VBT (Valence Bond Theory) [By Heitler & London]
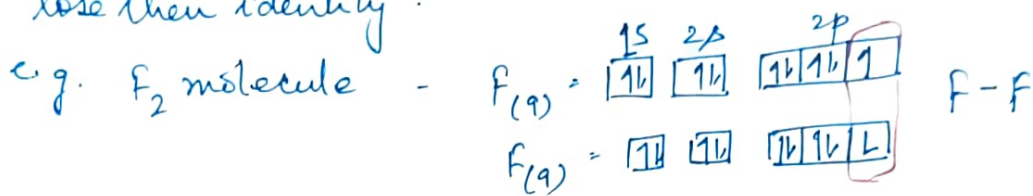
Only the half filled atomic orbitals of the combining atoms interact with each other and the inner filled atomic orbitals (AOs) remain intact i.e. they donot lose their identity.

e.g. F_2 molecule -

$F_{(9)} =$ [$1s$: ↑↓] [$2s$: ↑↓] [$2p$: ↑↓|↑↓|↑]   F - F

$F_{(9)} =$ [↑↓] [↑↓] [↑↓|↑↓|L]

Limitations :-

1- Paramagnetic nature is not explained by VBT.
2- Odd e^- bond formation is not explained.
3- Directional nature of covalent bond is not explained.
4 -
5 -

Molecular Orbital Theory (MOT)

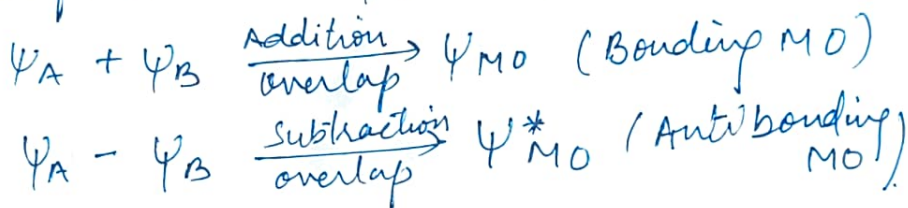This theory was developed by Hund & Mulliken

Postulates (Main features) -

1- The atomic orbitals of the combining atoms overlap and form molecular orbitals. Therefore these AOs lose their identity.

2- Molecular orbitals are associated with the entire molecule.

3- The electrons in the AOs are influenced by one nucleus while the electrons in the MOs are influenced by all the nuclei combining nuclei. Therefore MOs are called as POLYCENTRIC in nature.

4- The no. of MOs formed = The no. of AOs combining

5- The filling of electrons in MOs is same as that in AOs i.e. according to Hund's Rule of maximum multiplicity (pairing of e^- in the degenerate MO cannot occur until each of them is singly filled), Aufbau Principle (in order of increasing energy of the

MOs) and Pauli's exclusion Principle (Maximum no. of e̅ in each M.O. is 2 and each one of them is having opposite spin).
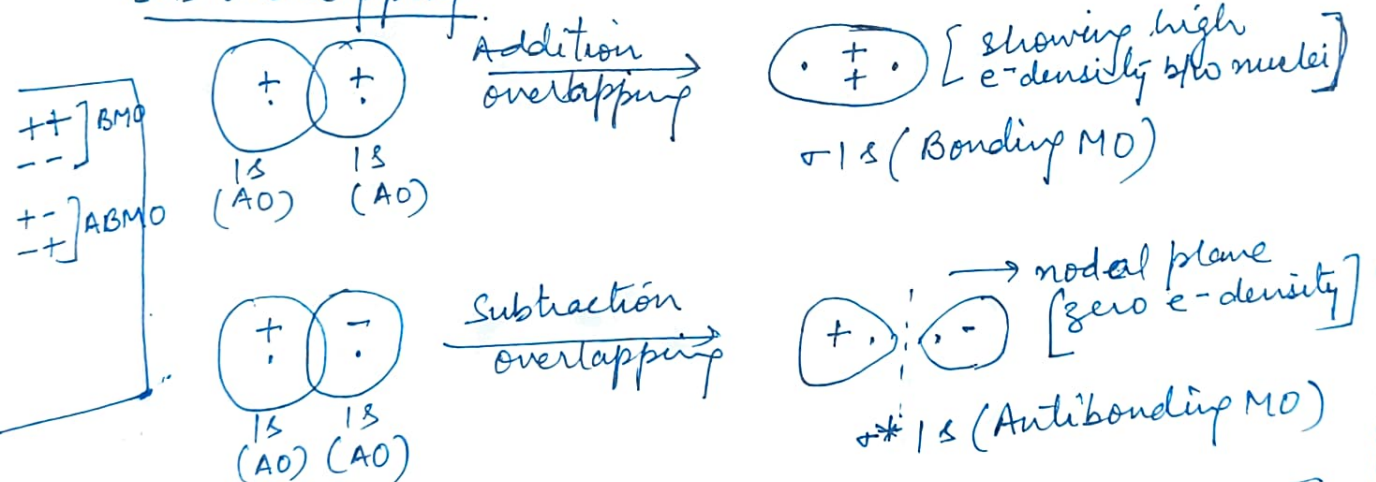
6. Molecular orbitals are formed by the linear combination of Atomic orbitals (LCAO method). The linear combination of AOs can take place by addition or subtraction of the wave functions of atomic orbitals involved i.e. ψ. (wave mechanics expresses AOs as ψ.

