

Quantum Chemistry

At molecular level, classic mechanics given by Newton cannot be applied and hence here comes the part of quantum chemistry.

If we shoot bullets from 2 slits in a single wall, we would get a flat density of bullets in figure (1). As electrons were considered as particles, same experiments was performed but the result was not same. The result was figure (2). Hence the electron was seen as wave nature.

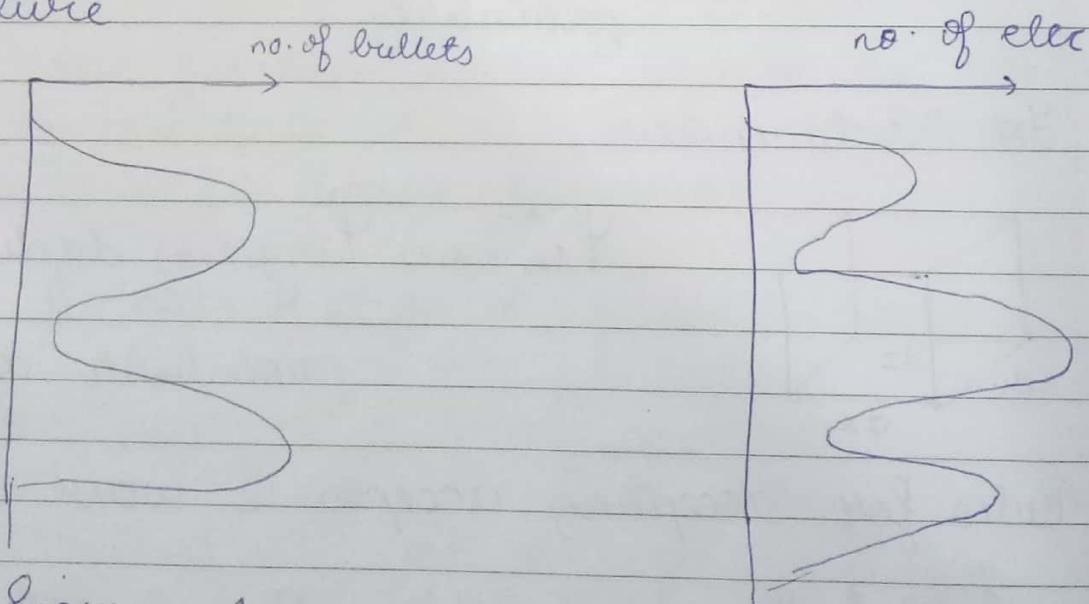


Figure - 1

#

$\Psi(x, y, z, t)$ (denotes for co-ordination)

wave / state function.

$\Psi(x, t) \rightarrow$ wave moves only in one direction



If we talk about He, the wave function of $2e^0$,
 (one direction) of He

$$\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)$$

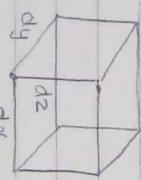


: probability of finding electron in

$$\Psi_{(x,t)}^* \Psi_{(x,t)} dx \Rightarrow |\Psi(x)|^2 dx$$

probability

for 3 dimensions,



$$\Psi_{(x,y,z,t)}^* \Psi_{(x,y,z,t)} dx dy dz$$

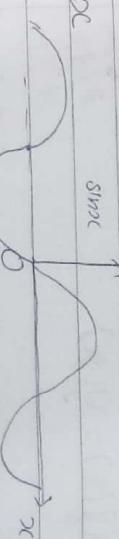
probability density

Rules for accepting acceptable wave function

$$\phi(x) = \frac{e^{-x^2}}{1 + e^{-x^2}} \quad \text{at } x = \infty$$

(2) It should be single valued (one-one)

$$\phi(x) = \sin x$$



: one function value can't be obtained by multiply x, : not acceptable wave function

(3) The function should be continuous

$$\begin{aligned} \phi(x) &= \frac{e^{-x^2}}{1 + e^{-x^2}} & \text{at } x = \infty \\ \text{at } x = 0.00, & \quad \phi(x) = \infty \\ \phi(x) \rightarrow 0, & \quad \phi(x) = \infty \\ \text{at } x = -0.00, & \quad \text{not an acceptable} \\ \phi(x) &\rightarrow 1 & \text{wave function} \end{aligned}$$

doing normalisation for making it acceptable wave function.

$$\frac{\int \phi^*(x) \phi(x) dx}{\int \phi^*(x) dx} = 1$$

Postulate - 2 -

For every observable \hat{A} physical observable,
there corresponds a linear Hermitian
operator.

\hat{A} physical observable $\rightarrow x \rightarrow$ position
 $\hat{P}_x \rightarrow$ momentum

$$KE = \frac{\hat{P}_x^2}{2m}$$

Operator $\rightarrow \hat{A}$

\hat{A}	$f(x)$	$g(x)$
$\frac{d}{dx} f(x)$	$\frac{x^2}{2}$	$2x$
$\frac{d^2}{dx^2} f(x)$	x^2	x
$\int f(x) dx$	$x^2/2$	$x^2/2$
$\sqrt{f(x)}$	x	x

