

Date: 17/11/21 | Atomic and Molecular structures

de Broglie hypothesis :-

Every material particle has a wave counterpart having wave length, $\lambda = h/p$

For a particle of Mass m , moving with a velocity of v this become, $h/mv = \lambda$ [$p = mv$]

$$\lambda = \frac{h}{\sqrt{2mE}}$$

de Broglie wavelength in terms of kinetic energy -

$$K = p^2/2m$$

$$\text{therefore } p = \sqrt{2mK}$$

$$\lambda = \frac{h}{\sqrt{2mK}}$$

Derivation :- de Broglie hypothesis

From the law of relativity,

$$E^2 = p^2c^2 + m_0^2c^4 \rightarrow ①$$

where E = Energy, c = velocity of light

m_0 = Rest Mass.

Photon having rest mass, $m_0 = 0$

$$E^2 = p^2c^2$$

$$E = \sqrt{p^2c^2}$$

$$E = pc$$

$$\boxed{p = \frac{E}{c}} \rightarrow ②$$

From Planck relation we know,

$$E = h\nu \rightarrow ③$$

$$\therefore P = \frac{E}{c} = \frac{h\nu}{c} \quad [c = \lambda]$$

$$P = \frac{h}{\lambda}$$

$$\left[\frac{1}{\lambda} = \frac{v}{c} \right]$$

Thus momentum of photon given by
the above relation,

If this expression is extended to a
material particle of mass m and
velocity v , its momentum

$P = mv$ will be related to wavelength
as,

$$P = \frac{h}{\lambda}$$

$$mv = \frac{h}{\lambda}$$

$$\text{or, } \lambda = \frac{h}{mv} \rightarrow \text{de Broglie}$$

$$\lambda = \frac{h}{P}$$

de-Broglie hypothesis in terms of Kinetic
Energy \rightarrow

$$K = \frac{1}{2}mv^2 = \frac{1}{2} \times \frac{1}{m} m v^2$$

$$= \frac{(mv)^2}{2m}$$

$$\Rightarrow K = \frac{P^2}{2m}$$

$$\text{or } P^2 = 2mk$$

$$\text{or, } P = \sqrt{2mk} \rightarrow ⑥$$

from de-Broglie

$$\lambda = \frac{h}{P} \Rightarrow \left[\frac{h}{\sqrt{2mk}} = \lambda \right]$$

Summaries :-

★ Statement

$$\textcircled{1} \quad \lambda = \frac{h}{p} \rightarrow ①$$

$$\textcircled{2} \quad \lambda = \frac{h}{mv} \rightarrow ②$$

$$\textcircled{3} \quad \lambda = \frac{h}{\sqrt{2mk}}$$

Problem

- ① A cricket ball having a mass of 9 g is moving with a speed of 2 m/s, what will be its wavelength?
will this wavelength be observable?

→ We know from de-Broglie relation-

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.63 \times 10^{-34} (\text{Js})}{9 \times 10^{-3} \times 2}$$

$$= \frac{(\text{kg}) \times (\text{m/s})}{}$$

$$= 3.68 \times 10^{-32} \text{ m} \quad (\text{not be observ})$$

- ② calculate the de-Broglie wave-length of an electron moving with a speed of $1/1000$ th of light

→ speed of light $\rightarrow 3 \times 10^8 \text{ m/s}$

Hence, speed of will be $\rightarrow \frac{1}{1000} \times 3 \times 10^8$
 $= 3 \times 10^6 \text{ m/s}$

Now, mass of electron

$$= 9.11 \times 10^{-31} \text{ kg}$$

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34} (\text{Js})}{9.11 \times 10^{-31} (\text{kg}) \times 3 \times 10^6 (\text{m/s})}$$

$$= 2.42 \times 10^{-10} \text{ m}$$

= 2.42 A° (Not negligible for electrons)

③ Find out de-broglie wave length of electrons moving with kinetic energy of 200 eV.



$$\lambda = \frac{h}{\sqrt{2mE}} \text{ where, } E \rightarrow \text{kinetic energy}$$

$$= \frac{6.63 \times 10^{-34} \text{ Js}}{\sqrt{2 \times 9.11 \times 10^{-31} \times 200 \times 1.6 \times 10^{-19}}}$$

Uncertainty principle:

It is not possible to determine the position and momentum of the subatomic particle simultaneously with equal exactness, more exactly we determine the position the less exact become the moment.

Mathematically,

$$\langle \Delta x \Delta p \rangle \geq \frac{h}{4\pi} \quad h = \text{Planck Constant}$$

$$\text{or, } \langle \Delta x \Delta p \rangle \geq \frac{h}{2}$$

$$\langle \Delta x \Delta p \rangle \geq 5.3 \times 10^{-35}$$

- ① Calculate the uncertainty in the position of an electron moving with a speed of $2.2 \times 10^6 \text{ m/s}$

$$\text{Given } \Delta p = 10^3 \text{ kg m/s}$$

$$\left\{ \begin{array}{l} 5 \times 2 = 10 \\ 2 \times 5 = 10 \\ 1 \times 10 = 10 \\ 10 \times 1 = 10 \end{array} \right.$$

⇒ We know, $\langle \Delta x \Delta p \rangle \geq \frac{h}{4\pi}$

$$\Delta P = 9.11 \times 2.2 \times 10^{-25} \text{ kg m/s} \quad \Delta P = 10^{-3} P \quad P = mv$$

$$\times 10^{-3} \quad P = 9.11 \times 10^{-31} (\text{kg}) \quad \times 2.2 \times 10^4 \text{ m/s}$$

$$\Delta x = \frac{\hbar}{4\pi \Delta P}$$

$$= \frac{\hbar}{4\pi \times 9.11 \times 2.2 \times 10^{-28}} \\ = 10^{-10} \times 263 \\ = 263 \text{ A}^\circ$$

(2) calculate the uncertainty in the position of an position having mass 1 g and moving with a speed of 1.5 m/s

Given: $\Delta P = 10^{-3} P$

$$\Rightarrow P = mv = 1.0 \times 10^{-3} \text{ kg} \times 1.5 \text{ m/s}$$

$$\Delta P = 1 \times 1.5 \times 10^{-6} \text{ kg m/s}$$

$$\Delta x = \frac{\hbar}{4\pi \times 1.5 \times 10^{-6}}$$

$$\Delta x = 3.5 \times 10^{-29} \text{ m}$$

$$= 3.5 \times 10^{-19} \text{ A}^\circ$$

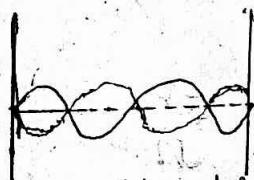
$$A^\circ = 10^{10}$$

Schrodinger wave equation

(1) Standing wave \rightarrow

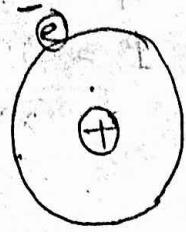
(2) progressive wave. \rightarrow Can transfer energy

The crest and trough of the wave move in the forward direction. \rightarrow From one location of medium to another location.



Standing wave

Crest and trough of the wave appear and disappear in the same position.



* The behaviour of electron in an atom is also standing or stationary wave type.