ψ ∿∿∿

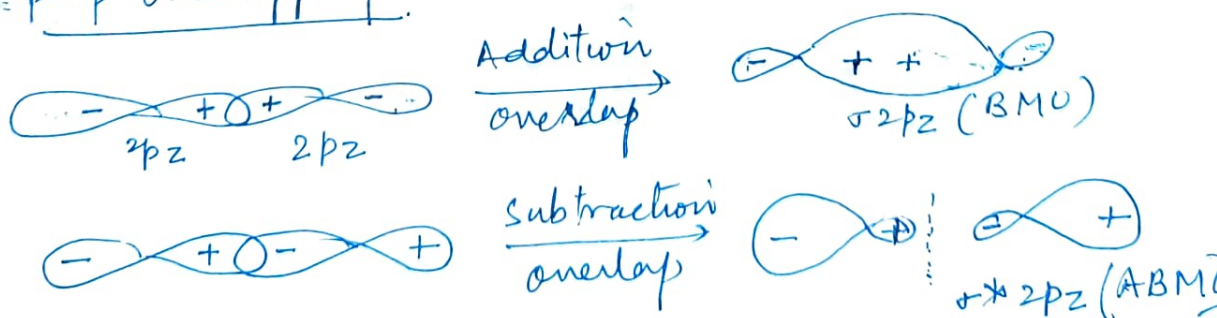For e.g. For H_2 molecule

Two atoms of Hydrogen H_A H_B
Their wave functions ψ_A ψ_B

$$\psi_A + \psi_B \xrightarrow[\text{overlap}]{\text{Addition}} \psi_{MO} \text{ (Bonding MO)}$$

$$\psi_A - \psi_B \xrightarrow[\text{overlap}]{\text{Subtraction}} \psi^*_{MO} \text{ (Antibonding MO)}$$

s-s overlapping.

$$\left.\begin{array}{c} ++ \\ -- \end{array}\right] BMO$$

$$\left.\begin{array}{c} +- \\ -+ \end{array}\right] ABMO$$

1s (AO) 1s (AO)   Addition overlapping → [showing high e-density b/w nuclei] $\sigma 1s$ (Bonding MO)

1s (AO) 1s (AO)   Subtraction overlapping → nodal plane [zero e-density] $\sigma^* 1s$ (Antibonding MO)

p-p overlapping.

2pz 2pz   Addition overlap → $\sigma 2pz$ (BMO)

Subtraction overlap → $\sigma^* 2pz$ (ABMO)

Addition → π 2px (BMO)

2px 2px

Subtraction → π* 2px (ABMO)

2px 2px

Addition → π 2py (BMO)

2py 2py

Subtraction → π* 2py (ABMO)

2py 2py
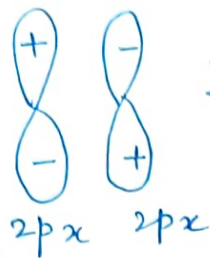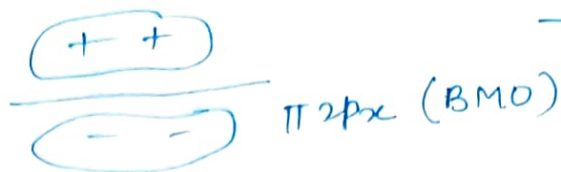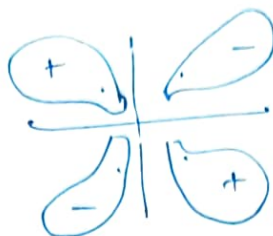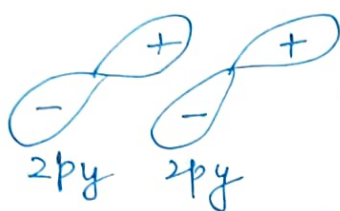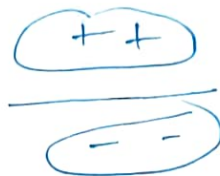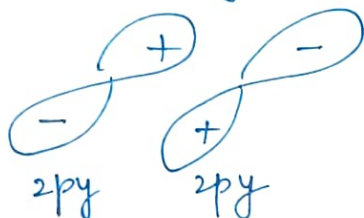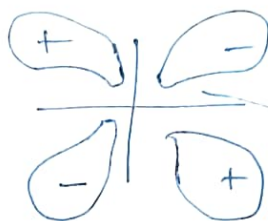
| BMO (Bonding MO)	ABMO (Antibonding MO)
1. formed by the addition of overlapping of AOs. $\Psi_{MO} = \Psi_A + \Psi_B$	- formed by the subtraction of overlapping of AOs. $\Psi_{MO}^{*} = \Psi_A - \Psi_B$
2. formed by the combination of same sign (++ or --)	- by the combination of opposite signs (+ -)
3. In a BMO, the attraction of both the nuclei for both the e's increases, which favours the bond formation (Stablize the molecule)	- In an antibonding MO, the repulsion of both the nuclei increases as the e-density removes from the centre which does not favour bond formation (destablise the molecule)
4. Have lesser energy than AOs.	- Have higher energy than AOs.