Linear \rightarrow

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

$$\hat{P}_x \rightarrow \hat{A} \Rightarrow \frac{d}{dx}$$

$$\frac{d}{dx} (\cos x + e^x) = \frac{d(\cos x)}{dx} + \frac{d(e^x)}{dx}$$

$$\begin{aligned} KE &= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \\ &= -\frac{\hbar^2}{2m} \nabla^2 \end{aligned}$$

$$\hat{A} = \int$$

$$\int \cos x + e^x \neq \int \cos x + \int e^x$$

Hermitian condition :- Det ψ, ϕ be distinct
function

$$\therefore \int \phi^* \hat{A} \psi = (\int \psi^* \hat{A} \phi)^*$$

In quantum chemistry we don't use
momentum & position directly, instead
we use ψ as an operator

$$x \rightarrow x \quad \rightarrow \quad \hat{P}_x \rightarrow -i\hbar \frac{\partial}{\partial x} \quad (\hbar = \frac{k}{e\pi})$$

$$i = \sqrt{-1}$$

Postulate - 3

Measurement of an observable would give one of the eigen values of corresponding operator.

$$\hat{A}\phi(x) = K(\phi)(x) \rightarrow \text{Eigen function}$$

constant

$$\frac{d}{dx} (\sin kx) \rightarrow k \cos kx$$

$$\frac{d^2}{dx^2} (\sin kx) \rightarrow -k^2 \sin kx$$

$\therefore -k^2 \rightarrow \text{Eigen value}$

Postulate - 4

$$i\hbar \frac{d\psi(x,t)}{dt} = \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right\} \psi(x,t)$$

Success@ for one dimension,

Assuming time independent Potential Energy.

$$\hat{H} = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right)$$

$$\hat{H}\phi(x) = E\phi(x) \quad \therefore E = \left(n + \frac{1}{2} \right) \hbar\nu$$

$$\Psi(x,t) = \psi(x)\phi(t)$$

$$i\hbar \frac{d\Psi(x,t)}{dt} = \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right\} \Psi(x,t)$$

For any experiment performed, $a_1 \rightarrow a_1 a_1$
 $\& n_1 \text{ times}, \quad a_2 \rightarrow a_2 \text{ times}, \quad \dots$

$$\text{Average value} = n_1 a_1 + n_2 a_2 + n_3 a_3 + \dots$$

$$g(t) = g(x) = E$$

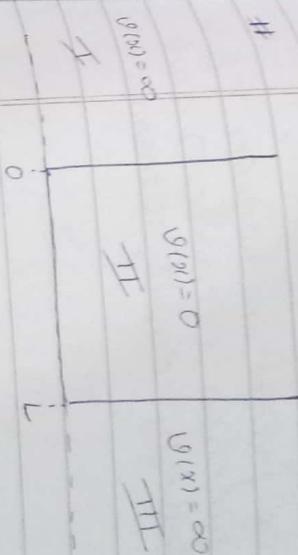
$$i\hbar \frac{d\phi(t)}{dt} = \frac{1}{\psi(x)} \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right\} \psi(x)$$

$$\therefore \frac{i\hbar}{\phi(t)} \frac{d\phi(t)}{dt} = E$$

$$\frac{d\phi(t)}{\phi(t)} dt = \frac{-iE}{\hbar}$$

$$\ln(\phi(t)) = -\frac{iE}{\hbar}t + C$$

IV



particle in a box

$d\mathcal{L} \rightarrow dx dy dz$ if 3 dimensional.

$$\langle \hat{A} \rangle = \int_{-\infty}^{\infty} \psi^{*}(x, t) \hat{A} \psi(x, t) dx$$

$$= \int_{-\infty}^{\infty} \psi^{*}(x, t) \psi(x, t) dx$$

$$\psi(x) = \Psi(x)\phi(t) = \Psi(x)e^{-\frac{iEt}{\hbar}}$$

$$\Psi(x, t) \Psi^{*}(x, t) \Rightarrow A^2 \Psi^{*}(x) \cdot \Psi(x)$$

: Probability density is time independent

$$\therefore E_n = \left(n + \frac{1}{2}\right) \hbar \nu \quad \varepsilon_1, \varepsilon_2, \varepsilon_3$$

$$E_0 = \frac{1}{2} \hbar \nu \quad H \quad H \quad H$$

$$\varepsilon_1 = \frac{3}{2} \hbar \nu$$

$$\psi(x, t) = \phi(t) \psi(x)$$

$$\text{but } g(x) \rightarrow \infty$$

for region I & III,

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) = E \psi(x)$$

$$\left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) = E \psi(x)$$

$$\therefore -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} \propto \psi(x) = E \psi(x)$$

$$\frac{-\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = \psi(x) \cdot (E - \infty)$$

$$\therefore \psi(x) \approx 0$$

\therefore Particle will not be found in regions I & III as the wave function becomes 0 and therefore the probability density becomes zero.