The wave equation for standing wave

$$\frac{d^2 \psi}{dx^2} = -\frac{4\pi}{\lambda^2} \psi \quad [\psi \rightarrow \text{Amplitude}] \quad \text{①}$$

$\lambda = \frac{h}{mv} \rightarrow \text{de Broglie}$

or $\frac{d^2 \psi}{dx^2} = -\frac{4\pi^2 m v^2}{h^2} \psi \quad \text{②}$ [Kinetic energy]
 $\qquad \qquad \qquad T = \frac{1}{2} mv^2$

or $\frac{d^2 \psi}{dx^2} = -\frac{4\pi^2 m \cdot 2T}{h^2} \psi \quad \text{③}$ [mv^2 = 2T]

$= -\frac{8\pi^2 m \psi T}{h^2}$ [E = T + V]

or $\frac{d^2 \psi}{dx^2} = -\frac{8\pi^2 m (E-V)}{h^2} \psi$ [where V is Potential energy]

Schrodinger eqn for one dimension.

$$\Rightarrow \frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m (E-V)}{h^2} \psi = 0$$

if we extend the equation in 3D,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E-V) \psi = 0$$

$$\Rightarrow \psi \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{8\pi^2 m}{h^2} (E-V) \psi = 0$$

Laplacian operator (∇^2)

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\therefore \psi \nabla^2 = -\frac{8\pi^2 m (E-V)}{h^2} \psi$$

$$\text{or, } -\frac{\hbar^2}{8\pi^2 m} \nabla^2 \psi = (E\psi) \psi$$

$$\text{or, } -\frac{\hbar^2}{8\pi^2 m} \nabla^2 \psi + v\psi = E\psi \rightarrow \textcircled{3}$$

$$\text{or, } \left[-\frac{\hbar^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + v \right] \psi = E\psi$$

$$\psi = (x, y, z)$$

$$v = (x, y, z)$$

$$\Rightarrow \boxed{\hat{H}\psi = E\psi} \quad \hat{H} = \frac{-\hbar^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + v(x, y, z)$$

Schrodinger eqn or

Eigen eqn

$$\frac{-\hbar^2}{8\pi^2 m} \nabla^2 \psi + v\psi = E\psi$$

Required planck constant $\rightarrow \hbar = \frac{\hbar}{2\pi}$

$$\hbar^2 = \frac{\hbar}{4\pi^2}$$

$$\hbar^2 = \hbar^2 \cdot 4\pi^2$$

putting the value of \hbar^2 in eqn,

$$-\frac{\hbar^2 \cdot 4\pi^2}{8\pi^2 m} \nabla^2 \psi + v\psi = E\psi$$

$$\text{or, } -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + v\psi = E\psi$$

$$\text{or, } -\frac{\hbar^2}{2m} \nabla^2 \psi + v\psi = E\psi$$

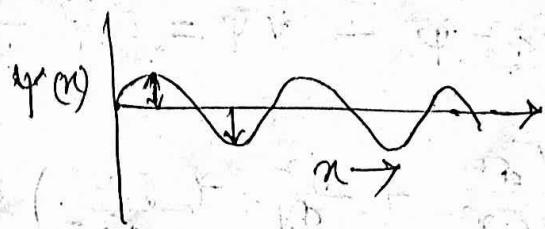
$$\hat{H}\psi = E\psi$$

\downarrow Hamiltonian operator

$$\psi \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + v \right] \psi = E\psi$$

* $|\psi|^2 \rightarrow \text{probability density}$

$$|\psi|^2 dx \rightarrow n \text{ and } n+dx$$



$\psi(n) \rightarrow$ it self here no meaning

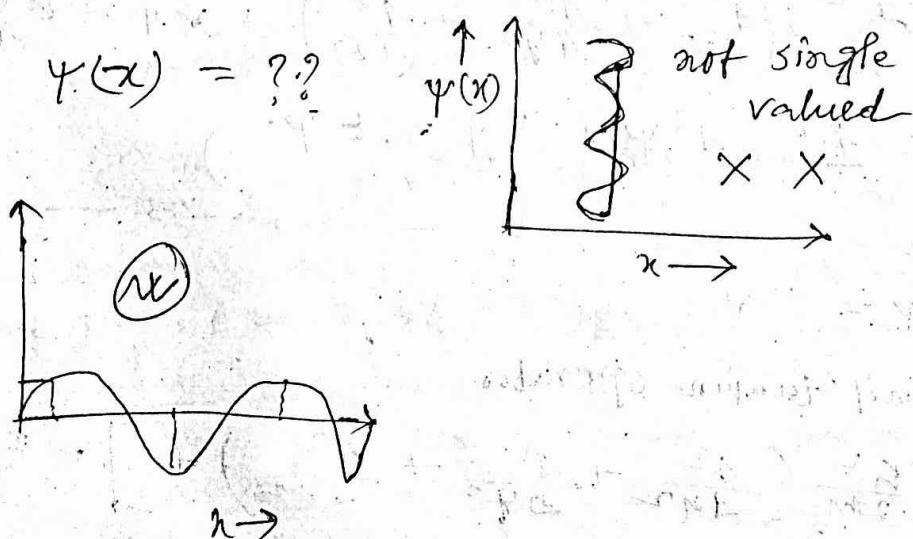
but according to max bond

$|\psi|^2 dx$ or $\psi^* \psi dx$ indicates
the number of finding the particle
between x and $x+dx$

- (*) only certain values of ψ are acceptable.

Acceptable Condition of ψ

- ① ψ should be finite.
- ② ψ must be single valued at all points.
- ③ ψ and its first derivative must be continuous.



- ① finite
- ② single valued
- ③ ψ and its 1st derivative should be continuous.

operator

An operator is a mathematical tools for transforming one function into another.

$$\hat{A} f(x) = g(x)$$

$$\begin{aligned}\frac{d}{dx} f(x) &= \frac{d(fx^2)}{dx} & f(x) &= cx^2 \\ &= 2cx \\ &= g(x)\end{aligned}$$

Eigen function

Eigen function is type of function such that when a particular operator acts upon that function, the function will be re-generated multiplied by a constant is known as eigen value.

$$e^{mx} \rightarrow \frac{d}{dx}$$

$$\frac{d(e^{mx})}{dx} = m(e^{mx}) \rightarrow \text{eigen function.}$$

eigen value

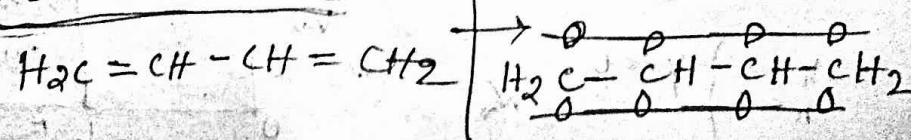
$e^{mx^2} \rightarrow$ eigen function of $\frac{d}{dx}$ is not

$$\therefore \frac{d}{dx} (e^{mx^2}) = \frac{2mx e^{mx^2}}{\downarrow}$$

not a constant because
n is there.

partical in one dimension

1,3-butadiene

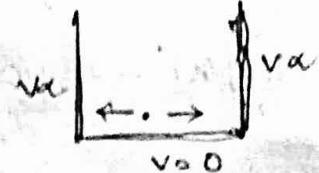


$$V = \frac{K q_1 q_2}{r} \quad [k \rightarrow \text{constant}]$$

$$K = \frac{1}{4\pi\epsilon_0}$$

$$\therefore V_e = k_e + \frac{2e^2}{r} - e$$

$$= k_e - \frac{2e^2}{r}$$



* $\hat{H}\psi = E\psi \rightarrow \text{one Schrodinger equation.}$

Hamiltonian operator.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi = E\psi$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2} + V \right] \psi = E\psi$$

$$\Rightarrow \left[-\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} \right] \psi = E\psi$$

$$\Rightarrow \frac{-\hbar^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} = E\psi$$

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} = -\frac{8\pi^2 m E}{\hbar^2} \psi} \rightarrow ①$$

$$\therefore \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m E}{\hbar^2} \psi = 0 \rightarrow ②$$

$$\therefore \boxed{\frac{d^2\psi}{dx^2} = -K^2 \psi} \rightarrow ③$$

$$\psi = A \sin kx + B \cos kx \rightarrow ④$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$\hbar \rightarrow \text{reduced Planck constant}$

$$\hbar = \frac{h}{2\pi}$$

$$\hbar^2 = \frac{h^2}{4\pi^2}$$

$\rightarrow ①$

$$K^2 = \frac{8\pi^2 m E}{\hbar^2}$$

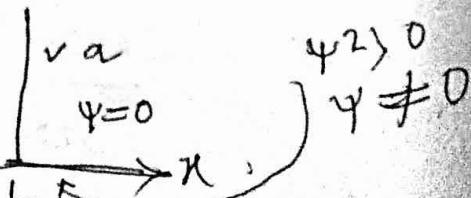
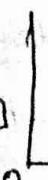
$$\psi = A \sin kx + B \cos kx$$

