$\sin^2\theta$

(i.e $L = 0, 1, 2, 3 \cdots$)

$\dfrac{d^2\phi}{d^2\phi}$

Atomic Orbital

If

→ Atomic Orbital

(where ϕ^2 is maximum)

Electron Cloud Picture

Atomic orbital is a three dimensional space around the nucleus within the probability of finding the electron is maximum (ψ^2).

The wave function ψ for election is known as atomic orbital.

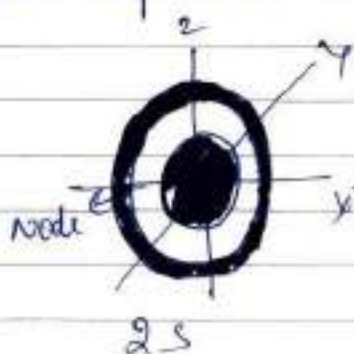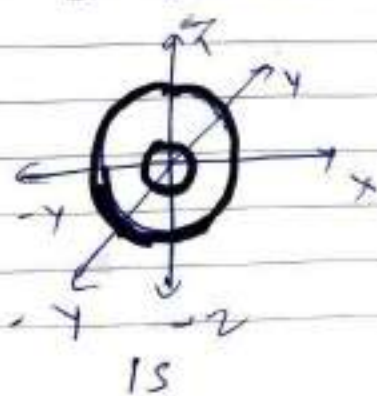There are four types of atomic orbitals based on Quantum No.

1) **S - Orbital :-** $l = 0$ and $m = 0$

$$\Theta_{0,} \cdot \Phi_{0} = \frac{1}{\sqrt{4\pi}} = \frac{1}{2\sqrt{\pi}}$$

$(\Theta$ and $\phi)$ Radial wave functions

Angular wave equation for s orbital is independent of angles Θ and ϕ.

S - orbitals are spherical symmetrical
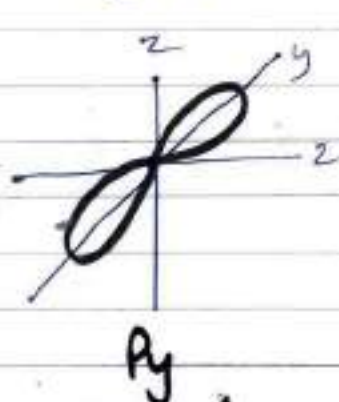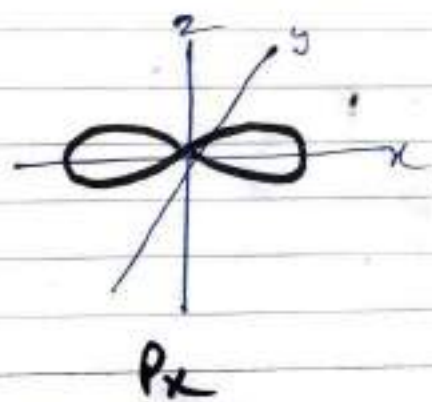

1s   Node   2s   3s   node

(2) __P - orbital__ → for this $l = 1$

and $m = \not{1}, -1, 0$

corresponding wave functions are

1) $\Theta_{1}, \Phi_{+1} = \left(\dfrac{3}{4\pi}\right)^{1/2} \sin\theta \cos\phi$ P_x

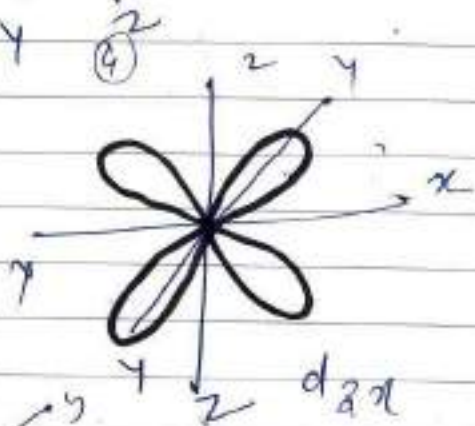2) $\Theta_{1}, \Phi_{-1} = \left(\dfrac{3}{4\pi}\right)^{1/2} \cos\theta \sin\phi$ P_y

3) $\Theta_{1}, \Phi_{0} = \left(\dfrac{3}{4\pi}\right)^{1/2} \cos\theta$ P_z

P_x P_y P_z

3. $\underline{\text{d - orbitals}}$ → $n = 3$

$\ell = 0, 1, 2,$

so m is $+2, +1, 0, -1, -2$

①

d_{xy}

②

d_{yz}

③

d_{z^2}

④

d_{zx}

⑤

$d_{x^2-y^2}$
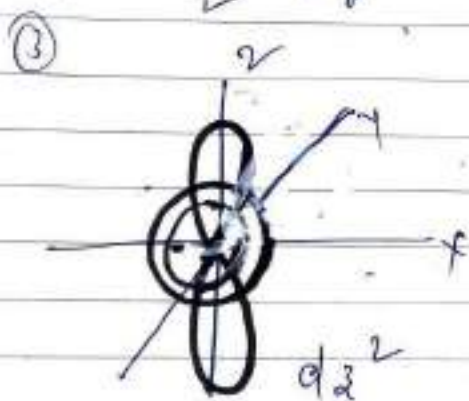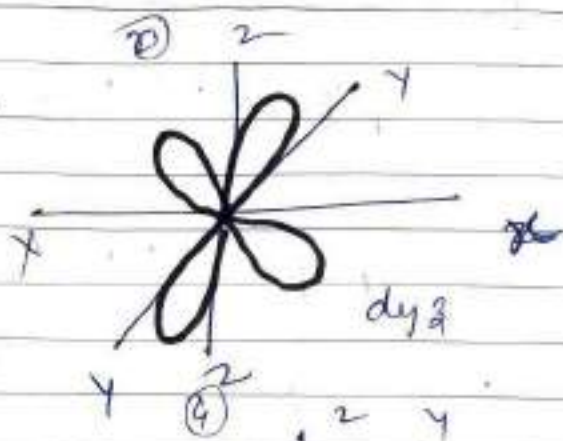
Dumb-bell shape

4. **f - orbitals** :- $n = 4$ $l = 0, 1, 2, 3$

$m = +3 \quad +2 \quad +1 \quad 0 \quad -3 \quad -2 \quad -1$

Molecular Orbitals :- (LCAO)

Molecular Orbitals are formed by the linear Combination of atomic Orbitals

$\psi \rightarrow$ Represents the atomic orbital
(electron in an atom)

"Behaviour of an electron in a molecule is described by a molecular wave function Known as Molecular orbital"

Acc to Quantum Mechanics $\rightarrow$ Linear Combination method gives two types of Molecular orbital