For II,

$$\frac{-\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E \psi(x) \quad [V(x) = 0]$$

$$\therefore \frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \psi(x)$$

$$\therefore \frac{d^2\psi(x)}{dx^2} = -K^2 \psi(x)$$

$$\psi(x) = A \sin(kx) + B \cos(kx)$$

$$\therefore \text{From } -\infty < x < 0, L < x < \infty \Rightarrow \psi(x) = 0$$

\therefore For acceptable wave functions, it should be continuous.

$$\therefore \psi(x) = 0, x = 0$$

$$\psi(x) = 0 + B \times 1 = 0$$

$$\therefore B = 0$$

$$\therefore \text{at } x = L, \psi(0) = 0$$

$$\psi(x) = A \sin(kL) = 0$$

but $A \neq 0$ because this well make $\psi(x) = 0$ & there will be no probability to find the electron.

$$\therefore KL = n\pi$$

$$\therefore K = \frac{n\pi}{L}$$

$$\psi(x) = A \sin\left(\frac{n\pi}{L}x\right)$$

$$K^2 = \frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2} \quad (\hbar = h/2\pi)$$

$$\therefore E = \frac{n^2\hbar^2}{8mL^2}$$

$$\therefore \int_0^L \psi(x)^* \psi(x) dx = 1$$

$$\therefore \int_0^L \psi(x)^* \psi(x) dx = 1$$

$$\therefore \int_0^L (A \sin\left(\frac{n\pi}{L}x\right))^* A \sin\left(\frac{n\pi}{L}x\right) dx = 1$$

$$\therefore A^2 \int_0^L 1 - \cos\left(\frac{n\pi x}{2}\right) dx$$

$$\therefore A^2 \left(\frac{L}{2} - \frac{\sin(n\pi x)}{n\pi} \times \frac{2L}{n\pi} \right) \Big|_0^L = 1$$

for jump from HOMO to LUMO

$$\begin{array}{c} n=5 \\ n=4 \\ n=3 \\ n=2 \\ n=1 \end{array}$$

$$\underline{E_s - E_u} = \text{Energy for jump}$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$



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

$$\underline{n=1}$$

\therefore no node for

$$E_1 = \frac{4h^2}{8mL^2}$$

$\therefore E_1 = \frac{4h^2}{8mL^2} \rightarrow$ zero point energy

$$E_2 = \frac{4h^2}{8mL^2}$$

$$\underline{n=1}$$

$$\therefore E_3 = \frac{5h^2}{8mL^2}$$

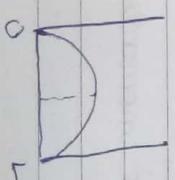
1 node
 $(n=2)$

$$E_2 = \frac{4h^2}{8mL^2}$$

$$E_1 = \frac{4h^2}{8mL^2}$$

\therefore $n =$ large number

$$\psi^2(x) \Big|_0^L$$



\therefore for E_1 the average position should be at $L/2$ as if it is symmetrical

$$\Big|_0^L$$

$$C = C - c = c - c = c - c = c - c$$



$$\therefore \langle \hat{A} \rangle = \int_{-\infty}^{\infty} \Psi(x, t)^* \hat{A} \Psi(x, t) dx$$

$$= \int_0^L \int_L^{\infty} \frac{2}{L} \sin\left(\frac{n\pi x}{L}\right) - itn \frac{d}{dx} \Psi(x, t) \Psi(x, t) dx$$

$\Psi(x, t)$ is acceptable
wave function

$$\langle \hat{A} \rangle = \int_0^L \Psi(x, t)^* \hat{A} \Psi(x, t) dx$$

\hookrightarrow (abs $\Psi(x, t)$) is dependent
on time as e^{-it} it will
be cancelled

$$\langle \hat{x} \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) - itn \frac{d}{dx} \cos\left(\frac{n\pi x}{L}\right) dx$$

$$= - \int_0^L \frac{2}{L} \times itn \times \frac{\pi}{L} \times \int_0^L \sin\left(\frac{n\pi x}{L}\right) dx$$

$$\langle \hat{x} \rangle = \int_0^L \frac{2}{L} x \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$\stackrel{=} 0 \rightarrow$ same as if goes & comes back
the same path hence average
momentum = 0

$$\therefore \int_0^L \frac{2}{L} x \left(1 - \cos\left(\frac{2n\pi x}{L}\right)\right) dx$$

• Calculating $\langle p_x^2 \rangle$

$$\begin{aligned} & \approx \frac{1}{L} \int_0^L x dx - \frac{1}{L} \int_0^L x \cos\left(\frac{2n\pi x}{L}\right) dx \end{aligned}$$

$$= \frac{1}{L} \times \frac{L^2}{2} = \frac{L^2}{2} \text{ Hence } \underline{\text{force}}$$

Let us calculate average momentum.

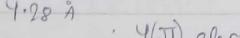
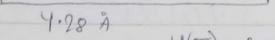
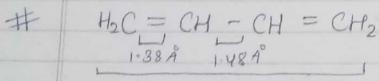
$$\begin{aligned} & = \int_0^L \int_L^{\infty} \frac{2}{L} \sin\left(\frac{n\pi x}{L}\right) \left(\frac{-t n^2}{4m^2}\right) \frac{d^2 \Psi(x, t)}{dx^2} dx \end{aligned}$$

$$= \int_0^L \frac{2}{L} \sin\left(\frac{n\pi x}{L}\right) \left(\frac{+t n^2}{4m^2}\right) \times \frac{n^2 \pi^2}{L^2} \left(\frac{\sin(n\pi x)}{1 + \cos(n\pi x)}\right) dx$$

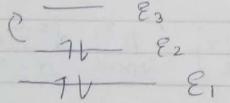
$$\begin{aligned}
 &= \int_0^L \frac{n^2 \pi^2 h^2}{8L^3} \times 2 \sin^2\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi z}{L}\right) dx \\
 &= \int_0^L \frac{2n^2 \pi^2 h^2}{8L^3} \sin^2\left(\frac{n\pi x}{L}\right) dx \\
 &= \int_0^L \frac{2n^2 \pi^2 h^2}{8L^3} \left(1 - \frac{\cos(2n\pi x/L)}{2}\right) dx \\
 &\stackrel{\text{Integration}}{=} \frac{2n^2 \pi^2 h^2}{8L^3} \left(L - \frac{1}{2}\right)
 \end{aligned}$$

$$\langle P_x^2 \rangle = \frac{n^2 \pi^2}{8L^2} \times \frac{h^2}{4\pi^2} = \frac{n^2 h^2}{4L^2}$$

