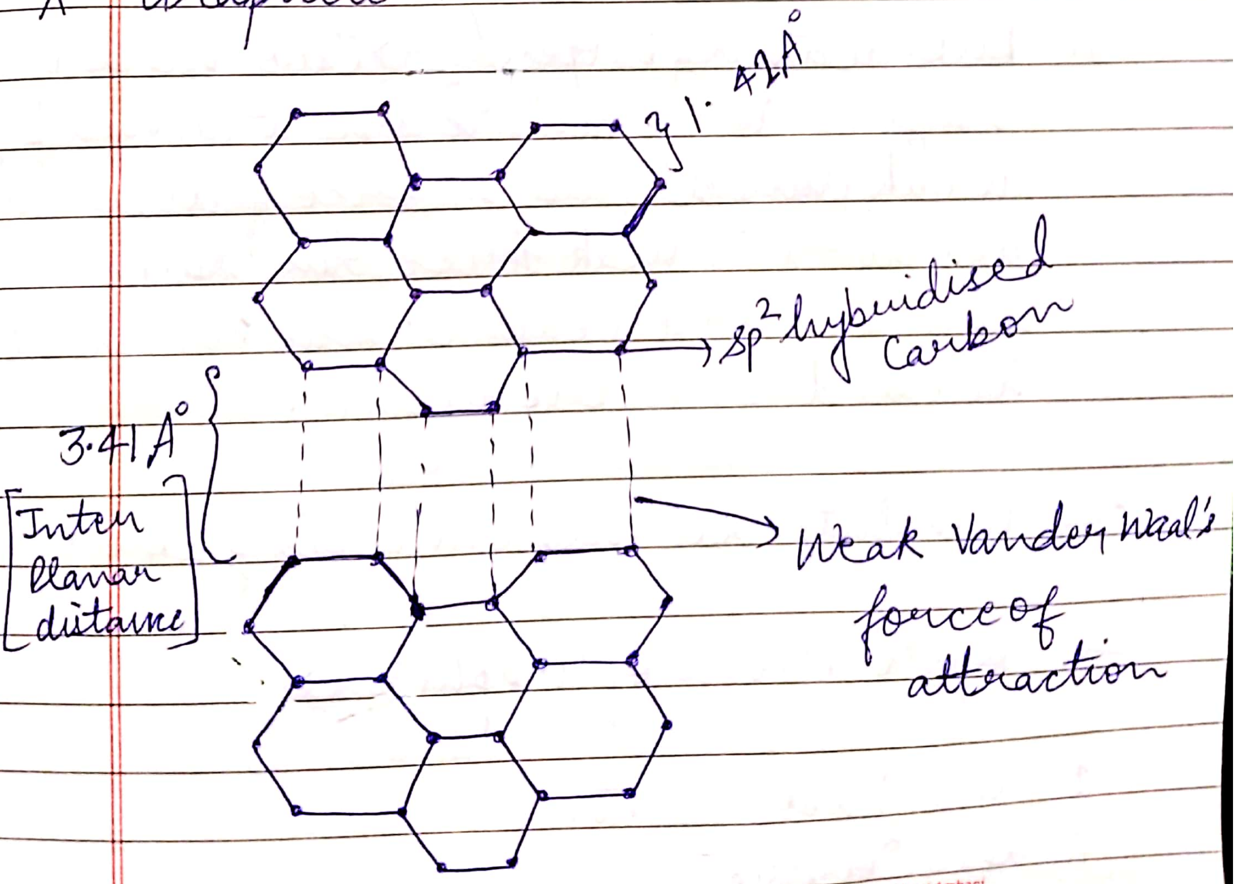
→ For testing of radiations.

→ Used as a lubricant.

→ Used in LCDs

→ Used in mood rings.

✗ Graphite →



"You have to take the calculated risk, to earn something." – Dhirubhai Ambani

* Allotropy → A property of certain element to exist in two or more different forms is known as allotropy.

* Structure Of Graphite → In Graphite, each carbon is sp^2 hybridised and is attached with other 3 Carbon atoms by single covalent bond.