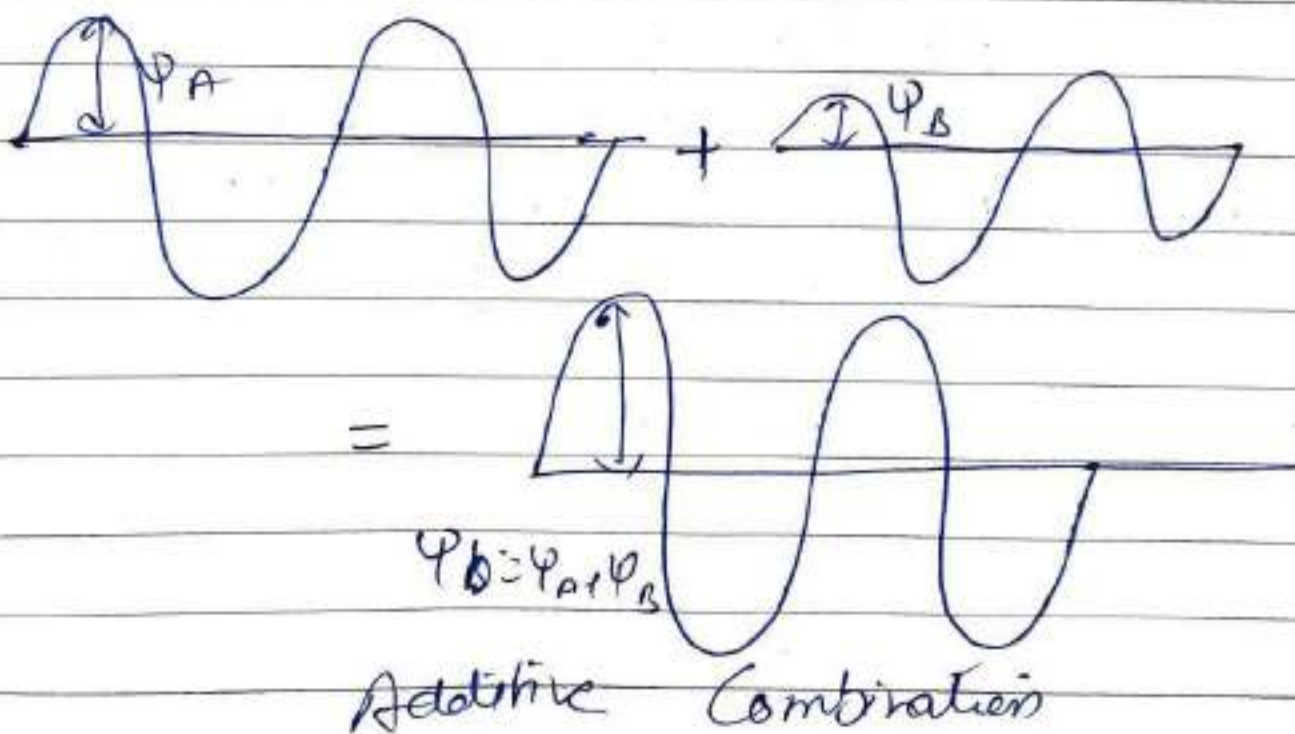1) Bonding Molecular orbital
2) Anti Bonding Molecular orbital

Molecular Orbitals are formed by the addition when two waves are in phase
Or
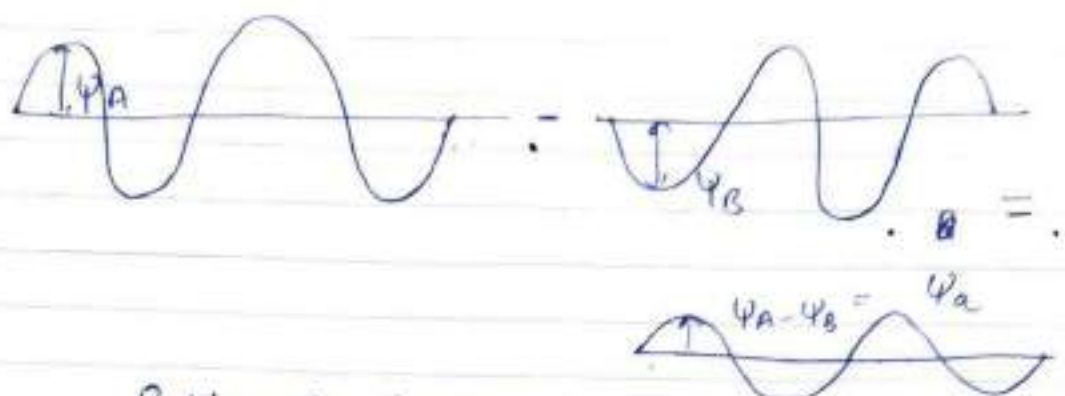They are formed by subtraction when two waves are not in phase.

So if ψ_A and ψ_B are the atomic orbitals then

$$\psi_A + \psi_B = \psi_b \quad \text{(Bonding molecular orbital)} \quad \text{——①}$$

$$\psi_A - \psi_B = \psi_a \quad \text{(Anti Bonding molecular orbital)} \quad \text{——②}$$

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

Additive Combination

$\angle I.\Psi_A$

Ψ_B

$\cdot B =$

$\Psi_A - \Psi_B = \Psi_a$

Subtractive Combination of waves

By Squaring ef ① and ② It becomes

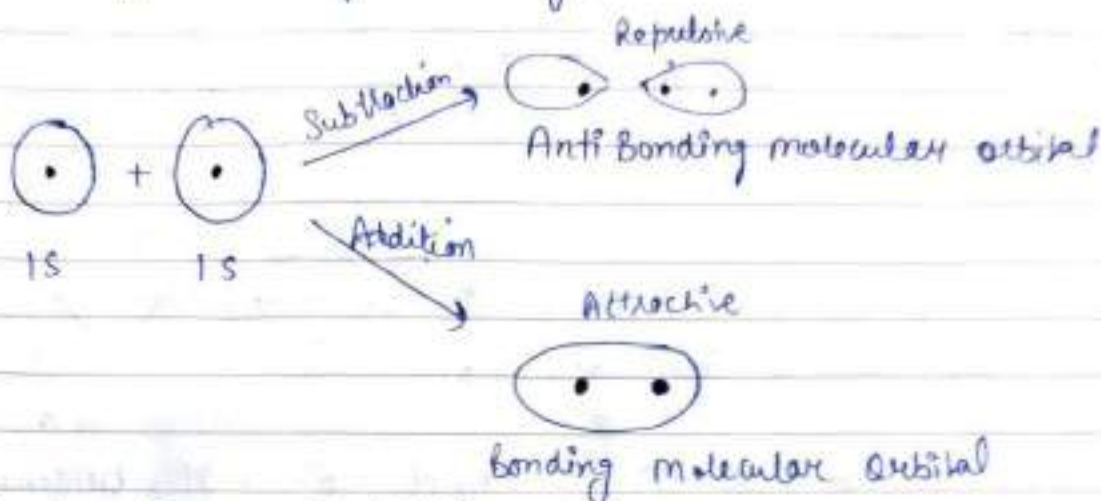$$\Psi_b^2 = (\Psi_A + \Psi_B)^2 = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$$

③

Ψ_b^2 is the probability of e^- density of the bonding molecular orbital

$$\Psi_a^2 = (\Psi_A - \Psi_B)^2 = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B$$

Ψ_a^2 is the probability of electron density of the anti bonding molecular orbital

Antibonding orbitals do not lead to formation of a chemical bond.

① Another form of Molecular orbitals

Repulsive

$\underset{1s}{\textcircled{\bullet}}$ + $\underset{1s}{\textcircled{\bullet}}$ $\xrightarrow{\text{Subtraction}}$

Anti Bonding molecular orbital

$\xrightarrow{\text{Addition}}$ Attractive

Bonding molecular orbital

Molecular Orbital Theory

Molecular orbitals are formed by the Addition or Subtraction of ~~overlap orbits~~ atomic orbitals as discussed above.