Energy level sequence and diagrams
for the filling of electrons in Molecular oilbitals.

Case-I: Homoatomic or Homonuclear molecules -
For H_2, He_2 (hypothetical), Li_2, Be_2, B_2, C_2 N_2 and their ions :-

(atoms having atomic no. < 7)
(Diatomics of 2nd period)

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \Pi 2p_x = \Pi 2p_y, \sigma 2p_z, \Pi^*_2 p_x = \Pi^* 2p_y, \sigma^*_2 p_z$$

Case-II. For O_2, F_2, Ne_2 (hypothetical) (atoms having and their ions :- atomic no. > 7)

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \Pi 2p_x = \Pi 2p_y, \Pi^*_2 p_x = \Pi^*_2 p_y \sigma^*_2 p_z$$

(AO)   (MO)   (AO)   (AO)   (MO)   (AO)
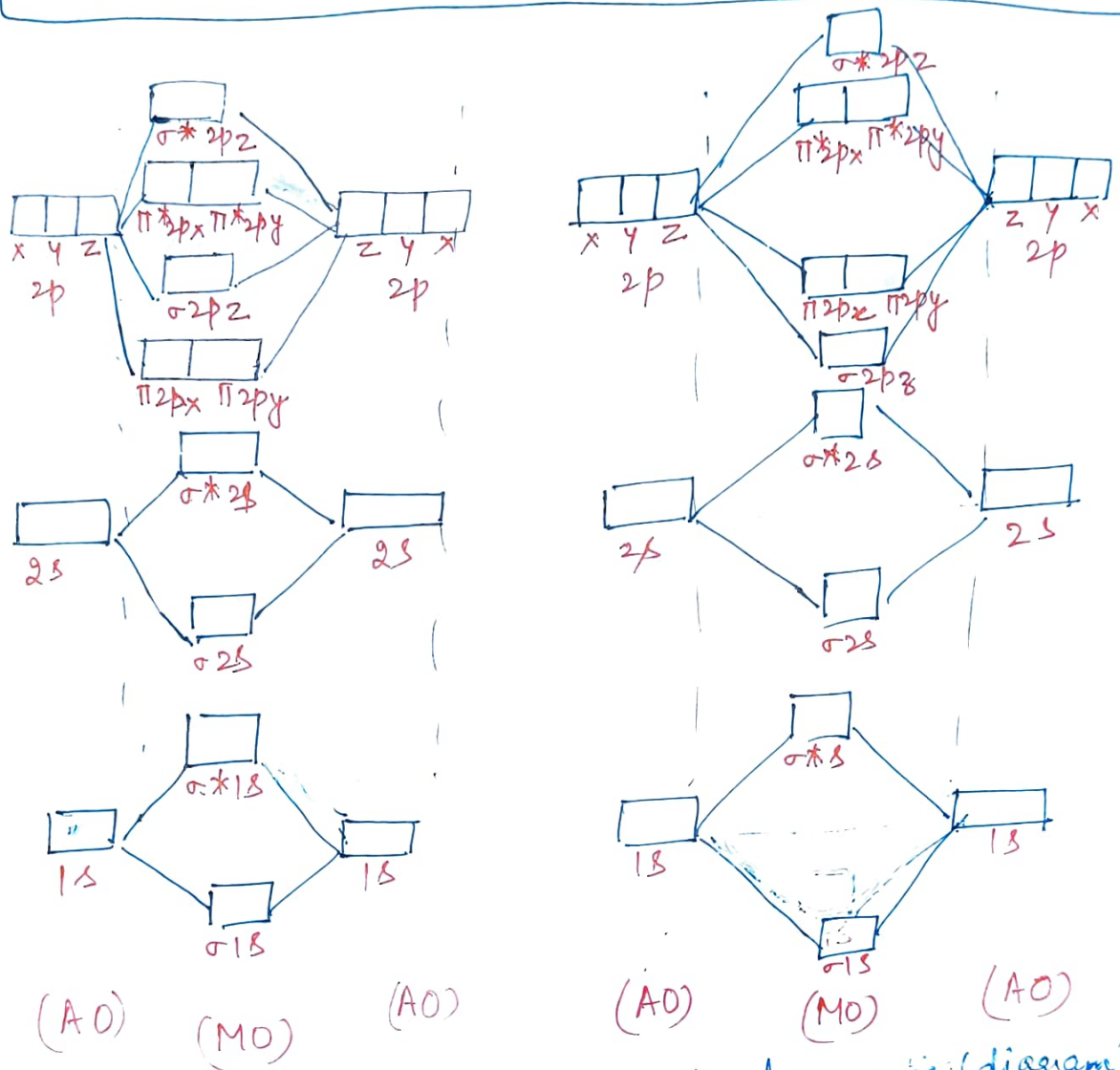
NOTE :- The difference in energy level sequence (diagram)
is because of the intermixing of the 2s and $2p_z$
atomic orbitals (in elements upto at.no. 7) as their
energy difference is very less, while the energy difference
is large in the atoms having at.no. > 7.