$\therefore \langle P_x^2 \rangle$ should give energy $\therefore E = \frac{n^2 h^2}{8mL^2}$
Hence true



$\therefore 4(J)$ electrons



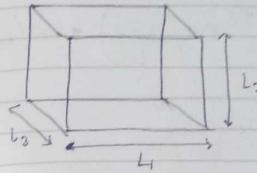
$$\therefore \Delta E = E_3 - E_2$$

$$h\nu = \frac{5h^2}{8mL^2}$$

$$\therefore L = \underline{5.6\text{ \AA}} \text{ (close)}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

$\therefore 3$ dimensional



$$\begin{aligned}
 &\therefore V(x) = 0 \quad \text{for } 0 < x < L_1 \\
 &\therefore V(y) = 0 \quad \text{for } 0 < y < L_2 \\
 &\therefore V(z) = 0 \quad \text{for } 0 < z < L_3
 \end{aligned}$$

$$\text{Assuming} \rightarrow \Psi(x, y, z) = f(x)g(y)h(z)$$

$$-\frac{\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\} f(x)g(y)h(z) = E f(x)g(y)h(z)$$

Applying partial derivative

$$\begin{aligned}
 &-\frac{\hbar^2}{2m} \left\{ g(y)h(z) \frac{\partial^2 f(x)}{\partial x^2} + f(x)h(z) \frac{\partial^2 g(y)}{\partial y^2} + f(x)g(y) \frac{\partial^2 h(z)}{\partial z^2} \right\} \\
 &= E f(x)g(y)h(z)
 \end{aligned}$$

$$\therefore E = -\frac{\hbar^2}{2m} \left\{ \frac{\partial^2 f(x)}{\partial x^2} + \frac{\partial^2 g(y)}{\partial y^2} + \frac{\partial^2 h(z)}{\partial z^2} \right\}$$

\therefore Solving individually,

$$f(x) = \sqrt{\frac{2}{L_1}} \sin\left(\frac{n\pi x}{L_1}\right), \quad g(y) = \sqrt{\frac{2}{L_2}} \sin\left(\frac{n\pi y}{L_2}\right)$$

$$h(z) = \sqrt{\frac{2}{L_2}} \sin\left(\frac{n_2 \pi z}{L_2}\right)$$

Taking $L_1 = L_2 = L_3 = L$

$$\therefore \Psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \sin\left(\frac{n_3 \pi z}{L}\right)$$

$$\therefore E = \frac{(n_x^2 + n_y^2 + n_z^2)}{8mL^2} \frac{\hbar^2}{2}$$

\therefore Standard deviation :-

$$\text{SD of momentum} = \langle p_x^2 \rangle - \langle p_x \rangle^2$$

$$\text{SD of position} = \langle x^2 \rangle - \langle x \rangle^2$$

$$\Psi(x, y, z) = \frac{(2)^{3/2}}{\sqrt{L_1} \sqrt{L_2} \sqrt{L_3}} \sin\left(\frac{n_1 \pi x}{L_1}\right) \sin\left(\frac{n_2 \pi y}{L_2}\right) \sin\left(\frac{n_3 \pi z}{L_3}\right)$$

$$E = \frac{\hbar^2}{8m} \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) \quad L_1 = L_2 = L_3$$

(2, 2, 2)

(3, 1, 1) (1, 3, 1) (1, 1, 3)

(2, 2, 1) (2, 1, 2) (1, 2, 2)

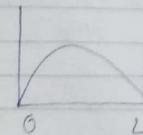
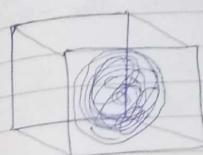
(2, 1, 1), (1, 1, 2) (1, 2, 1)

(1, 1, 1)

$$n_1 = 1, n_2 = 1, n_3 = 1$$

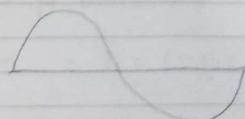
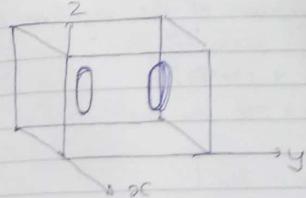
$$\text{For one dimension} \Rightarrow \frac{2}{L} \sin\left(\frac{\pi z}{L}\right)$$

For three dimensions



seen as 's' orbital

$$\text{For } n_1 = 1, n_2 = 2, n_3 = 1$$



For breaking degeneracy change length of box.

$$E = \frac{\hbar^2}{8m} \left(\frac{n_1^2}{L^2} + \frac{n_2^2}{L^2} + \frac{n_3^2}{(L+\Delta L)^2} \right)$$

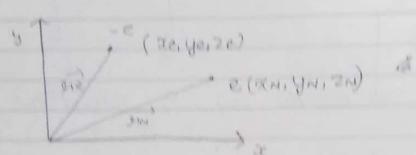
(2, 4, 1) (1, 2, 4)

$$[\hat{A} \cdot \hat{B}] \Psi = \underline{(\hat{A} \hat{B} - \hat{B} \hat{A}) \Psi} \quad (1, 1, 2)$$