Hence electron in an atom are not confined only to atom but to a molecule also.

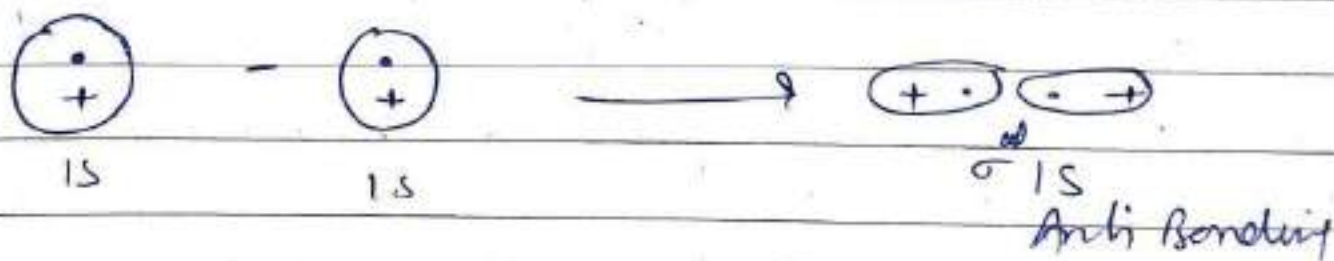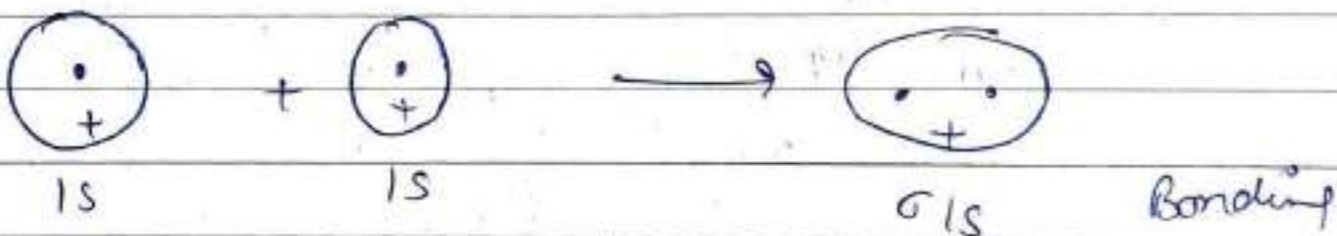## Features of molecular Orbital Theory

Developed by Mullican (1932)

① Like an atomic orbital which is around the nucleus of an atom there are molecular orbitals

② Molecular orbitals are entirely different from the atomic orbitals.

③ The molecular orbitals posses different energy levels like atomic orbitals in an atom.

④ Shapes of molecular orbitals are dependant upon the shapes of atomic orbitals from which they are formed. T

⑤ The number of molecular orbitals formed is equal to the number of atomic orbitals in a bond formation

⑥ Like atomic orbitals, electron filling in molecular orbitals follows three principles such Afbau, Pauli's Exclusion and Hund's Rule.

⑦ molecular orbitals are arranged in order of increasing energy.

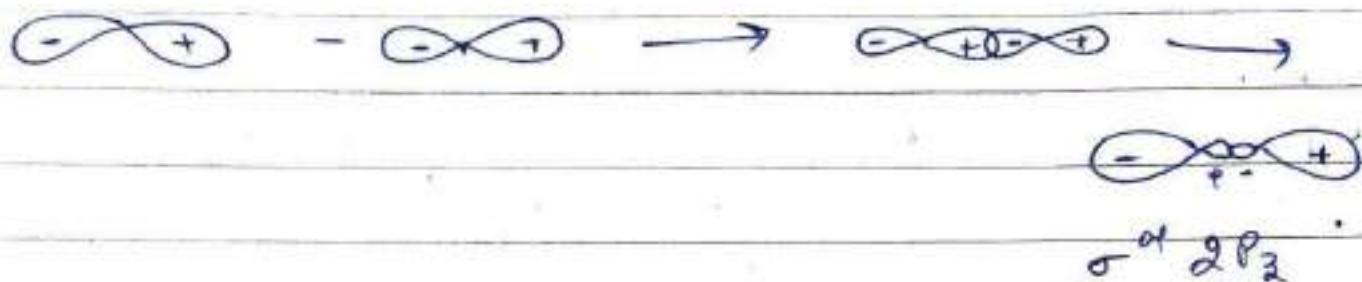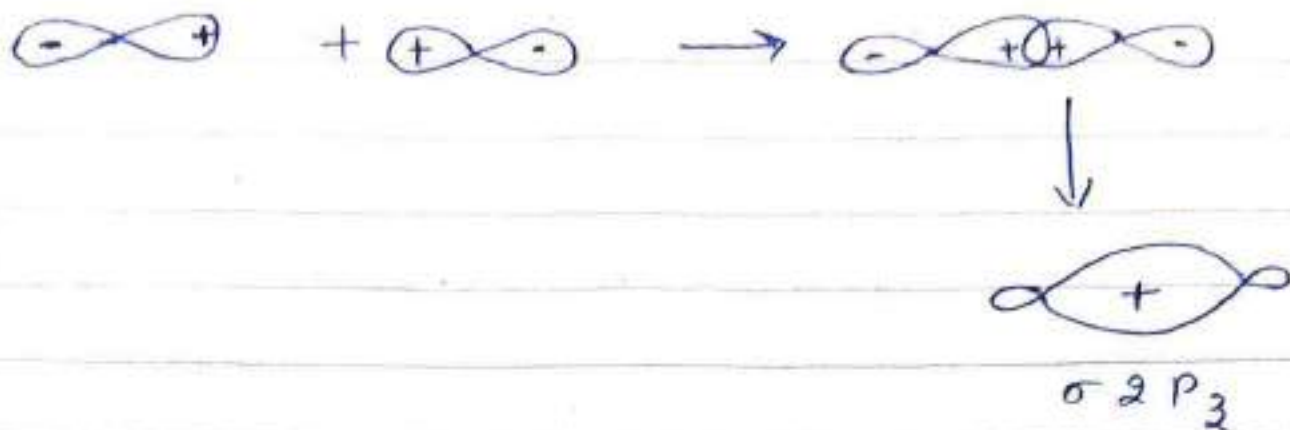Bonding molecular orbital (MO) have low energy than Anti Bonding molecular orbital.