→ One e^- over each carbon atom is free to move under the influence of applied potential so it is used as a good conductor.

* Lubricating Property → Two hexagonal layers in graphite are attached by weak Vander Waal's force of attraction, due to this weak force, two layers can slip over each other. Hence it is used as a Lubricant.

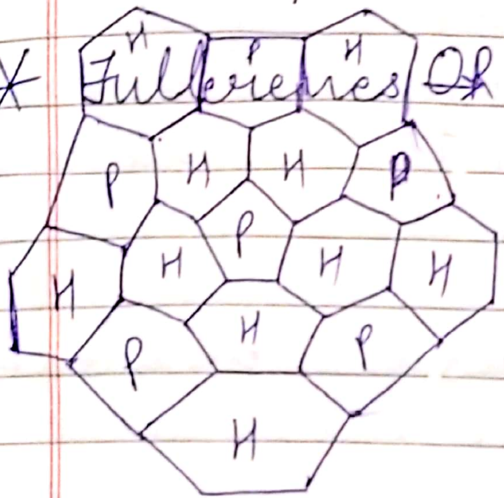
→ Graphite has high melting point.

* Applications of Graphite →

1. As a Lubricant.
2. As a Conductor.

3. In batteries.
4. In pencil lead.
5. In Nuclear reactor.
6. For preparation of fullerenes.

* Fullerenes OR Buckminster Fullerene→ OR C_{60} OR Bucky Ball



Pentagons = 12
Hexagons = 20

→ Buckminster Fuller has described the skeleton of fullerene.

→ It is discovered by Kroto and Smalley in Rice University [USA].

→ Buckmister fuller is an Architect.

* Structure of Fullerene→

→ In C_{60}, each carbon is sp^2 hybridised & attached with other 3 carbon atoms by using 2 single bonds & one double bond.

→ Fullerenes have 60 vertices, 32 faces out of which 12 are Pentagons & 20 hexagons.

→ Fullerenes have Truncated Icosahedron geometry.

→ Molecules are aromatic in nature due to presence of alternate double & single bond.

* Preparation → Fullerene is prepared by Vapourising graphite rod in inert atmosphere at low pressure where black soot C mixture of (C_{70}, C_{60}, C_{80}, C_{90}, ... is formed which further dissolves in benzene and are separated by solvent extraction method then pure C_{60} is isolated by column chromatography.

$$\text{Graphite Rod} \xrightarrow[\text{Electric spark [Low pressure]}]{\text{inert atmos.}} \text{Black soot } [C_{60}, C_{70}, C_{80}, C_{90}, \ldots]$$

↓

Dissolve in benzene

↓

Solvent Extraction

↓

C_{60} isolated by column Chromatography

Date __/__/____ Page No. ______

* Properties of Fullerenes →

1. Fullerene is black powdery material.

2. It is very tough and thermally stable.

3. It forms deep magenta coloured solution when dissolved in C_6H_6.

4. It can compress upto 30% of its volume without destroying carbon skeleton.

5. Endohederal Compounds → Alkaline metal may occupy the hollow cage like Structure and form Endohederal compound which is used as super conducting material.

→ Example → $C_{60}K_3$

6 Exohedral Compounds →

→ If the radicals are attached outside the hollow cage like structure then it is known as Exo-hedral compound and it is used as a ferro-magnetic material.

→ Example → TDAE
Tetrakis Dimethyl amino ethylene

✗ Applications of Fullerenes ~~Exohederal Compounds~~ →

1. Used as a superconducting material.
2. Used as a ferromagnetic material.
3. Used as a lubricant.
4. In electronic & optical devices
5. To produce small diamond and diamond film.
6. Used in nano-technology.