You can find out A and B by applying boundary condition and normalization

Condition:

$$\begin{cases} u=0 \\ x=L \end{cases} \quad \psi=0$$

$$x=0 \quad \boxed{\psi=0}$$



At $n=0$

$$\psi = A \sin kx + B \cos kx$$

$$\psi = A \sin kx + B \cos kx = 0$$

$$\psi = 0$$

At $n=0$

$$\psi = A \sin kx$$

the other boundary condition

$$x=L, \psi=0$$

$$A \sin kL = 0 \quad \text{if } (n=0) \quad \text{or } (\sin kL = 0) \quad \checkmark$$

(2)

$\sin kL = 0$

$$A \neq 0 \rightarrow \sin kL = 0$$

$$\rightarrow kL = n\pi$$

$$\rightarrow k = \frac{n\pi}{L}$$

$[n=1, 2, 3, \dots]$

$$\left[k^2 = \frac{8\pi^2 m E}{h^2} \right] \Rightarrow \left[k^2 = \frac{n^2 \pi^2}{L^2} \right]$$

$$k^2 = k^2$$

$$\Rightarrow \frac{n^2 \pi^2}{L^2} = \frac{8\pi^2 m E}{h^2}$$

$$\Rightarrow E = \frac{n^2 h^2}{8m L^2}$$

$n=1$

$$E = \frac{h^2}{8m L^2}$$

$n=2$

$$E = \frac{4h^2}{8m L^2} = \frac{h^2}{2m L^2}$$

$$\psi = A \sin kx$$

$$k = \frac{n\pi}{L}$$

$$\boxed{\psi_n = A \sin \frac{n\pi}{L} x}$$

$$\textcircled{1} \quad E_n = \frac{n^2 h^2}{8mL^2} \rightarrow \textcircled{2}$$

$$E_1 = \frac{h^2}{8mL^2}$$

Energy of the particle will never be zero,

or $\rightarrow E_1 = \frac{h^2}{8mL^2} \rightarrow$ zero point Energy.

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \left. \begin{array}{l} E_n \text{ and } E_{n+1} \\ E_1 \text{ and } E_2 \\ E_2 \text{ and } E_3 \text{ so one} \end{array} \right\}$$

$$\begin{aligned} \Delta E_n &= \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} \\ &= \left\{ (n+1)^2 - n^2 \right\} \frac{h^2}{8mL^2} \\ &= \left\{ n^2 + 2n + 1 - n^2 \right\} E_1 \cancel{, (n+1) E_2} \\ &= (2n+1) E_1 \end{aligned}$$

$$\Delta E_n = (2n+1) E_1$$

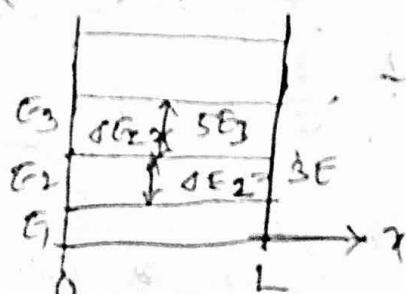
E_1 and E_{1+1} (E_2)

$$\Delta E_3 = E_2 - E_1 = (2 \cdot 1 \cdot 1) E_1$$

$$\Delta E_1 = 3E_1$$

$$\Delta E_2 = 5E_1$$

$$\Delta E_3 = 7E_1$$



⑧ Energy remain constant with change in n value.

'Conservative system'

$$③ E_1 = \frac{h^2}{8mL^2}$$

$E_1 \propto \frac{1}{L^2}$ } if the box size increases the energy gap between two layers will decrease \rightarrow large system continuous energy?

Mass increases $\rightarrow \Delta E$ decreases

$$\Delta E = (2n+1)E_1$$

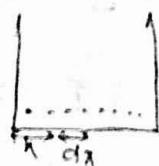
④ Atomic system

② \rightarrow very low mass dimension $\rightarrow 1^{\circ}$ Level

$$\begin{array}{l} L \rightarrow \text{low} \\ m \rightarrow \text{low} \end{array}$$

⑤

$$\boxed{\Psi_n = A \sin \frac{n\pi}{L} x} \rightarrow ① \quad A = \text{constant}$$



$$\int_{0}^{L} \Psi \Psi^* dx = 1$$

Ψ and Ψ^* \rightarrow same

$$\Rightarrow \int_{0}^{L} A^2 \sin^2 \frac{n\pi}{L} x dx = 1 \quad \downarrow \quad A \sin \frac{n\pi}{L} x \quad | \quad \Psi^* = \sin \frac{n\pi}{L} x$$

$$\Rightarrow \int_{0}^{L} A^2 \sin^2 \frac{n\pi}{L} x dx = 1$$

$$\Rightarrow A^2 \int_{0}^{L} \left(1 - \cos \frac{2n\pi x}{L} \right) dx = 1$$

\Rightarrow

$$\Psi_1 = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

$$\Psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2n\pi}{L} x$$

$$\boxed{\Psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x}$$

plot of ψ_1 vs. x

ψ_2 against x

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x$$

at $x=0$,

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} \cdot 0$$

$$\boxed{\Psi = 0}$$

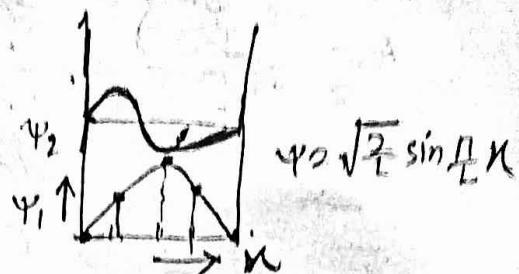
at $x = \frac{L}{4}$

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x \frac{K}{4}$$

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{4}$$

$$\psi_1 = \frac{\sqrt{2}}{\sqrt{L}} \frac{1}{\sqrt{2}}$$

$$\boxed{\psi_1 = \frac{1}{\sqrt{L}}}$$



at $x = \frac{L}{2}$

$$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x \frac{K}{2}$$

$$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{2}$$

$$\boxed{\psi_2 = \sqrt{\frac{2}{L}}}$$

at $x = \frac{3L}{4}$

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x \frac{3K}{4}$$

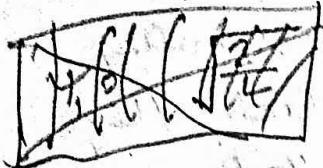
$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{3\pi}{4}$$

$$= \sqrt{\frac{2}{L}} \sin (90 + 45^\circ)$$

$$\boxed{\psi_1 = \sqrt{\frac{2}{L}}}$$

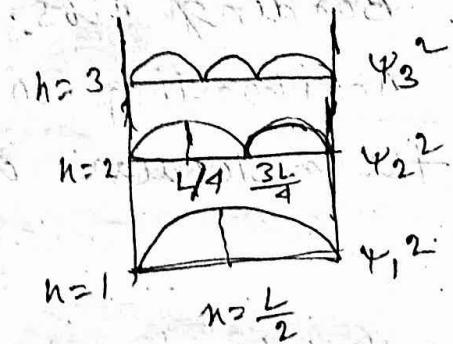
at $n=1$

$$\psi_1 = \frac{1}{\sqrt{2}} \sin \frac{\pi}{L} x L$$



$$(\psi = 0)$$

② $\psi^2 \rightarrow$ Against n



① Molecular orbital

- ① the atomic orbital must have comparable energies.
- ② they must overlap appreciably.
- ③ they must have the same symmetry with respect to the bonding molecular axis.
- ④ the number of the molecular orbital will be same to that of participating atomic orbital.
- ⑤ for even no of molecular orbital half will be bonding and remaining half will be anti bonding mos.
- ⑥ for odd no of mos \Rightarrow one will be non bonding mos and the remaining orbitals angular half will be anti bonding mos.