In molecular orbital theory, orbitals are identified as σ or π depending upon Symmetry of the (MO)

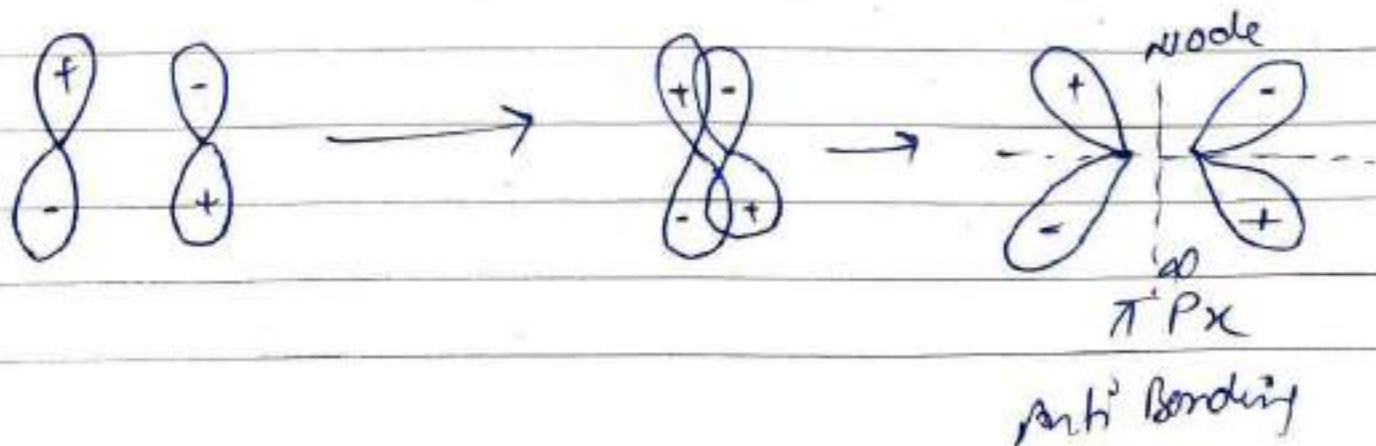A Sigma Bond (M·O) is one that has cylindrical Symmetry. A Sigma molecular orbital have
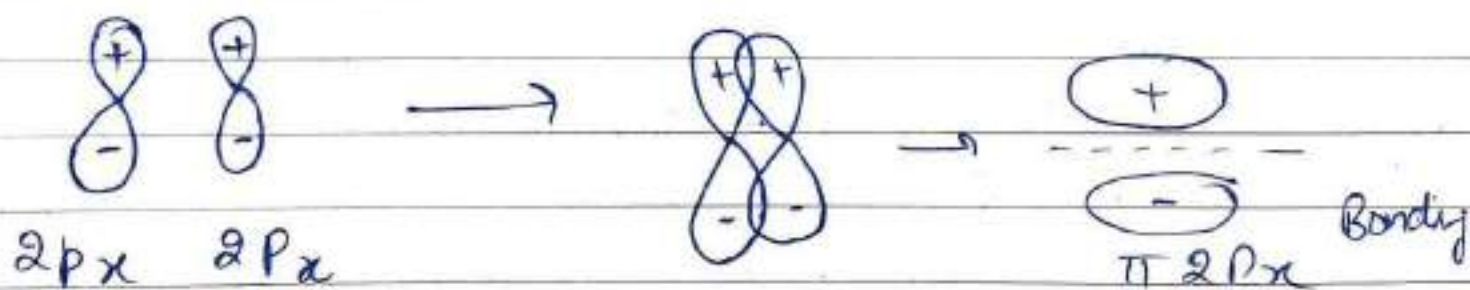
(i) σ Bonding MO

(ii) σ^* ~~bonding~~ Anti Bonding MO

1S + 1S → σ1S   Bonding

1S - 1S → σ^*1S
Anti Bonding

A σ Bond is formed when P orbitals Combines specially $2P_z$

$\sigma \, 2P_z$

$\sigma^a \, 2P_z$

(2) A π m.o is formed as

$2px$ $2P_x$

$\pi \, 2Px$ Bonding

Node

$\pi^* Px$

Anti Bonding

Relative energies of the molecular orbital are

$$\sigma 1s < \sigma^{*}1s < \sigma 2s < \sigma^{*}2s < \sigma 2P_{\tilde{z}} < \pi 2P_x$$
$$= \pi 2P_y <$$
$$\pi^{*}2P_x = \pi^{*}2P_y$$
$$< \sigma^{*}2P_{\tilde{z}}$$
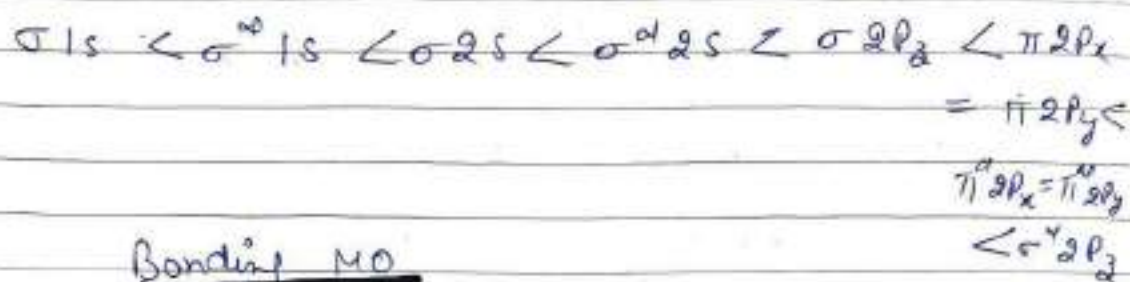
Bonding MO

$\pi 2P_y$ and $\pi 2P_x$ are degenerate
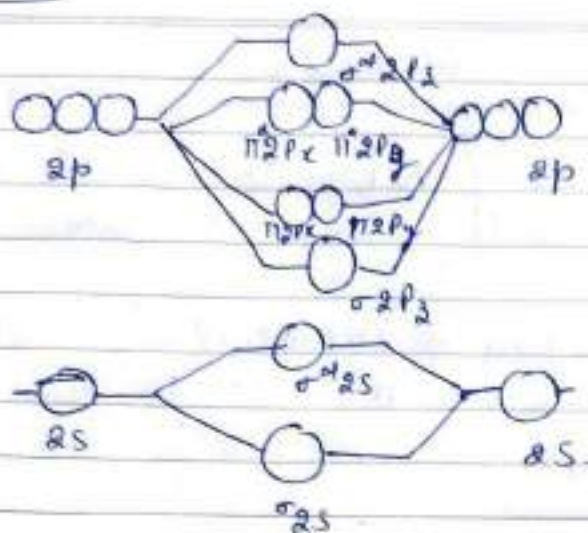(same energy)

Antibonding MO

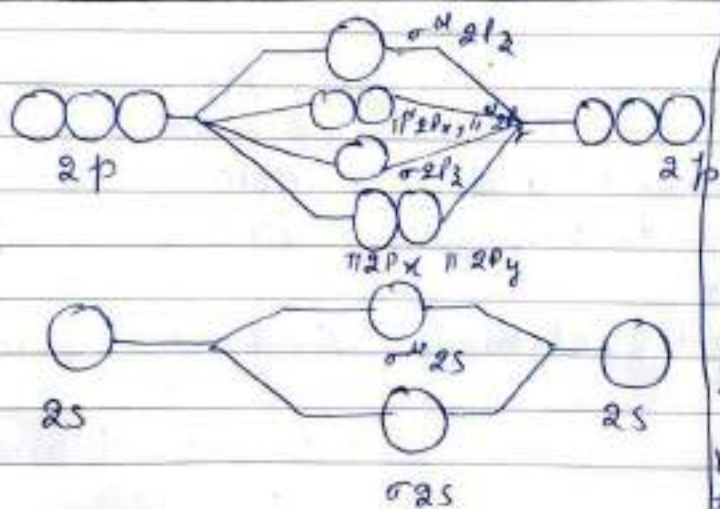$\pi^{*}2P_x$ and $\pi^{*}2P_y$ are degenerate
(same energy)

Molecular Orbital Diagram for Diatomic molecules:

Diatomic molecules like O_2, F_2 and Ne_2 and Li_2, Be_2, B_2 and N_2 have different diagram.