Bond order :- No. of covalent bonds in a molecule.

$$B.O. = \frac{Nb - Na}{2}$$

[Where Nb = No. of e^- in Bonding MO &
Na = " " " " Anti bonding MO].

B.O. = 1 → single bond
     = 2 → double "
     = 3 → triple "
     = fractional → Odd e^- bond.

If $Nb > Na$ → Stable molecule
    $Nb = Na$ → molecule does not exist
    $Nb < Na$ → "

Bond order α Bond strength
    " α Bond dissociation energy.

Bond order $\alpha \frac{1}{Bond\ length}$

e.g.	Bond length	Bond order	Bond energy
N_2 molecule (N≡N)	110 pm	3	945 KJ/mol
O_2 molecule (O=O)	121 pm	2	495 KJ/mol

Magnetic character :- when all the electrons in a molecular orbital are paired up, (the molecule is repelled in the magnetic field), it is a <u>Diamagnetic molecule</u> and when one or more electrons are unpaired in the molecular orbitals of a molecule, it is a <u>Paramagnetic molecule</u> (it is attracted by the magnetic field).

[NOTE :- The molecular orbitals that do not participate in bond formation are called as Non-bonding M.O. & their energies are equal to the energy of Atomic orbitals].
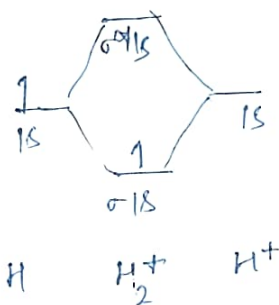
BONDING IN DIATOMIC MOLECULES

① **Homonuclear** - H_2
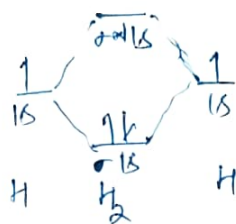
$H_2 = \sigma 1s^2$

$$B.O. = \frac{Nb - Na}{2} = \frac{2 - 0}{2} = 1 \ (\text{single bond})$$

NO unpaired e^- → diamagnetic

H_2^+

$H_2^+ = \sigma 1s^1$

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

Paramagnetic
Bond length is larger than H_2'
H and bond e is lesser thus
weaker ionthan H_2 molecule.

Hypothetical He_2 molecule :-

$He_2 = 2 + 2 = 4 \ e^-$, $\sigma 1s^2$, $\sigma^* 1s^2$

$$B.O. = \frac{2 - 2}{2} = 0 \quad i.e. \ NO \ bonding$$
betn He - He
no existence.

Helium molecule ion He_2^+ :-

$He_2^+ = 2 + 1 = 3$, $\sigma 1s^2, \sigma^* 1s^1$

$$B.O. = \frac{2 - 1}{2} = \frac{1}{2}, \quad Paramagnetic$$

Li₂

$3h + 6e$

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$

B.O. $= ?$; $= 1$

Be₂ $= 4+4 = 8e$

$\sigma 1s^2, \sigma^* 2s^2 \ldots \sigma^* 2p_z^1$

$2\dfrac{-?}{?} = 0$

Molecule does not exist.

N₂ molecule: $7+7 = 14e$

$KK\ (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2, (\pi 2p_y)^2,$
$(\sigma 2p_z)^2$

B.O. $= ?$; $= 3$

One sigma and 2 π bond
Diamagnetic

O₂⁺ $8+7 = 15e$

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

B.O. $= ?$; $= ?$

Paramagnetic.

Since the B.O of O₂⁺ is greater than O₂, the bond strength of O₂⁺ will be more than O₂ and bond is ~~stronger~~ stronger than O₂

O₂⁻ (superoxide ion) $8+9 = 17e$

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

B.O. $= \dfrac{8-5}{2} = 1.5$ Paramagnetic. The B.O of O₂⁻ is less than O₂, the bond in O₂⁻ will be weaker than O₂ and bond length is more than O₂.

F₂

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

B.O. $= ?$; $= 1$

Paramagnetic

C₂ $= 6+6 = 12e$

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

B.O. $= 6-2 = 2$

Diamagnetic

O₂ molecule: $8+8 = 16e$

$KK\ \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$
$\pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^1,$
$\pi^* 2p_y^1$ Paramagnetic B.O. $= \dfrac{8-4}{2}$

(3') O_2^- (Superoxide)

8 + 10 = 18 e⁻

KK $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_3^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^2, \pi^* 2p_y^1$

B.O. : $\frac{8-6}{2} = 1$

weaker bond than O_2

higher bond length than O_2.