① Bonding Mo :- $\text{Mo} \rightarrow \text{Molecular orbitals}$

the molecular orbitals whose energy is lower than the corresponding atomic orbitals from which they have been formed are called Bonding Mo.

② Antibonding Mo :-

The molecular orbitals

③ Non bonding Mo :-

The molecular orbitals whose energy are is equal to the atomic orbitals

Bond order :-

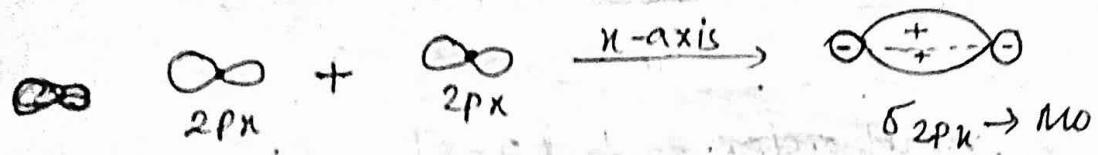
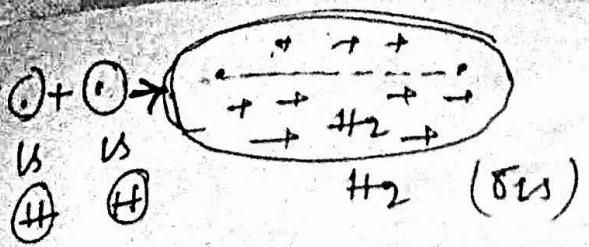
Bond order may be defined in the following way -

$$\text{Bond order} = \frac{1}{2} [\text{No. of electrons in the bonding molecular orbitals} - \text{no. of electrons in the anti bonding Mo}]$$

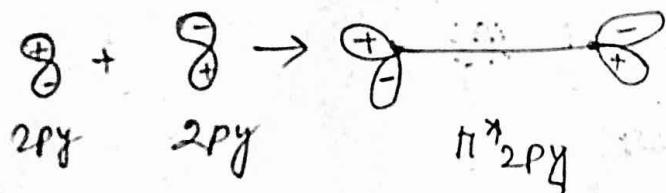
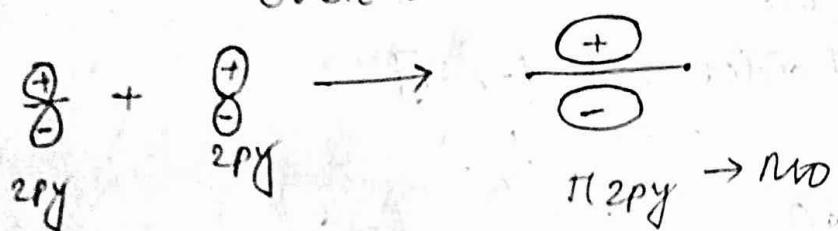
8 Molecular orbital (MOs)

Head on overlap between two molecular orbitals will give rise to atomic σ molecular orbitals.

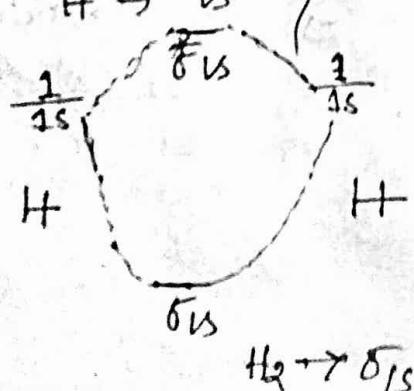
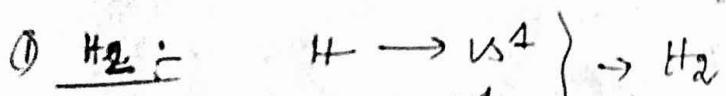
$$\text{MO} = \text{H}_2 \rightarrow \text{molecule.}$$



$\pi \rightarrow \text{MO} \rightarrow$ lateral overlap between two atomic orbitals.



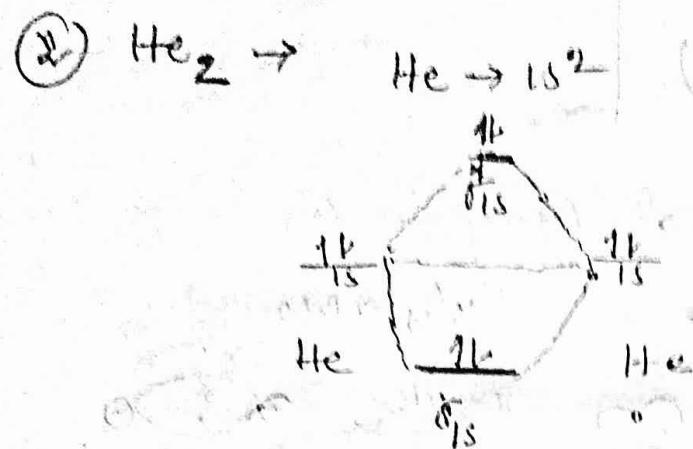
① $\text{H}_2, \text{He}, \text{Li}_2, \text{Be}_2, \text{Ne}$



② Bond order = $\frac{1}{2} [2 - 0] = 1$

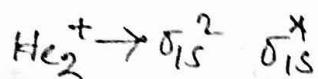
$\text{H}_2 \rightarrow$ single bonds
1s present

* Bond order ≥ 0



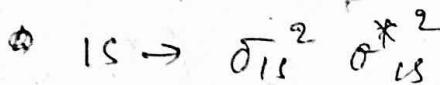
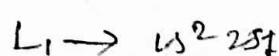
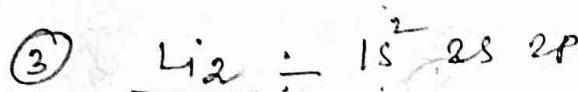
$$\text{Bond order} = \frac{1}{2} [2 - 2]$$

$\text{He}_2 \rightarrow$ is not possible.