For a H atom

When H atom is moving, the nucleus and the electron both is moving

$$\hat{H} = \frac{-\hbar^2}{2m_N} \nabla_N^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\epsilon_0} (\vec{r}_{ie} - \vec{r}_{in})$$



i.e. the centre of the mass of the system is :-

$$(x, y, z) = \vec{R} = \frac{m_N \vec{r}_{in} + m_e \vec{r}_{ie}}{m_N + m_e}$$

$$(x, y, z) = \vec{r}_1 = |\vec{r}_{ie} - \vec{r}_{in}|$$

$$\hat{H} \Psi_{\text{total}} = \left(\frac{-\hbar^2}{2(M_N + M_e)} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_{\vec{r}_1}^2 - \frac{e^2}{4\pi\epsilon_0 \delta} \right) \Psi_{\text{total}} = E \Psi_{\text{total}} \quad (1)$$

$$\therefore \Psi_{\text{total}} = \Psi_{\text{cm}} \Psi_{\text{rel}}$$

$$\hat{H} = \frac{-\hbar^2}{2m_N} \left(\frac{\partial^2}{\partial x_N^2} + \frac{\partial^2}{\partial y_N^2} + \frac{\partial^2}{\partial z_N^2} \right) + \frac{-\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) - \frac{e^2}{4\pi\epsilon_0 \delta} (\vec{r}_{ie} - \vec{r}_{in})$$

$$\frac{\partial}{\partial x_N} = \left(\frac{\partial x}{\partial x_N} \right)_{\text{constant}} \frac{\partial}{\partial x} + \left(\frac{\partial x}{\partial x_N} \right)_{\text{not constant}} \frac{\partial}{\partial x}$$

$$\frac{\partial}{\partial x_e} = \left(\frac{\partial x}{\partial x_e} \right)_{\text{constant}} \frac{\partial}{\partial x} + \left(\frac{\partial x}{\partial x_e} \right)_{\text{not constant}} \frac{\partial}{\partial x}$$

$$\therefore \frac{\partial}{\partial x} = \left(\frac{m_e}{m_e + m_N} \right) \frac{\partial}{\partial x_N} + \left(\frac{m_N}{m_e + m_N} \right) \frac{\partial}{\partial x_e}$$

[Ψ continuing ①]

$$E \Psi_{\text{cm}} \Psi_{\text{rel}} = \left[\Psi_{\text{cm}} \left(\frac{-\hbar^2}{2(m_N + m_e)} \nabla_{\vec{r}_1}^2 \right) \Psi_{\text{cm}} - \Psi_{\text{cm}} \frac{\hbar^2}{2\mu} \nabla_{\vec{r}_1}^2 \Psi_{\text{cm}} - \Psi_{\text{cm}} \frac{e^2}{4\pi\epsilon_0 \delta} \Psi_{\text{cm}} \right] = E \Psi_{\text{cm}} \Psi_{\text{cm}}$$

i.e. Comparing,

$$\frac{-\hbar^2}{2(m_e + m_N)} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi_{\text{cm}} = E \Psi_{\text{cm}}$$

considering e^2 at origin

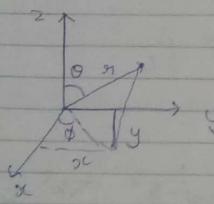
$$\therefore \left\{ \frac{-\hbar^2}{2\mu} \nabla_{\vec{r}_1}^2 - \frac{e^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}} \right\} \Psi_{\text{cm}} = E \Psi_{\text{cm}}$$

$$\frac{-\hbar^2}{2(m_e + m_N)} \nabla_{cm}^2 \Psi_{cm}(\vec{R}) = E_{cm} \Psi_{cm}(\vec{R})$$

$$\left[\frac{-\hbar^2}{2\mu} \nabla_{\vec{r}_1}^2 - \frac{e^2}{4\pi\epsilon_0 r_1} \right] \Psi_{nm}(\vec{r}_1) = E_{nm} \Psi_{nm}(\vec{r}_1)$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$(x, y, z) \rightarrow (r_1, \theta, \phi)$$



$$z = r_1 \cos \theta$$

$$x = r_1 \sin \theta \cos \phi$$

$$y = r_1 \sin \theta \sin \phi$$

$$r_1 \rightarrow (0, \infty)$$

$$\theta \rightarrow (0, \pi)$$

$$\phi \rightarrow (0, 2\pi)$$

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r_1} \times \frac{\partial r_1}{\partial x} + \frac{\partial}{\partial \theta} \times \frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \phi} \times \frac{\partial \phi}{\partial x}$$

$$\left[\frac{-\hbar^2}{2\mu} \left\{ \frac{1}{r_1^2} \frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1^2 \sin \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{1}{r_1^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} - \frac{e^2}{4\pi\epsilon_0 r_1} \right] \Psi = E \Psi(r_1, \theta, \phi)$$

$$\Psi(r_1, \theta, \phi) = R(r_1) \Phi(\phi) \Theta(\theta)$$

$$\frac{-\hbar^2}{2\mu} \left\{ \frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1^2} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{1}{r_1^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} R(r_1) \Phi(\phi) \Theta(\theta) + \frac{R(r_1) \Phi(\phi) \Theta(\theta)}{4\pi\epsilon_0 r_1} = E R(r_1) \Phi(\phi) \Theta(\theta)$$