Bond dissociation e - $O_2^+ > O_2 > O_2^- \cdot > O_2^-$

Bond length - $O_2^- > O_2^- > O_2 > O_2^+$

(4) F_2 molecule / Ne_2 (Hypothetical) -

Heteronuclear Diatomic Molecules

Here, due to the difference in electronegativities of the atoms, the e's in a bonding MO spend more time near the more electronegative atom while the e's in an ABMO are closer to the less electronegative atom.

for e.g. CO Carbon monoxide molecule! -

6 + 8 = 14 e⁻
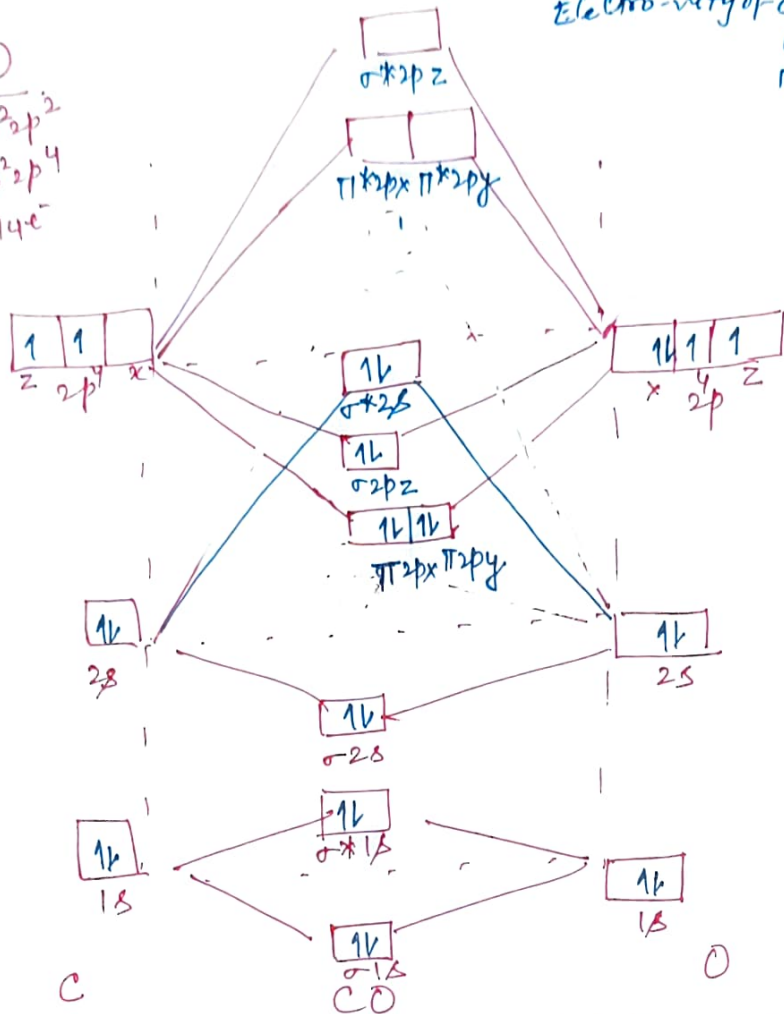
Becoz of higher electronegativity of O than c, the AOs of O will be of lower e than AOs of C. Thus BMOs recieves more contribution from AOs of lower e i.e. of O and would be closer to it in e and ABMOs recieve more contri than the ABMOs whi while ABMOs would be closer to it in e. the Carbon in e. The BMOs have more characteristics of AOs of O and ABMOs have more characteristics of AOs of C.

Electro-nity of C = 2·55
O = 3·44   ☞ 9.
N = 3·04

CO

$C = 1s^2, 2s^2 2p^2$
$O = 1s^2, 2s^2 2p^4$
Total $e^- = 14 e^-$

σ^*2p_z

π^*2p_x π^*2p_y

z $2p$ x

x $2p$ z

σ^*2s

$\sigma 2p_z$

$\pi 2p_x$ $\pi 2p_y$

$2s$

$2s$

$\sigma 2s$

σ^*1s

$1s$

$1s$

$\sigma 1s$
CO

C

O

$B.O. = \dfrac{Nb - Na}{2} = \dfrac{10-4}{2}$

$= 3$

Diamagnetic.

	Bond length	Bond order
CO	= 1·128 A°	3·5 (less stable) 1
CO$^+$	= 1·115 A°	3 (more stable)