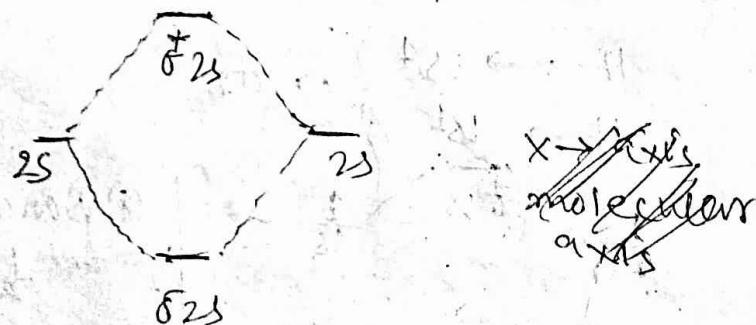


$$(\text{B.o}) \text{ Bond order} = \frac{1}{2} [2 - 1] = \frac{1}{2}$$

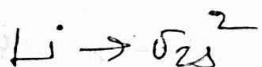
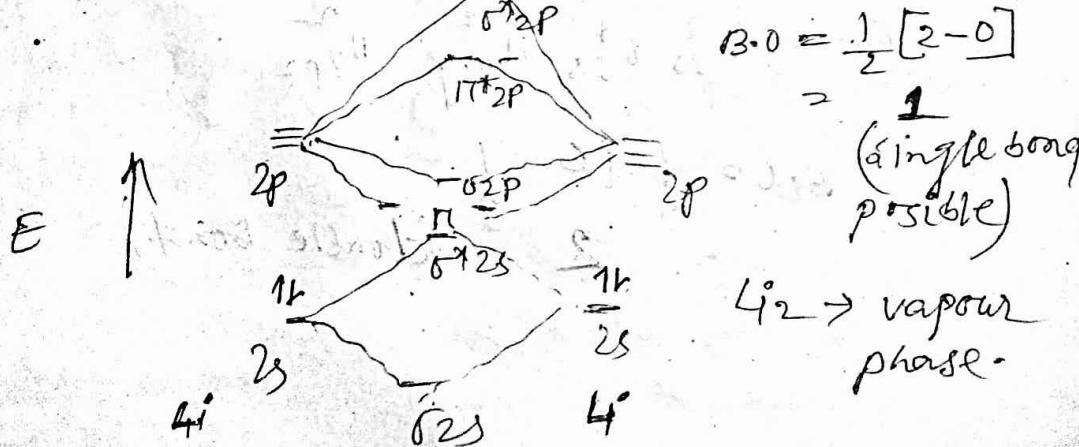
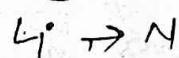
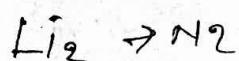
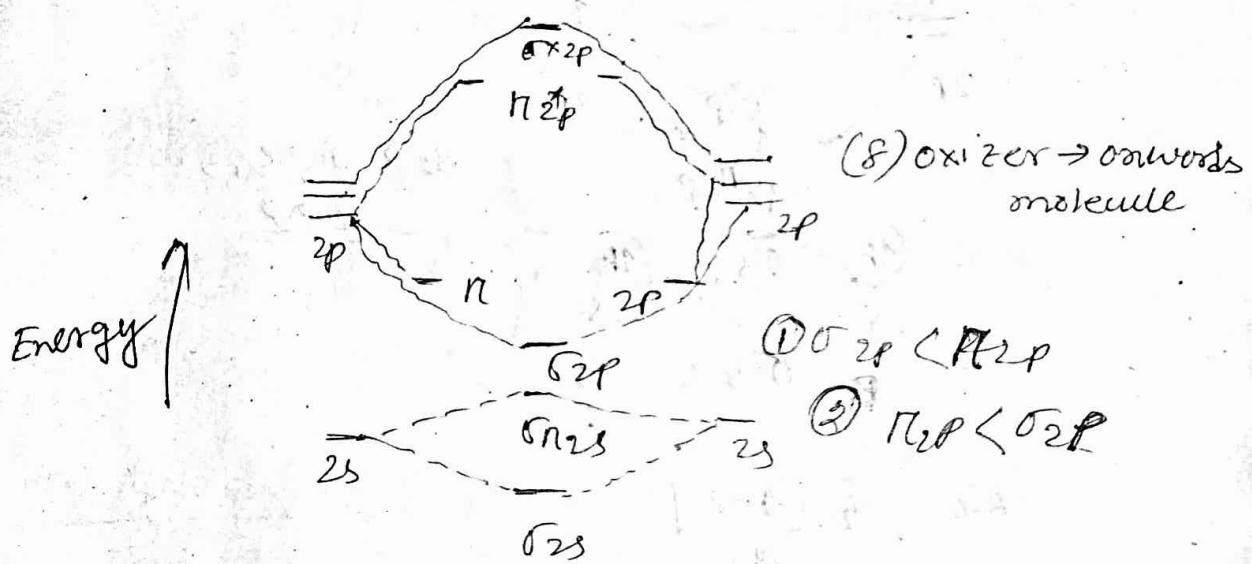
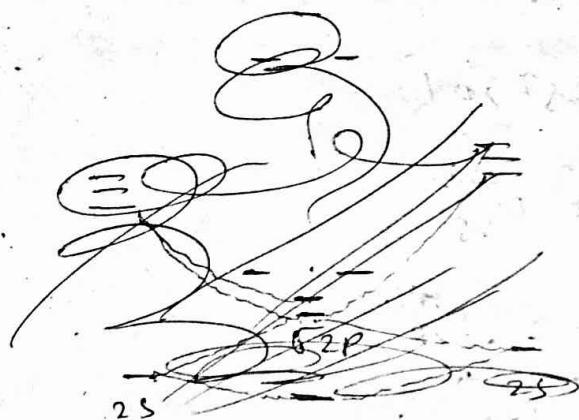
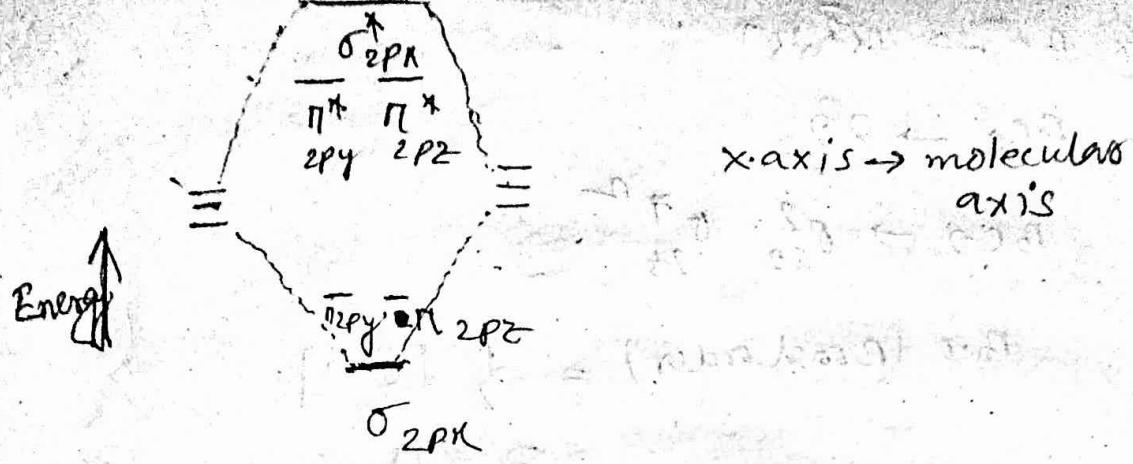
$$\oplus \text{B.o} > 0$$



$$\text{Bo} \Rightarrow 0$$



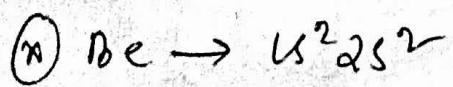
$\times \rightarrow \alpha_{1s}$
molecular
 α_{1s}



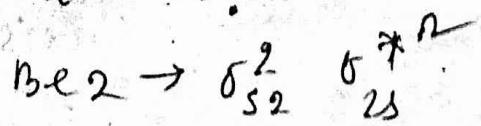
$$\text{B.O} = \frac{1}{2} [2 - 0]$$

= 1
(single bond possible)

$\text{Li}_2 \rightarrow \text{vapour phase}$

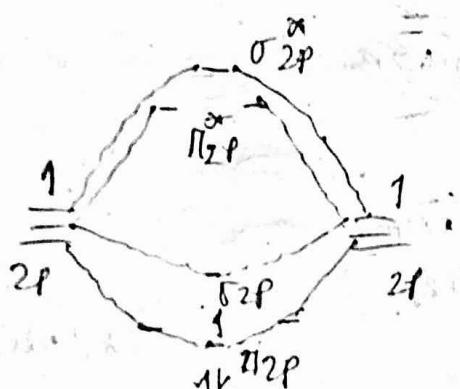
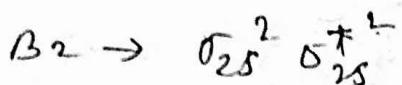
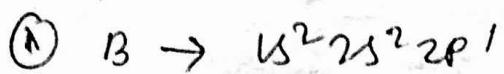


$\text{Be}_2 \rightarrow ? ?$

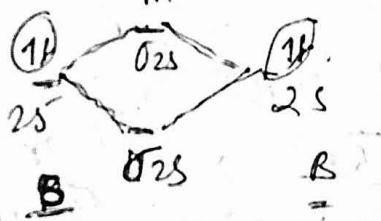


$$\text{B.O. (Bond order)} = \frac{1}{2} [2-2] \\ = 0$$

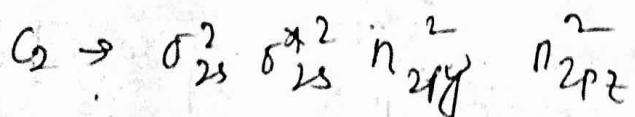
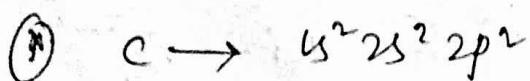
$\text{Be}_2 \rightarrow \times$ close not exist.