$$\frac{-\hbar^2}{2\mu} \left[\frac{1}{R(r_1)r_1^2} \frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1^2 \sin \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{1}{r_1^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Phi(\phi) \Theta(\theta) = E \Phi(\phi) \Theta(\theta)$$

$$\frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = -m^2$$

$$\left[\frac{-\hbar^2}{2\mu} \left\{ \frac{1}{R(r_1)r_1^2} \frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1^2 \sin \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{1}{r_1^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} - \frac{m^2}{r_1^2 \sin^2 \theta} \right] \Theta(\theta) = E \Theta(\theta)$$

$$\therefore \frac{1}{\sin \theta} \frac{\partial \sin \theta}{\partial \theta} \frac{\partial \theta}{\partial \theta} - \frac{m^2}{\sin^2 \theta} = \text{constant} = -\beta$$

$$\frac{-\hbar^2}{2\mu} \left[\frac{1}{R(r_1)r_1^2} \frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1^2 \sin \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{1}{r_1^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} - \beta \right] R(r_1) = E R(r_1)$$

$$\frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = -m^2$$

$$\Psi(x, y, z) = R(r_1) \Theta(\theta) \Phi(\phi)$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi^* \Psi \, dx dy dz = 1$$

$$\therefore \int_0^\infty R(r_1)^* R(r_1) r_1^2 dr_1 \int_0^\pi \Theta(\theta)^* \Theta(\theta) \sin \theta d\theta \int_0^{2\pi} \Phi(\phi)^* \Phi(\phi) d\phi = 1$$

$$\psi = R_m(\theta) \Theta_m(\theta) \phi_m(\phi)$$

$$\phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m = 0, \pm 1, \pm 2$$

$$\phi_{(0)} = A e^{im\phi}$$

$$R_m(\theta) = \sum_{j=0}^{n-p-1} b_j \sin^j \theta$$

$$b_{j+1} = \frac{2z}{n_q} \left(\frac{\sin^{j+\ell+1}\theta}{(j+1)(j+2\ell+2)} \right) b_j$$

$$\phi_{(0)} = A \cos m\phi$$

$$m = 0, \pm 1, \pm 2$$

$$\phi_{(0)} = A \cos m\phi$$

$$\Theta_m(\theta) = \int \frac{(2\ell+1)(\ell-m)!}{2} \frac{1}{(\ell+m)!} [N-1 \geq \ell]$$

$$\int_0^{2\pi} \phi^{*\ell} \phi d\phi = 1$$

$$\int_0^{2\pi} A \phi^{im\phi} A \phi^{im\phi} = 1$$

$$\rho_\ell^m(z) = \frac{1}{2^\ell \ell!} (1-z^2)^{1m/2} \frac{d^{\ell+m}}{dz^{\ell+m}} (z^{\ell+m})$$

$z \rightarrow \text{not atomic numbers}$

$$\psi_{100} \Rightarrow \psi_{nm}$$

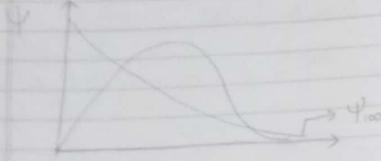
$$\phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$\phi_{(0)} = A \cos m\phi$$

$$\int_0^{2\pi} A \cos m\phi d\phi = 1$$

$$A = \frac{1}{\sqrt{\pi}}$$

$$\phi = \frac{1}{\sqrt{\pi}} \cos m\phi$$



$$|\Psi_{100}|^2 \propto 4\pi r^2 dr$$

$$\left(\frac{1}{a_0}\right)^3 e^{-2r/a_0} \propto \frac{1}{r^2} \propto 4\pi r^2 dr$$

↳ Radial distribution function

$$l=1, m=0$$

(n)

$$\Theta_{100} = \sqrt{(2l+1)!} P_1^0(z)$$

$$P_1^0(z) = \frac{1}{2!} (1-z^2)^0 \frac{d}{dz} (z^2 - 1)$$

$z \rightarrow \cos \theta$

$$\begin{array}{l} n=1 \\ l=0 \\ m=0 \end{array}$$

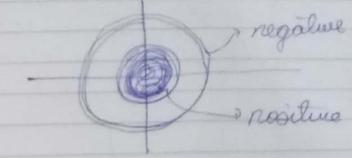
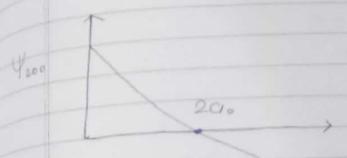
$$\begin{array}{l} n=2 \\ l=1, 0 \\ m=\pm 1, 0 \end{array}$$

$$\Psi_{100} = \Psi_{1s}$$

$$\Psi_{100} = R_{10}(r_1) \Theta_{100}(\theta) \Phi_{10}(\phi)$$

$$\Psi_{200} = R_{20}(r_1) \Theta_{00}(\theta) \Phi_{00}(\phi) \rightarrow Y_{00}(0, \phi)$$

$$= \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r_1}{a_0}\right) e^{-r_1/2a_0}$$