CO^+

σ^*2p_z

π^*2p_x π^*2p_y

σ^*2s

z $2p$ x

x $2p$ z

$\sigma 2p_z$

$\pi 2p_x$ $\pi 2p_y$

$2s$

$2s$

$\sigma 2s$

σ^*1s

$1s$

$1s$

$\sigma 1s$
CO^+

C

O
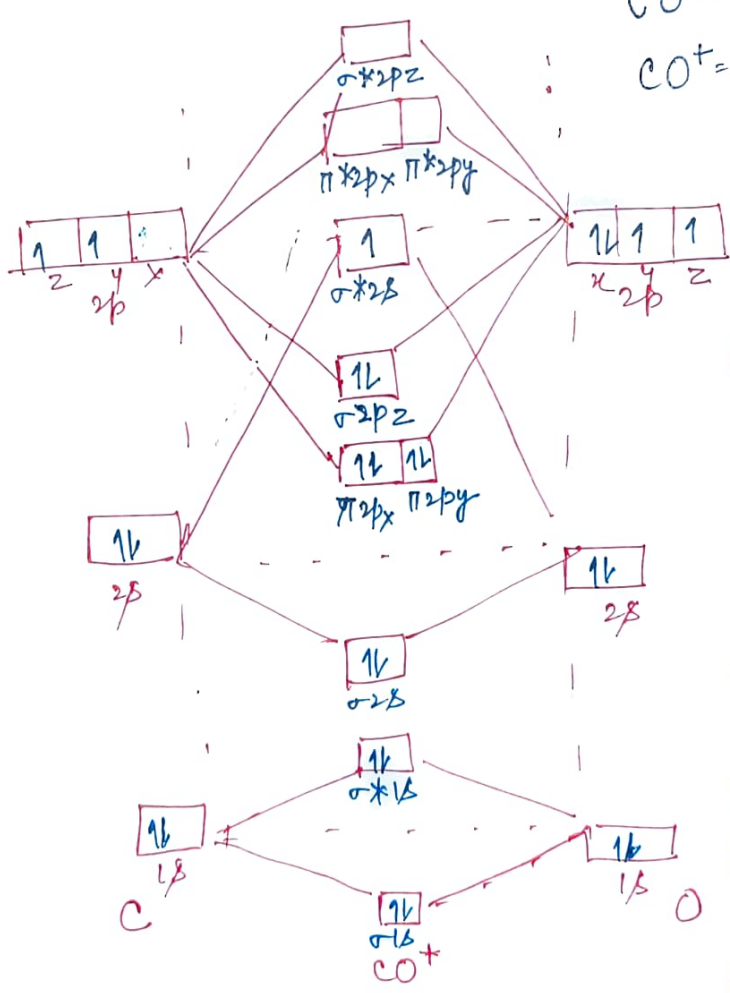
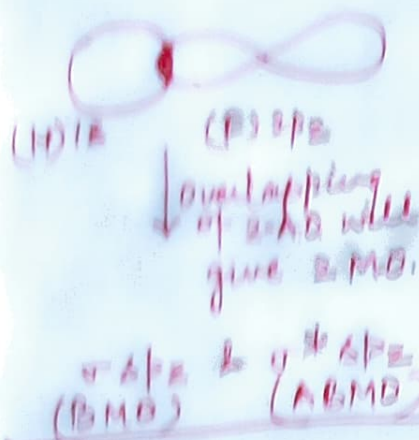$B.O. = \dfrac{Nb - Na}{2} = \dfrac{10-3}{2}$

$= 3·5$

Paramagnetic

NOTE:- electron in CO^+ is removed from σ^*2p orbital i.e. from antibonding orbital, therefore Bond order increases from 3 (in CO) to 3·5 in CO^+. Therefore bond length decreases.

HF

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

Overlapping only
between 1s of H
and 2p_z of F

(A) 1s   (B) 2p_z

Overlapping
of 2 A.O. will
give B.M.O.

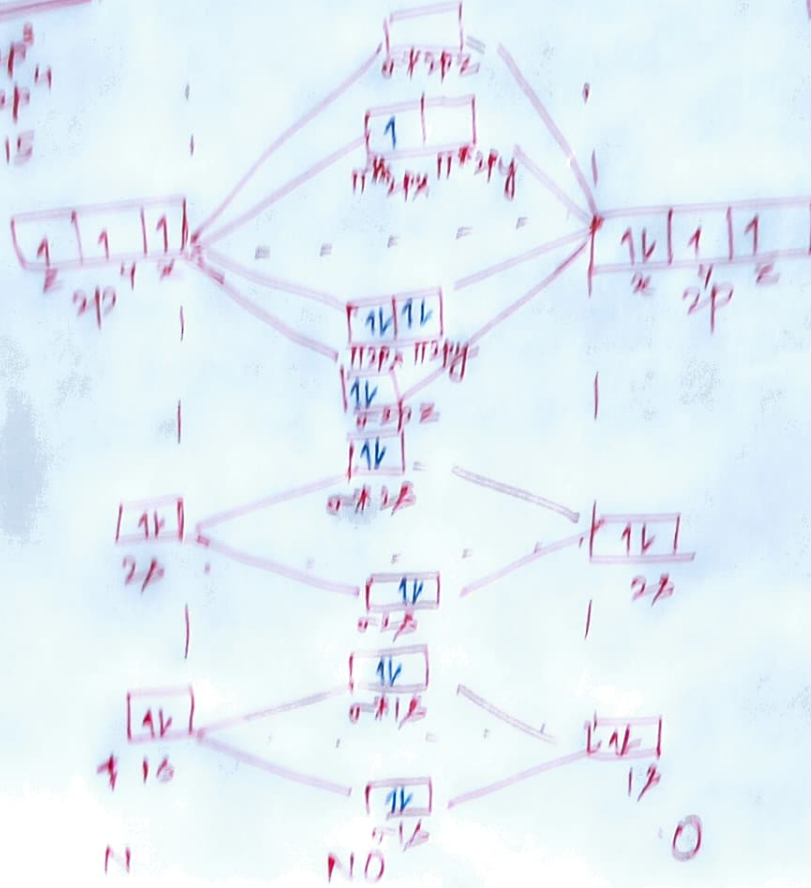σ^* A.O.$_z$ σ^* A.O.$_z$
(BMO)   (ABMO)