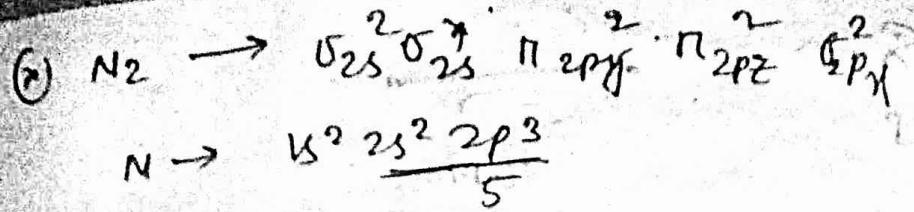
$\text{B}_2 \rightarrow \underline{\text{single bond}}$



$$\text{B.O.} = \frac{1}{2} [4-2] \\ = 1$$



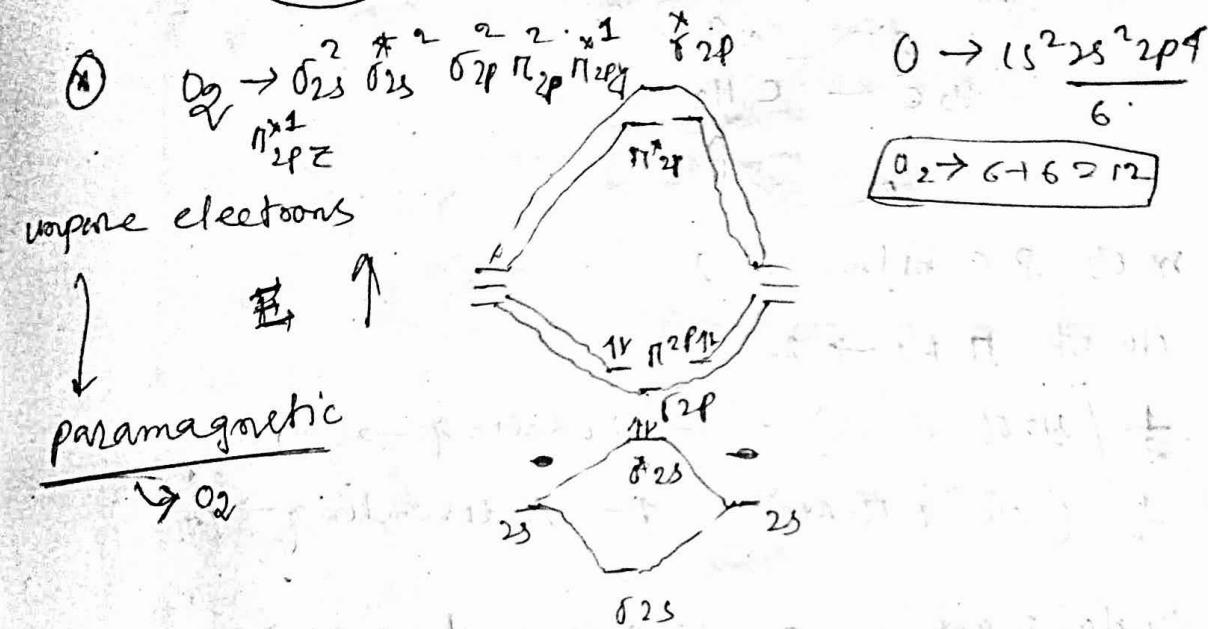
$$\text{B.O.} = \frac{1}{2} [6-2] \\ = 2 \quad (\text{double bond})$$



$$5+5=10$$

$$B.O. = \frac{1}{2} [8-2]$$

$\Rightarrow -3$



$$B.O. = \frac{1}{2} [8-4]$$

$\Rightarrow -2$

$\pi \rightarrow$ Molecule orbital :

- (1) $H_2C=CH_2$
- (2) $H_2C=CH-CH_2^+$
- (3) 1, 3-butadiene

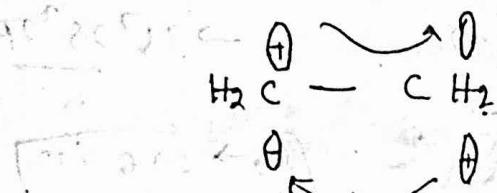
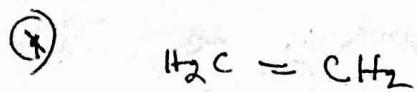
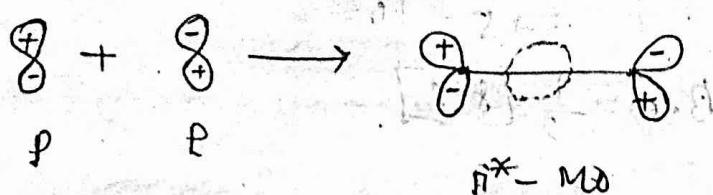
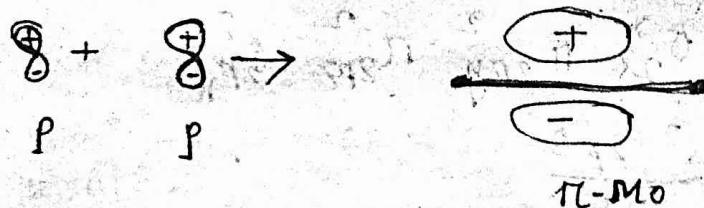
$HOMO \rightarrow$ highest occupied molecular orbital $\rightarrow (\psi_3)$

$LUMO \rightarrow$ lowest unoccupied $\rightarrow (\psi_5)$

Excited state \downarrow

$\psi_1, \psi_2, \psi_3, \dots, \psi_5, \psi_6^*, \dots, \psi_n^*$

$\pi_{1s}, \pi_2, \pi_3, \dots, \pi_5, \pi_6^*, \dots, \pi_n^*$



No of P orbital $\rightarrow 2$

No of $\pi\text{-Mo} \rightarrow 2$

$\frac{1}{2}$ (No of $\pi\text{-Mo}$) = 1 - bonding $\rightarrow \psi_1$

$\frac{1}{2}$ (No of $\pi\text{-Mo}$) = 1 - Antibonding $\rightarrow \psi_2^*$

Nodal plane \div e density will be zero.