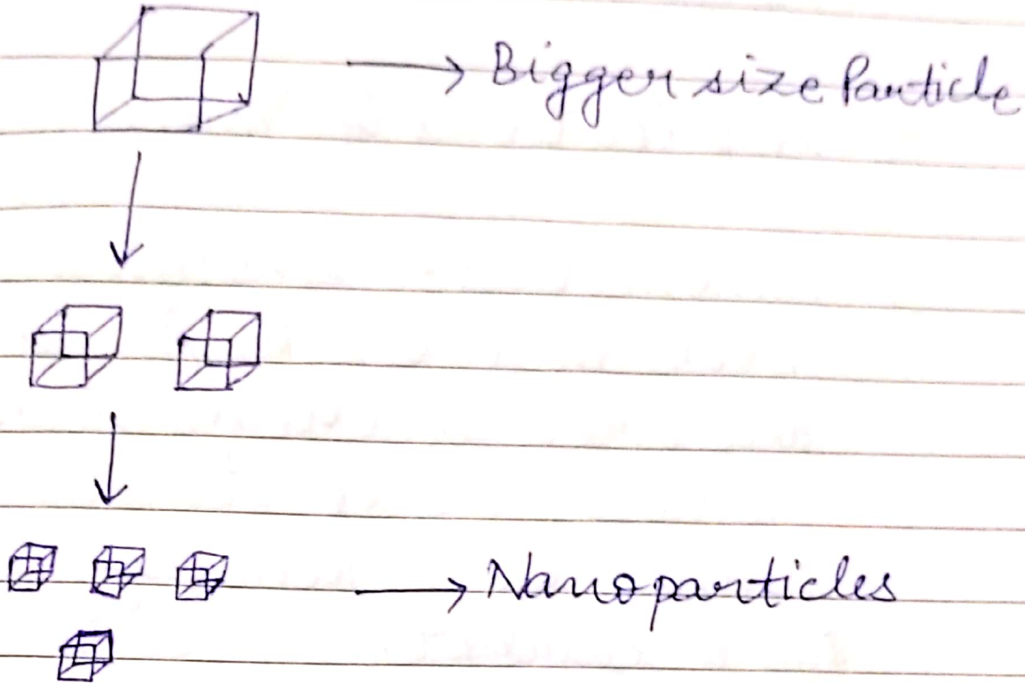
✗ Nanomaterials → [diameter → 1 - 100 nm]

→ They are materials with dimensions in the range of 100 to 1 nm.

→ They can be metal, ceramics, composites or polymers.

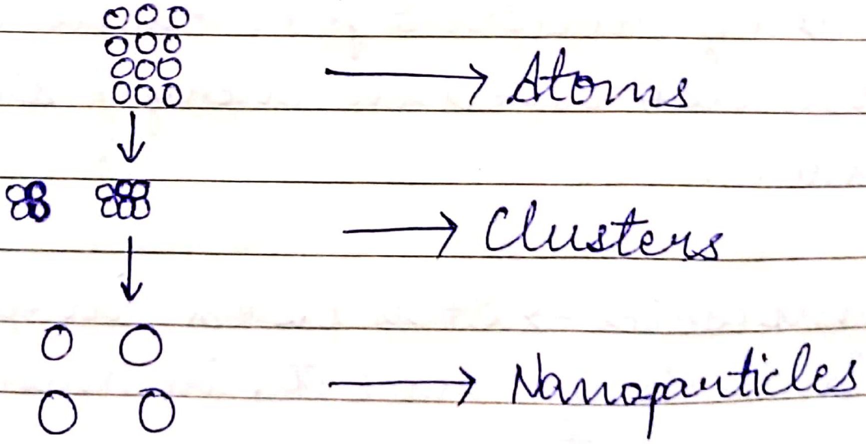
X Methods for Preparation →

1. Topdown Approach →



→ In this method, small features are created from large substract by grinding. Ex → Ballmill.

2. Bottom up Approach →



→ This method starts with very small units like molecules or atoms which are assembled together & form larger structure.

* Applications Of Nanomaterials →

1. Nanometals → Nanopowders of noble metals like Ag, Au, Pt, Pd are used in electronic energy devices, in construction, in Information Technology, in medicine & as a catalyst.