$$B.O. = \frac{Nb - Na}{2} = \frac{2-0}{2} = 1$$

Magnetic Behaviour
= Diamagnetic

NO
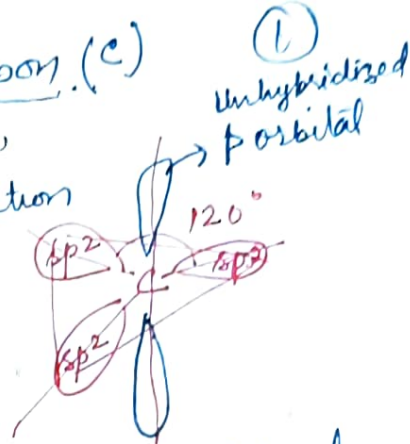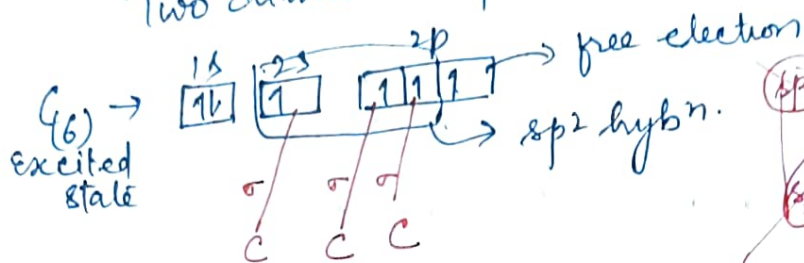
$N = 1s^2 2s^2 2p^3$
$O = 1s^2 2s^2 2p^4$
Total $e^- = 15$

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

$$= 2.5$$

Paramagnetic

N   NO   O

Graphite: An Allotrope of Carbon. (C)

Two dimensional structure

$C(6) \rightarrow$
Excited state

→ free electron
→ sp^2 hybn.

Unhybridized p orbital

$120°$

STRUCTURE:-

→ In Graphite each carbon atom is sp^2 hybridized. and is linked to 3 other carbon atoms in the same plane.

→ In this way hexagones of carbon atoms are formed in one layer which fuse together to form a plane or sheet called Graphene.

→ The bonding between atoms within a layer is strong covalent. C–C bond distance is $1.42 A°$

→ Graphite has two-dimensional layer (laminar / sheet) structure. These layers have a distance of $3.41 A°$ and are held together by weak Vander Waals forces.

→ Therefore, even a small force is sufficient to slide the layers parallel to each other and it has low co-efficient of friction.

→ Graphite is very soapy to touch, non-inflammable and can be used as a lubricant upto $370°$ (above this temp. it is oxidised). It is ineffective in vacuum conditions and above 370. However in the absence of air, it can be used upto much higher temp.

→ The 4th valence electron of each carbon atom is free which can move easily from one carbon atom to other, under the applied potential. Therefore, it is a good conductor of electricity.

→ It is greyish black substance having metallic ② lustre. M.P. is high (because of strong covalent bonds). Thermodynamically more stable than diamond.

→ Graphite exists in two forms :- α-Graphite (having ABABAB... type of structure arrangement) and β- Graphite (ABC A B C... type of arrangement).

→ Density 1.25g/cm³.

APPLICATIONS:-

→ Used as a (solid) lubricant (as layers can slide over one another due to weak vander waals forces).

→ Used in pencil leads (due to soft, slippery nature and leaves a black mark on paper when rubbed on paper).

→ It is used in the prepn of electrodes as it conducts electricity (due to presence of free electron on each carbon)

→ (Due to high M.P.) used to prepare crucible for making high grade steel!

→ It is used as moderator in nuclear reactors as it absorbs fast-moving neutrons.

→ used as conducting ink for screen printing.

1.42A° covalent bonds

carbon along (sp2 hybd.)

3.41A° vander waals forces b/w layers of graphite
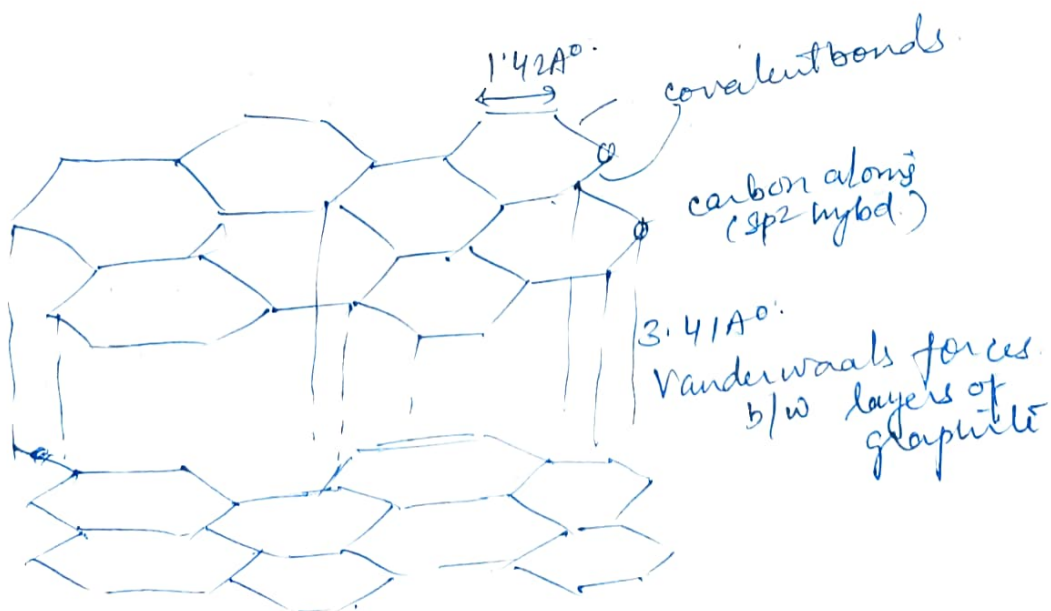
FULLERENES