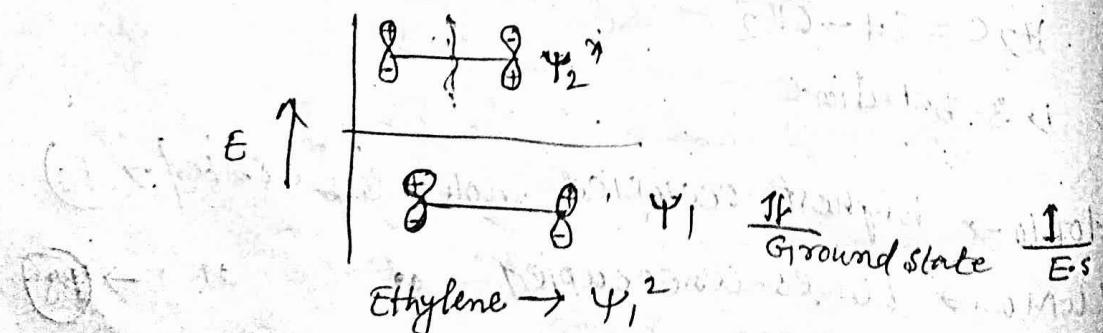
ψ_n No of nodal plane $\rightarrow n-1$

$$\psi_1 \rightarrow 0$$

$$\psi_2 \rightarrow 1$$

$$\psi_3 \rightarrow 2$$

* $\text{H}_2\text{C} = \text{CH}_2$



Ground State \rightarrow Ethylene $\rightarrow \psi_1$

Excited State \rightarrow $\psi_1 \psi_2$

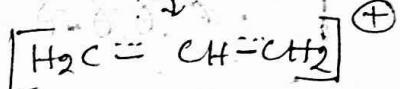
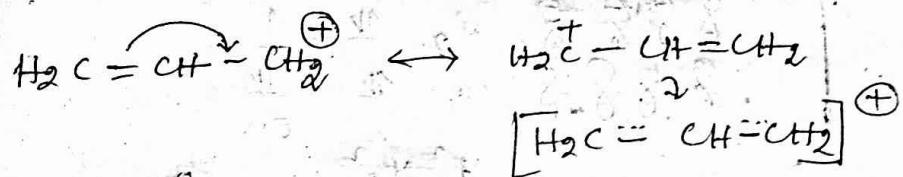
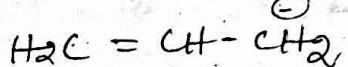
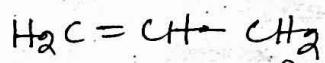
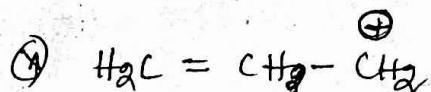
Ground state $\rightarrow \psi_1 \rightarrow \text{Homo}$

ψ_2^* $\rightarrow \text{LUMO}$

Excited state \rightarrow

$\psi_2^* \rightarrow \text{Homo}$

Lumo $\rightarrow X$



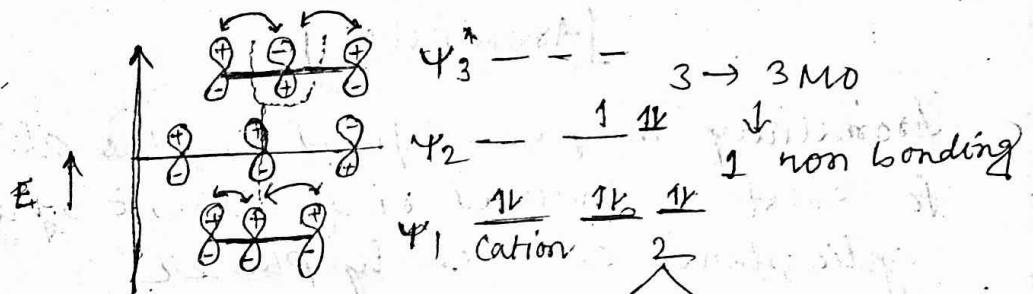
$\pi\text{-MO} \rightarrow \text{p orbitals} \rightarrow 3$

Allyl cation $\rightarrow e^+ s \rightarrow 2$

Allyl radical $\rightarrow e^+ s \rightarrow 3$

Allyl anion $\rightarrow e^+ s \rightarrow 1$

Some \rightarrow singly occupied molecular orbital.



Allyl cation $\rightarrow \text{Homo} \rightarrow \psi_1$

Allyl radical $\rightarrow \text{Homo} \rightarrow \psi_2$

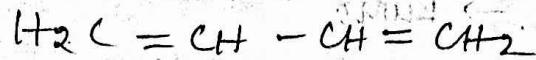
Some $\rightarrow \psi_2$

LUMO $\rightarrow \psi_3^*$

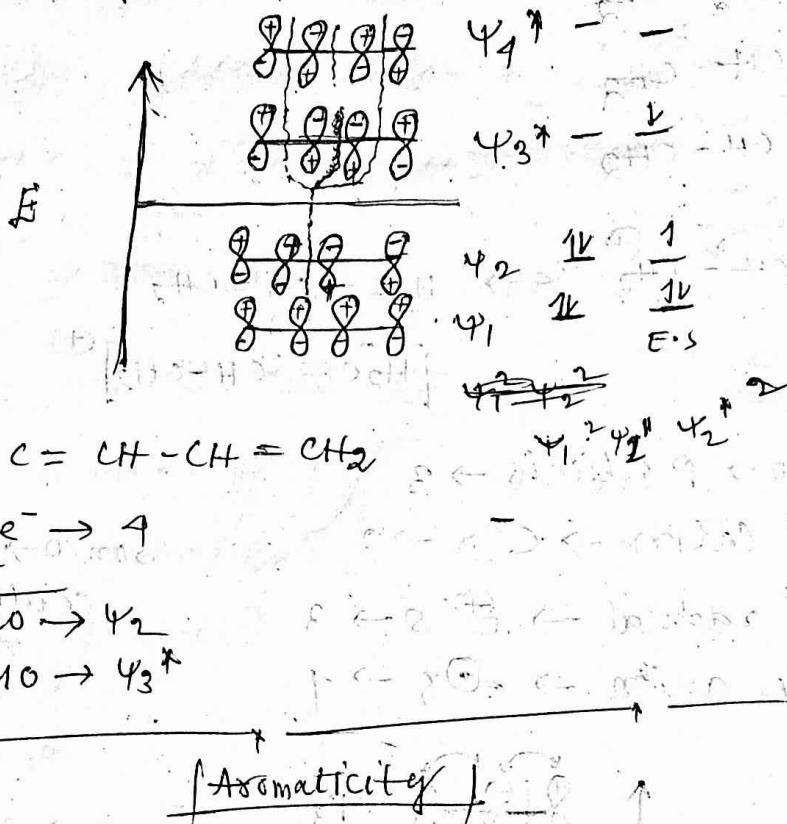
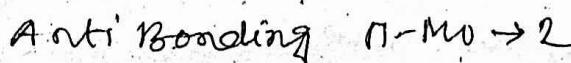
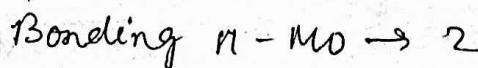
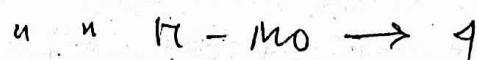
Allyl anion $\rightarrow \text{Homo} \rightarrow \psi_2$

LUMO $\rightarrow \psi_3^*$

① 1,3 di butadiene,



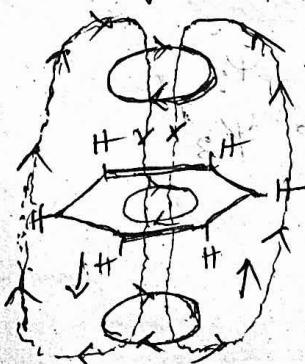
no of involved p-orbital = 4



Aromaticity may be defined as the ability to substant induced ring current by a cyclic planer or nearly planer system having $(n+2)$ no. of delocalized π electron where n is zero or any whole number.



$H \uparrow$ (applied magnetic field)



* when a magnetic field is applied to the perpendicular to the plane of the benzene ring is circulation of the delocalized π electrons

takes place in one direction and thereby
a ring current, which induces a magnetic
field as shown in the figure. thus benzene
has the ability to substantiate induced ring
current.

* Condition for aromaticity :-

Antiaromaticity :-

- ① The system must be cyclic.
- ② It must be planar.
- ③ It should contain Hückel no. of delocalized π -electrons,
i.e., $(4n+2)$ no. of π electrons where
 $n=0$ or any integer.