2. Carbon NanoTubes [CNT's] → CNT's are sheets of graphite, rolled upto make a tube having diameter 0.4 nm.

→ It is used as a needle to bring active agent into living cell for neuron growth & for regeneration, it is also used in energy storage devices.

3. Composites → It is used in space craft & , lawn tennis racket, in musical instruments.

4. Fullerenes → already done before.

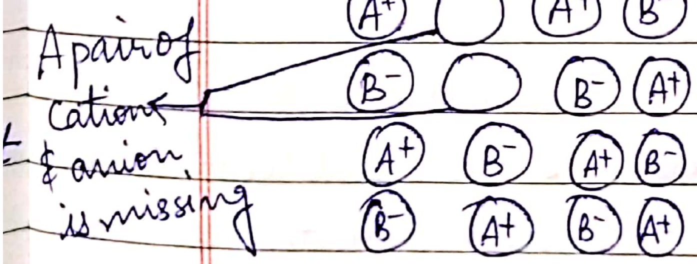
5. In Cosmetics → Nano size TiO_2 is currently used in sunscream as they reflect UV rays.

✱ Solid Defects → OR Solid Imperfections →

→ Deviation from the regular or periodic arrangement of a crystal is known as crystal defect.

✱ Stoichiometric Defects → The defects in which the stoichiometry [the ratio of +ve & −ve ions] do not disturb are known as Stoichiometric defects.

1. Schottky Defect → When a pair of cations & anions are missing from their lattice sites, then it is known as Schottky defect.

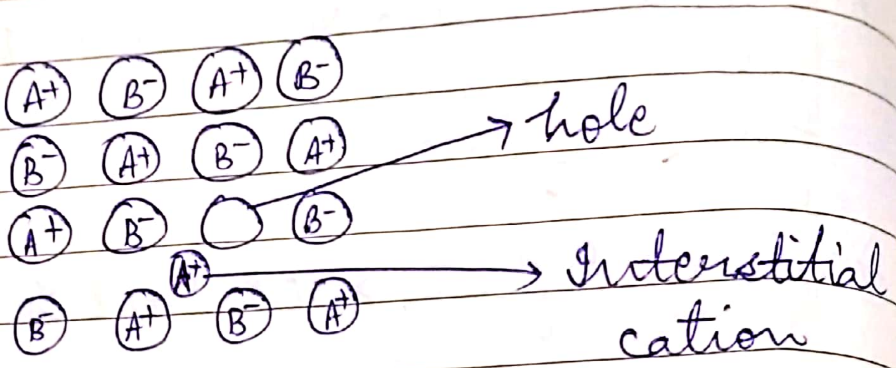


→ Density ~~remains same~~ decreases.

→ Generally found in high coord. no. compounds.

→ Ex → NaCl, AgBr.

2. Frenkel Defect →



→ When a cation or anion is moved to interstitial space, then it is known as frenkel defect.

→ Density will not change.

→ Generally found in lower Coord. no compounds

→ Generally cations move due to lower size than anions.

→ Ex → ZnS, AgBr, AgCl

* Non-Stoichiometric Defects →

→ Metal Excess defect → Excess of cation / deficiency of anion

→ Metal Deficiency defect → Excess of anion / Deficiency of cation

→ The defects defects which disturb the stoich. of compounds is known as non-stoichiometric defects. These defects are either due to presence of excess metal ions/deficiency of metal.

① Excess Cation → In this case there are extra positive ions occupying interstetial sites and e⁻ in another interstetial site to maintain electrical neutrality.

→ Ex → ZnO.

② Deficiency of anions → In this case, -ve ions may be missing from their lattice site leaving hole in which the e⁻ occupy to maintain the neutrality. Ex → NaCl, KCl.

③ Due to Excess anion → In this case, extra anions may occupy interstetial position & the extra -ve change is balanced by extra charge on adjacent metal ions. Ex → FeO, FeS.

④ Deficiency of cation → The +ve ion may be missing from their lattice sites and the charge is balanced by adjacent metal ions.