General

σ^*2P_z

$\pi2P_x \; \pi2P_y$

2p $\pi2P_x \quad \pi2P_y$ 2p

$\sigma2P_z$

σ^*2S

2S   2S.

$\sigma2S$

for O_2, F_2 and Ne.

σ^*2P_z

$\pi2P_x , \pi2P_y$

2p $\sigma2P_z$ 2p

$\pi2P_x \quad \pi2P_y$

σ^*2S

2S   2S

$\sigma2S$

for Li_2, Be_2, B_2 and N_2

difference b/w P_x and P_y is small.

As a result they are so close that repulsive forces b/w their e^- in them raise the level of $\sigma2P_z$

Stability of molecules

→ Bonding electron (N_b) are stable than the Anti Bonding (N_a) electron

Hence

(i) if $N_b > N_a$ molecule is stable

(ii) if $N_b < N_a$ molecule is unstable

(iii) $N_b = N_a$ molecule is unstable.

→ Bond Order $= \dfrac{1}{2}\left[\text{no. of Bonding electron} - \text{no. of anti Bonding electron}\right]$

$$\dfrac{1}{2}\left[N_b - N_a\right]$$

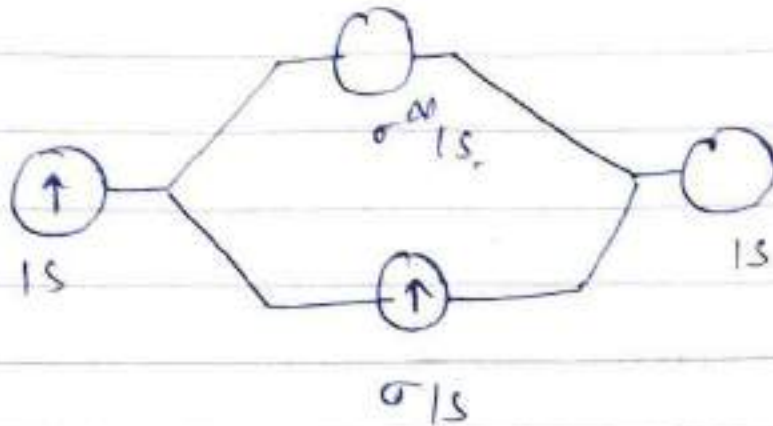→ High the Bond order , more stable is molecule

→ High Bond dissociation Energy, High Stability

→ Unpaired electron   — Leads to paromagnetic Character.

→ Paired Electron   → leads to Diomagnetic character

Examples

For $H_2^{\oplus}$ molecule
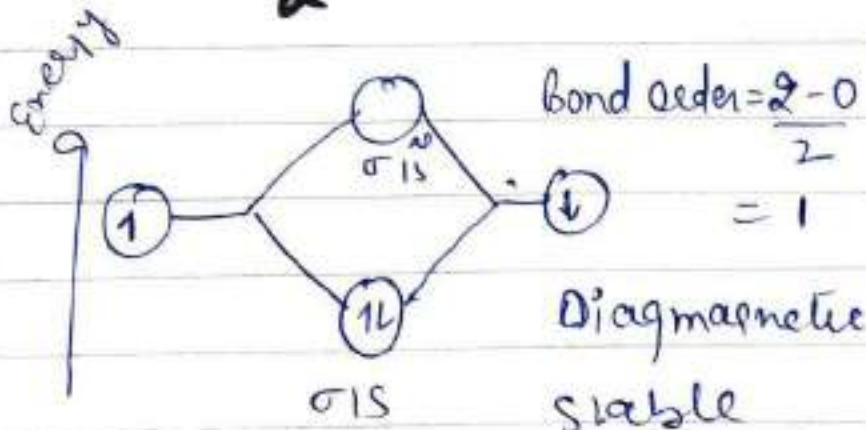

Molecular orbital energy level diagram.

$$H_2^+ = (\sigma_{1s})^1$$
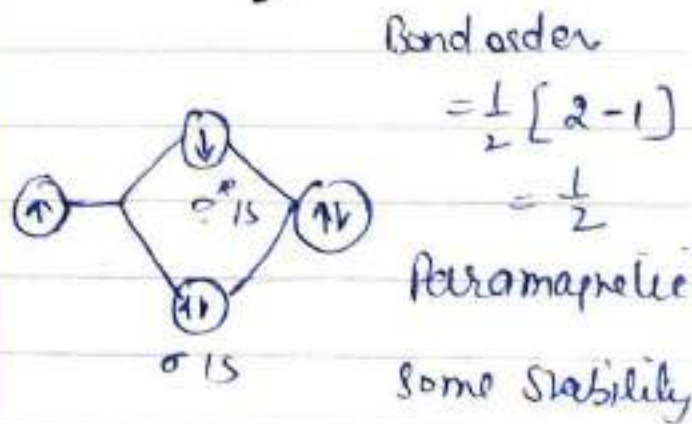
→ Bond order $= \dfrac{1}{2}[1-0] = \dfrac{1}{2}$

→ H_2^+ is paramagnetic

→ Stable

For H_2 molecule

Bond order $= \dfrac{2-0}{2} = 1$

Diagmagnetic

Stable

For H_2^-

Bond order

$= \dfrac{1}{2}[2-1]$

$= \dfrac{1}{2}$

Paramagnetic

Some stability

Comparision of the stabilities of H_2^+, H_2, H_2^-

(i) Since the bond order values are positive, all the hydrogen species H_2^+, H_2 and H_2^- are stable. Greater the bond order, more is the stability $H_2 > H_2^+ > H_2^-$

(ii) Although H_2^+ and H_2^- have the same bond order 1, yet H_2^- is slightly less stable than H_2^+. It is because H_2^- contains one electron in the anti-bonding orbital which results in repulsion and decreases the stability