Example :-

$\Delta \rightarrow$ cyclopropane.

$\begin{array}{c} \Delta \\ \equiv \end{array} \rightarrow$ cyclopropene.

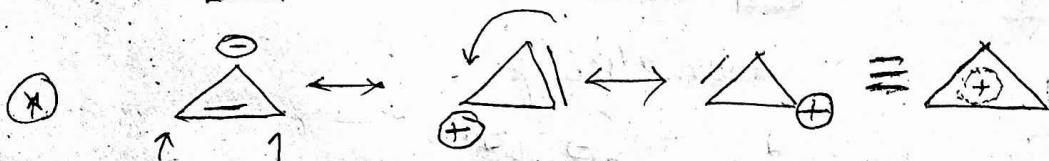
$\begin{array}{c} \Delta \\ \oplus \\ \ominus \end{array}$ or $\begin{array}{c} \Delta \\ \ominus \\ \oplus \end{array} \rightarrow$ cyclopropenyl cation.

$\begin{array}{c} \Delta \\ \ominus \end{array} \rightarrow$ cyclopropenyl anion.

$\begin{array}{c} \square \\ - \end{array} \rightarrow$ cyclobutadiene

$\begin{array}{c} \square \\ + \end{array} \rightarrow$ cyclopentadienyl cation.

$\begin{array}{c} \square \\ - \end{array} \rightarrow$ anion.

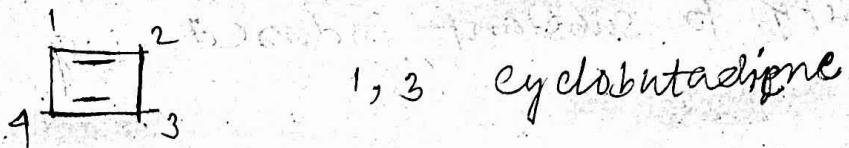
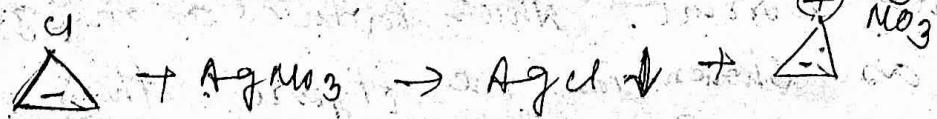


① it is cyclic

② planar ③ delocalized π electron. $2 \rightarrow$

$(4n+2) \xrightarrow{n=0} 2$ (This is aromatic system)

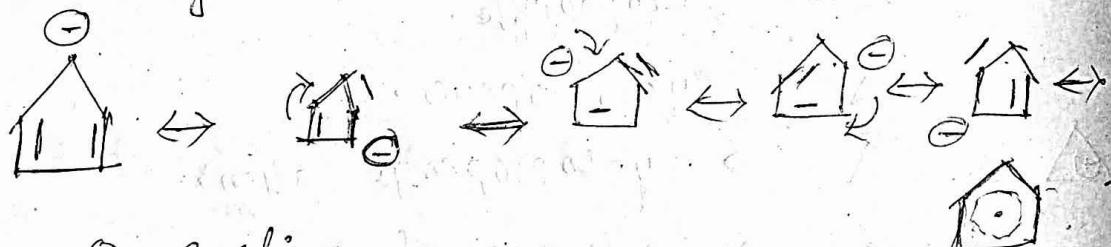
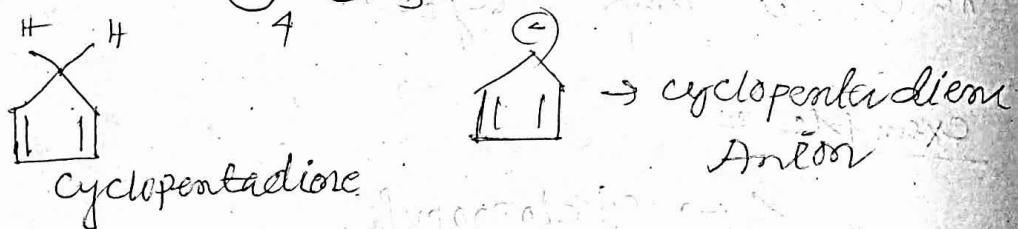
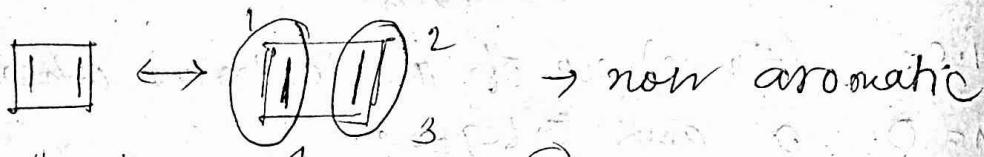
Extra stability



- ① cyclic system
- ② ~~planar~~ planar system
- ③ delocalization → 4-4W

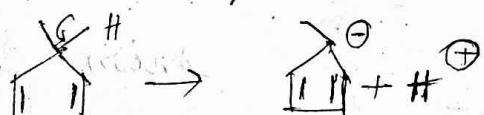


Anti-Aromatic

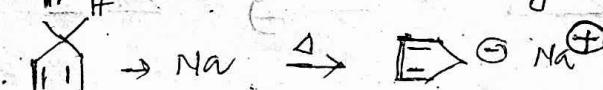


- ① cyclic
- ② planar
- ③ $5+1 = 6 \quad (4n+2)$ when $n=1$

Aromatic Acid

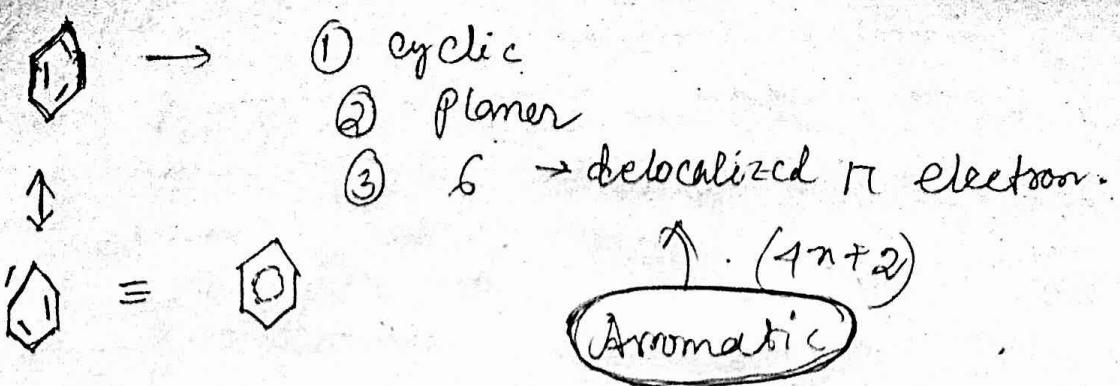


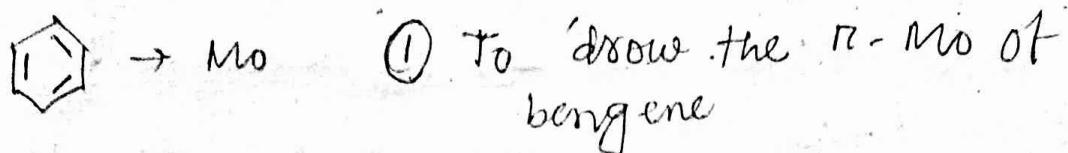
Aromaticity



- ① planar
- ② cyclic
- ③ $5-1=4$

} Anti-aromatic




 $\text{C}_6\text{H}_6 \rightarrow \text{Mo}$ ① To draw the π -MO of benzene

Frost diagram ② Aromaticity

1953 Frost \rightarrow

"A circle is inscribed with one in a polygon with one vertex pointing down ward; then the vertices which touched the circle at different parts will represent the energy level for the cyclic system".