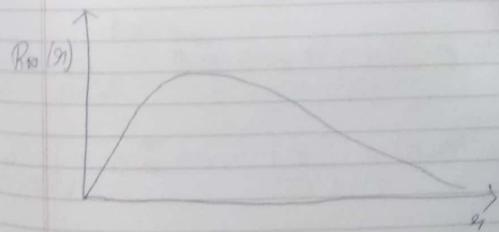


$$\text{Radial distribution} = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r_1}{a_0}\right)^2 e^{-r_1/2a_0} \times 4\pi r^2 dr$$

$$\Psi_{210} = R_{21}(r_1) \Theta_{10}(\theta) \Phi_{10}(\phi) \rightarrow Y_{10}(0, \phi)$$

$$\downarrow \\ Y_{10}(0, \phi) = \cos \theta$$

$$\Psi_{210} = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r_1}{a_0} e^{-r_1/2a_0} \cos \theta$$



Classified
 Date _____
 Page _____

$$\Theta \cos\theta$$

$$0 \quad 1$$

$$30^\circ \quad 0.85$$

$$45^\circ \quad 0.70$$

$$60^\circ \quad 0.5$$

$$90^\circ \quad 0$$

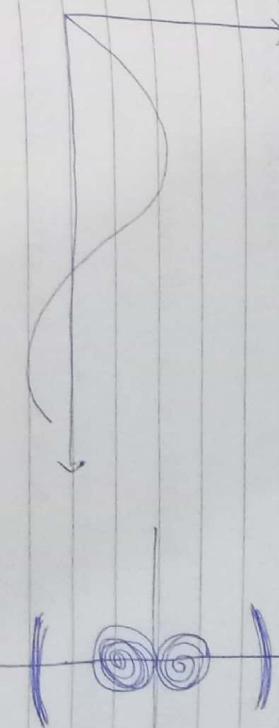
$$120^\circ \quad -0.5$$

$$135^\circ \quad -0.7$$

$$150^\circ \quad -0.85$$

$$180^\circ \quad -1$$

R_{in}



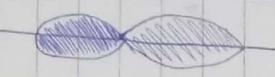
$$Z = 4 \cos\theta$$

$$x = g \sin\theta \cos\phi$$

$$\Psi_{310} = \frac{1}{8\sqrt{2}} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{1}{a_0} \right)^{3/2} \left(\frac{6g_1 - g_2^2}{a_0^2} \right) e^{-g_1/3a_0} \cos\theta$$

$$\Psi_{21\pm 1} = R_{21} g_1(\Theta_{1\pm 1}) \phi_{\pm 1}(\phi)$$

$$Y_{0m}(\theta, \phi)$$



constant evaluated
Ket basis applied

$$\Psi_{1+1}(\theta, \phi) = \left(\frac{3}{8\pi} \right)^{1/2} \sin\theta e^{i\phi}$$

$$\Psi_{1-1}(\theta, \phi) = \left(\frac{3}{8\pi} \right)^{1/2} \sin\theta e^{-i\phi}$$

$$P_x \rightarrow Y_{1+1}(\theta, \phi) = \left(\frac{3}{4\pi} \right)^{1/2} \sin\theta \cos\phi = \sqrt{\frac{3}{4\pi}} \frac{x}{2}$$

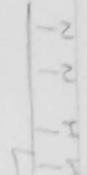
$$P_y \rightarrow Y_{1-1}(\theta, \phi) = \left(\frac{3}{4\pi} \right)^{1/2} \sin\theta \sin\phi = \sqrt{\frac{3}{4\pi}} \frac{y}{2}$$

Catalysis

Heterogeneous :-

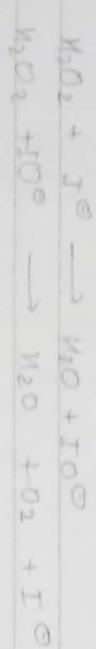
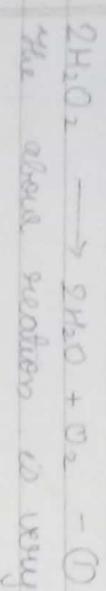


on iron catalyst



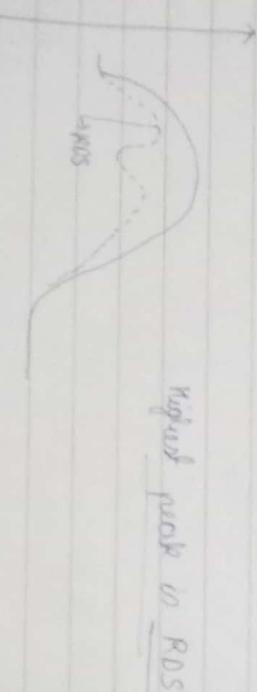
iron catalyst

Homogeneous equation :- $R = A e^{-E_a/RT}$



\Rightarrow For a catalyst to work, firstly, the reaction should be thermodynamically feasible ($\Delta H < 0$)

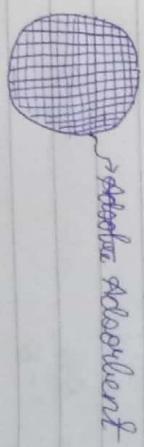
For reaction ①,



Langmuir Adsorption isotherm

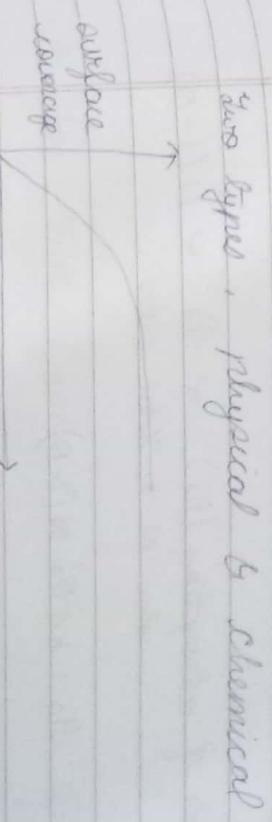
$$\text{Fractional coverage } (\theta) = \frac{\text{number of occupied sites}}{\text{Total number of sites available}} = \frac{x}{x_{\max}}$$

inhibitors slows down the reaction



while heterogeneous is in which all are not in same place.