(iii) H_2^+ and H_2^- molecule ions having an electron unpaired are paramagnetic while H_2 have paired $\bar{e}$ is diamagnetic
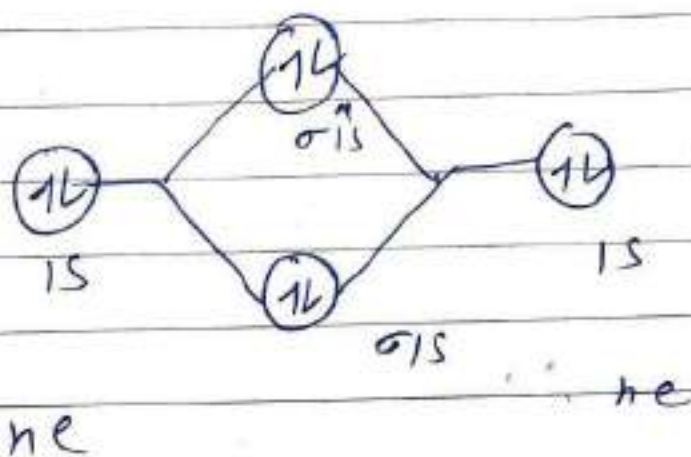
He_2^+
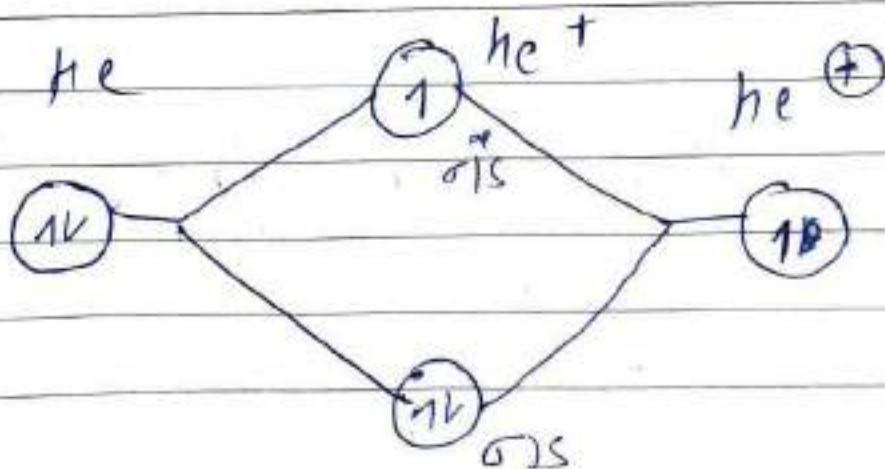
Bond order $= \frac{1}{2}[Nb-Na]$

$$= \frac{1}{2}(2-1) = \frac{1}{2}$$

Since $Nb > Na$
molecular ion is stable.

He_2 Hence He_2 do not exist

$\sigma 1s$

$1s$

$1s$

$\sigma 1s$

he

he

Bond order $= \frac{1}{2}[Nb-Na] = \frac{1}{2}(2-2) = 0$

Li_2, Be_2, B_2 and C_2 molecules

Bond order

$Li_2 \quad \frac{1}{2}(2-0) = 1$ $\qquad C_2 = \frac{1}{2}(6-2) = 2$

$Be_2 \quad \frac{1}{2}(2-2) = 0$

$B_2 \quad \frac{1}{2}(4-2) = 1$

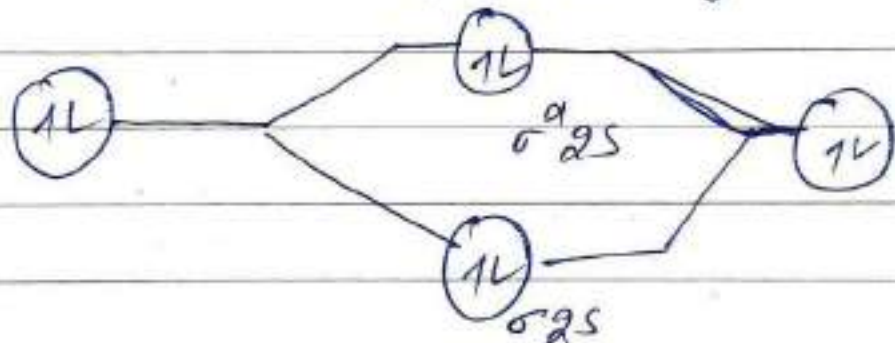C_2 molecule   atomic   number - 6
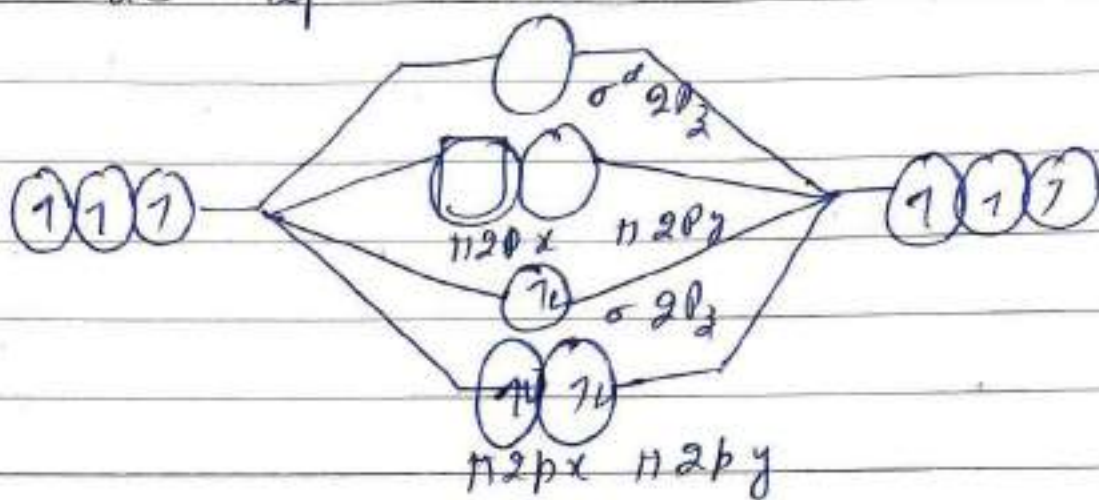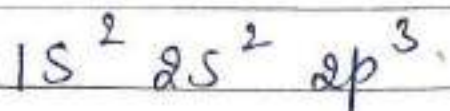
$1s^2 \, 2s^2 \, 2p^2$
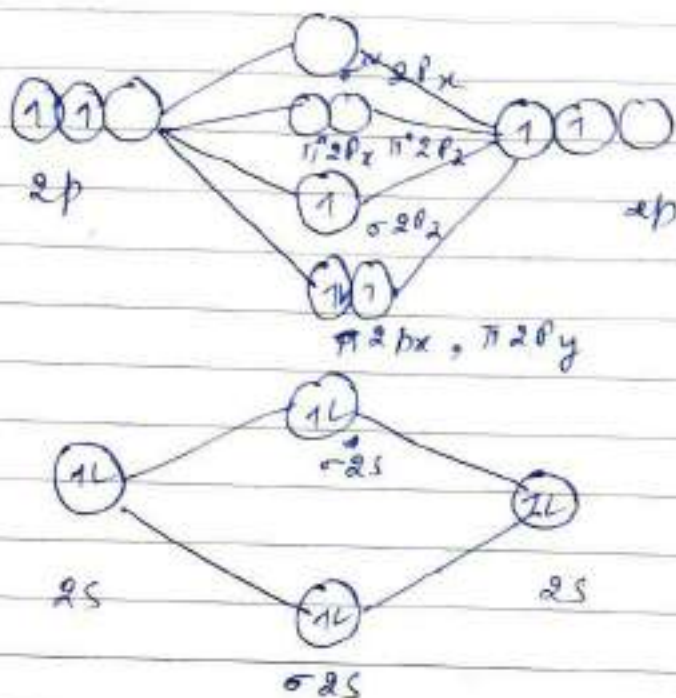
Bond order $= \dfrac{1}{2} \left[6 - 2 \right]$