It is an new allotropic form of carbon
- The first member of fullerene family was a molecule C_{60}, made up of 60 c-atoms, discovered by Harold Kroto & Richard Smalley in 1985. This is the most stable molecule fullerene. This new allotropic form of carbon C_{60} was given the name fullerene in the honour of Buckminster Fuller who described the geodesic domes and fullerene resemble these domes.
- C_{60} exist as a discrete molecule consisting of clusters of 60-carbon atoms. Other relatively common clusters are $C_{32}, C_{50}, C_{70}, C_{72}, C_{74}$ etc. These allotropes are collectively known as Fullerenes. C_{60} is also known as Buckminster fullerene.

STRUCTURE :-
- C_{60} has the most symmetrical 'soccer ball' shaped structure. It consists of 20 hexagons and 12-pentagons ie. Truncated icosahedran structure. The proposed st. of C_{60} is not planar. The angle b/w the p_2 axis and a c-c bond vector, θ is $101.6°$ as compared to $90°$ in planar graphite. Each c-atom is sp^2 hybd. There are 30 C=C, 60 vertices & 32 faces in C_{60}.

Fullerenes
can be diffent
shapes!-
1-spherical →
   buckyball
2- Cylindrical → Nanotubes
3- Planar → Graphene sheets

$\rightarrow p_2$
$\theta = 101.6°$
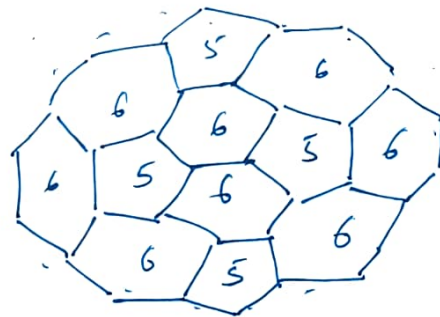
face-centred cubic pattern Tetrahedral & octahedral holes are present.

es can accomodate in octahedral holes.
Intercalation

PREPARATION :-
Graphite electrodes (Ar. atm. $P = 0.05 - 0.1$ atm) $\xrightarrow{electric spark}$ 5-15% Mixture of fullerenes + c-black. $\xrightarrow{800 l^-}$

↓ solvent extraction

mixture of fullerenes
↓ column chromatography

$\boxed{C_{60}}$

NOTE :-
Ar atm- prevents the formation of CO & CO_2 by oxidation.

PROPERTIES OF C_{60} :-

→ In C_{60} each carbon atom is sp^2 hybd.

* → Black mustard coloured (solid) powder, forms deep magenta soln in benzene.

→ Covalent in nature, soluble in aromatic hydrocarbons. Their chemical transformation is very difficult.

→ Metal ions can penetrate these hollow balls because of their smaller size. This structure is known as Endohedral structure, while if radicals are attached outside this hollow cage, Exohedral structure is obtained.

→ Some of the compounds of fullerenes possess remarkable properties of superconductors. e.g. $C_{60}K_3$ exhibits super conductivity upto 30K (critical temp.) (It's compds with alkali metals show superconductivity). This has created a great excitement in the field of - superconductivity.

* → C_{60} reacts with organic electron donors to form soft-ferromagnetic materials with zero remenance e.g. Tetrakis (dimethylamino) ethyene (TDAE) form (TDAE) C_{60} with C_{60}.

Applications :-
(i) In the preparation superconductors, with alkali metals. e.g. $C_{60}K_3$
(ii) Electronic devices
(iii) Microelectronic devices
(iv) Non-linear optical devices
(v) Batteries as charge carriers
(vi) Preparation of soft ferromagnets (with zero remenence) e.g. (TDAE)C_{60}
(vii) Fully fluorinated fullerenes are used as world's best lubricants. Suitable as a lubricant due to spherical shape, Bucky balls act as molecular Ball Bearings.

* Properties:- Very tough & thermally stable (it can be sublimed at 600°C under vacuum). It can be compressed to lose 30% of its volume without destroying its carbon cage str.

zero remenence → Power of a ferromagnetic material to retain the magnetism even at applied magnetic field (-H) = 0.