$= \dfrac{4}{2} = 2$

$N_2, \quad O_2, \quad Fe_2 \quad$ type molecules

1) N_2 — Nitrogen molecule

A. no. — 7

$$1S^2 \, 2S^2 \, 2p^3$$

Diamagnetic

Bond order $= \dfrac{1}{2}(8-2) = \dfrac{6}{2} = 3$

2) $N_2^+ = 1S^2 \, 2S^2 \, 2p^2$

orbital Conf.
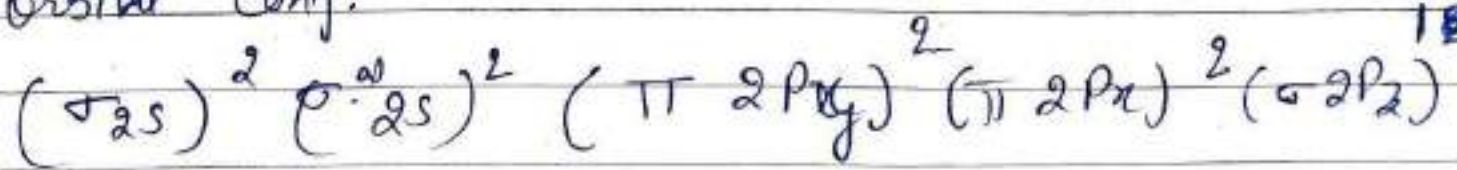
$$(\sigma_{2s})^2 \, (\sigma^*_{2s})^2 \, (\pi 2p_y)^2 \, (\pi 2p_x)^2 \, (\sigma 2p_z)^{1\varnothing}$$

Bond order $= \dfrac{1}{2}(7-2) = 2\dfrac{1}{2}$

Paramagnetic as it has one unpaired e^-

N_2^- $KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_y)^2 (\bar{\pi} 2p_x)^2 (\sigma 2p_z^2)$

$\qquad\qquad\qquad\qquad \pi^* 2p_x^1$
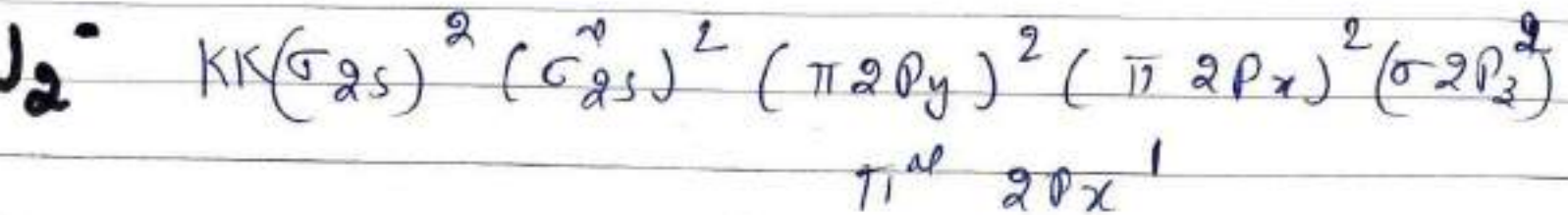
Bond order $\dfrac{1}{2}(8-3) = 2\dfrac{1}{2}$

Paramagnetic as it has one unpaired e^-

N_2^{2-}
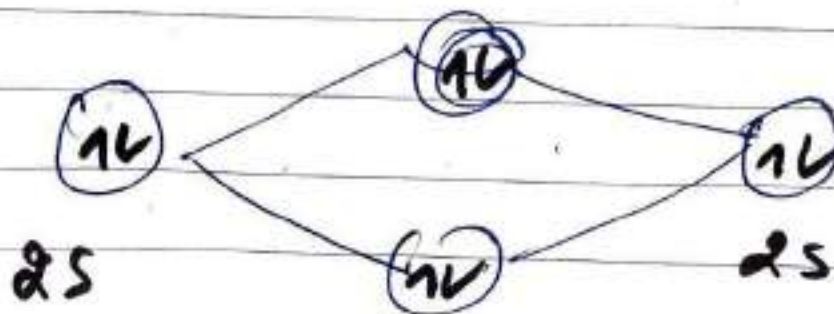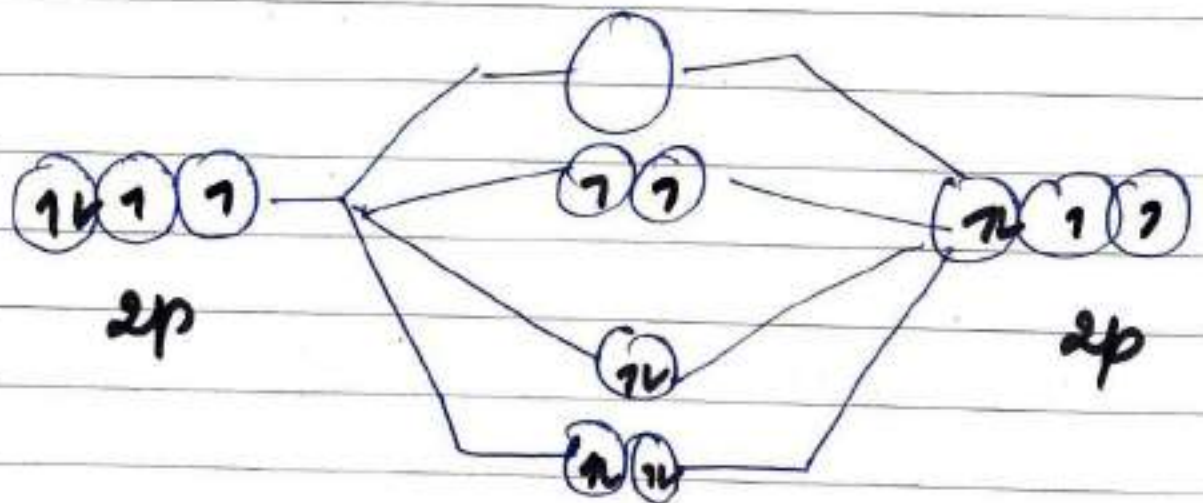
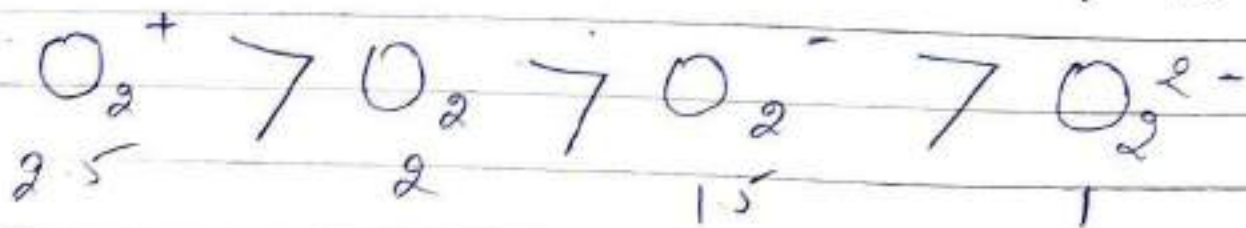Bond order $= \frac{1}{2}(8-4) = 2$

Paramagnetic

Stability order

$$N_2 > N_2^+ > N_2^- > N_2^{2-}$$

Diamagnetic   Para magnetic   Paramagnetic   Paramagnetic
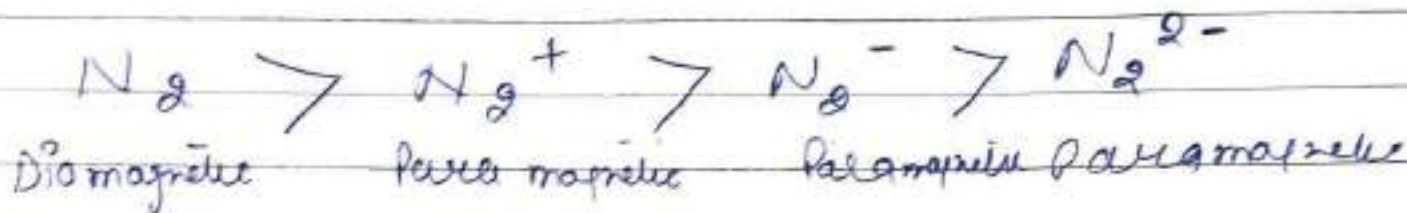
Oxygen molecule (O_2)

$1s^2 2s^2 2p^4$

$KK [\sigma_{2s}^2 \quad \sigma^*_{2s}^2 \quad \text{oooo} \quad \Pi 2p_x^2 \quad \Pi 2p_y^2 \quad \sigma 2p_z^2$

$\Pi 2p_x^1 \quad \Pi 2p_y^1]$

Bond order is same as that of N_2^{2-}

$\frac{1}{2}(8-4) = 2$

Stability order of $O_2, O_2^+, O_2^-, O_2^{--}$

$$O_2^+ > O_2 > O_2^- > O_2^{2-}$$

2.5 2 1.5 1

$\longrightarrow$ Bond order

Molecular orbital Electronic configurations
of Some Heteronuclear molecules

① N O
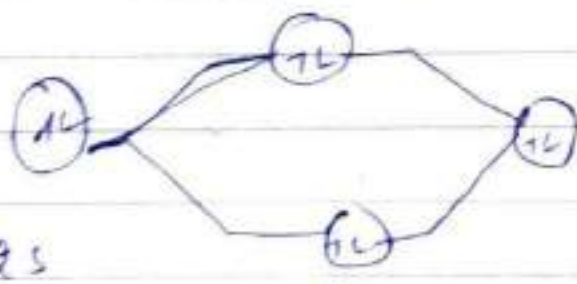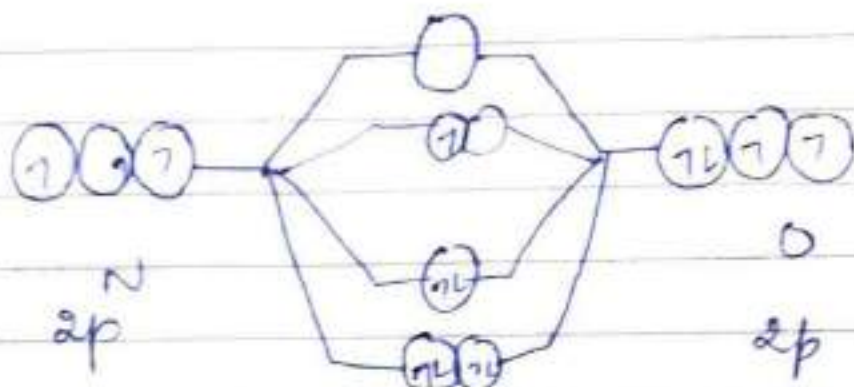
Bond order = $\frac{1}{2}(8-3) = 2\frac{1}{2}$

Paramagnetic

② $CN^{\ominus}$ Total no. of $\bar{e} = 6+7+1 = 14$

Bond order = $\frac{1}{2}(8-2) = \frac{6}{2} = 3$
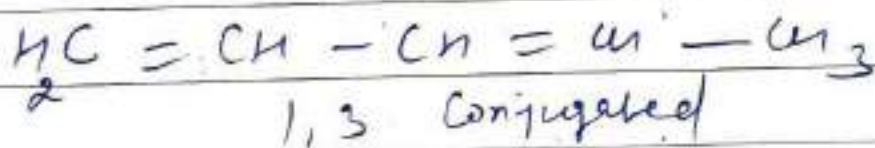
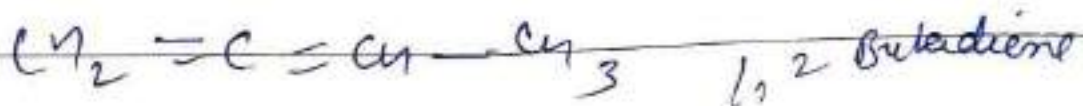# π molecular orbitals of Butadiene, Benzene aromaticity

When atomic orbitals overlap side wise a pi (π) molecular orbital is formed. π molecular orbital have a nodal plane. Presence of π molecular orbitals affect its physical and chemical properties.

π molecular orbital of Buta-di-ene

Conjugated dienes are more stable than non-conjugated dienes. 1,3 pentadiene is more stable than 1,4 Pentadiene

$$H_2C = CH - CH = CH - CH_3$$

1,3 Conjugated

$$CH_2 = C - C - C = CH_2$$

1,4 Conjugated (non)

Similarly

$$H_2C = CH - CH = CH_2 \qquad 1,3 \text{ Butadiene}$$

$$CH_2 = C = CH - CH_3 \qquad 1,2 \text{ Butadiene}$$
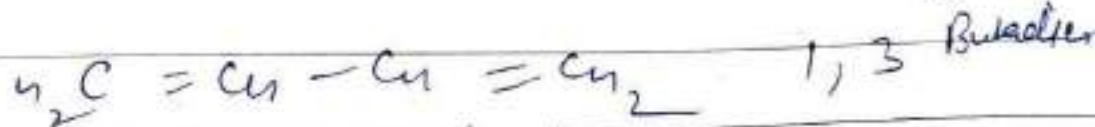
The relative stability of dienes is expressed in the following order

Conjugated diene > Isolated diene > Comulated diene

most stable   least stable

The Basis of stability is delocalisation of π electrons

Orbital Pictures of Dienes

For Example 1, 3, - Butadiene
→ each of the four Carbon atoms use three Sp^2 hybrid orbitals for the formation of σ bond and an unhybridised orbital for the formation of π bond.

The Linear Combination of these four P orbitals give four molecular orbitals having wave functions

$$\pi_1, \pi_2, \pi_3^{*} \text{ and } \pi_4^{*}$$

g.s   g.s
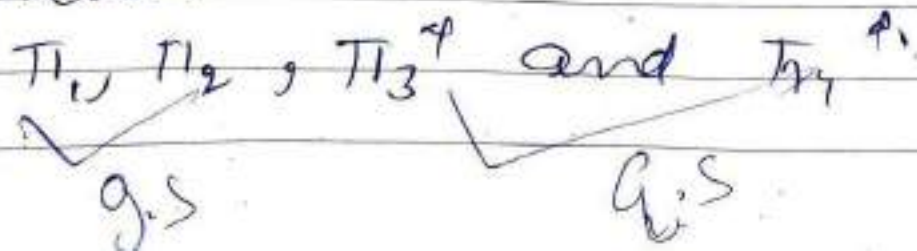
Π_1 and Π_2 are Bonding orbitals (Contain Two $\bar{e}$)
Π_3^a and Π_4^a are Anti Bonding orbitals (vacant)

Out of Two Bonding orbitals Π_1 is of lowest energy as it has no node and energy of Π_2 is higher because of one node. similarly two energies of Π_3^a and Π_4^a are more.

Ψ_4^{*} Three nodes

Ψ_3^{*} Two nodes

Ψ_2 One node

Ψ_1 no node

Energy

LCAO of Four P orbitals