Adsorption \rightarrow surface phenomena.



Homogeneous catalyst

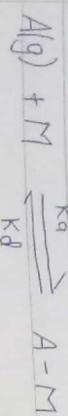
If the reactant, product, catalyst are all in same phase, then it is known as homogeneous catalyst



$$K\bar{P}_A - K\bar{P}_A \theta = 0$$

⇒ Assumptions taken for Langmuir assumption

- 1 Only monolayer
- 2 All are equivalent sites
- 3 No - adsorbate - adsorbate interaction
- 4 Adsorbate case immobile
- 5 Site independent

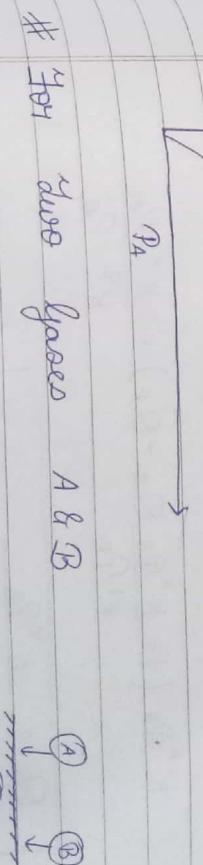


$k_a \rightarrow$ K for adsorption

$K_d \rightarrow K$ for desorption

$$K = \frac{k_a}{K_d} \quad (\text{for reaction})$$

∴ Rate of adsorption ($\dot{\gamma}_a$) $\propto P_A \propto N(1-\theta)$
where $N \rightarrow$ Total sites



For two gases A & B



Rate of desorption ($\dot{\gamma}_d$) $\propto N\theta$

$$\dot{\gamma}_{dA} = K_d N \theta$$

∴ At equilibrium, $\dot{\gamma}_a = \dot{\gamma}_{dA}$

$$\therefore P_A K_a / (1-\theta) = K_d N \theta$$

$$\frac{K_a}{K_d} = K = \frac{\theta P_A}{1-\theta}$$

$$\dot{\gamma}_a^A = \dot{\gamma}_{dA}^A$$

∴ At equilibrium,

$$K_a^A = K_d^A N \theta_A$$

when $K\bar{P}_A$ is very large, $\theta = 1$
when $K\bar{P}_A$ is very small, $\theta = K\bar{P}_A$

$$\boxed{\theta = \frac{K\bar{P}_A}{1 + K\bar{P}_A}}$$

$$P_A K^A (1 - \Theta_A - \Theta_B) = K^A \Theta_A$$

$$K^A P_A (1 - \Theta_A - \Theta_B) = \Theta_A$$

$$K^A P_A (1 - \Theta_A - \Theta_B) = \Theta_A \quad \text{--- (1)}$$

$$K^B P_B (1 - \Theta_A - \Theta_B) = \Theta_B \quad \text{--- (2)}$$

$\therefore (1) \div (2)$

$$\frac{K^A P_A}{K^B P_B} = \frac{\Theta_A}{\Theta_B} \quad \text{--- (3)}$$

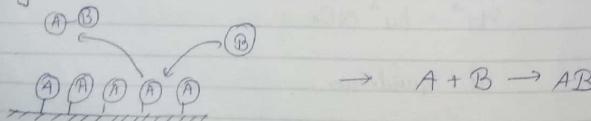
Putting (3) in (1)

$$K^A P_A (1 - \frac{K^A P_A}{K^B P_B} \Theta_B - \Theta_B) = \frac{K^A}{K^B} \frac{P_A}{P_B}$$

$$\Theta_B = \frac{K^B P_B}{1 + K^A P_A + K^B P_B}$$

Langmuir - Hinshelwood mechanism

Eley - Rideal Mechanism

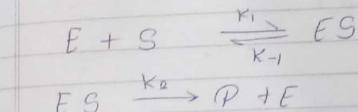
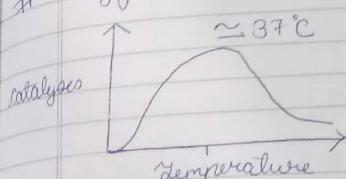


$$\Theta_A = \frac{K^A P_A}{1 + K^A P_A}$$

$$\therefore \text{Rate of Reaction} = K_2 P_B \Theta_A = K_2 P_B \times \frac{K^A P_A}{1 + K^A P_A}$$

$$= K_2 \frac{K^A P_B P_A}{1 + K^A P_A}$$

Enzyme catalysis



Michaelis menten equation

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_{-1}[ES] - k_2[ES] = 0$$

$$\boxed{\frac{d[ES]}{dt} = 0}$$

Steady state approximation

$$\therefore [ES] = \frac{k_1 [E][S]}{k_{-1} + k_2}$$

$$[E]_0 \rightarrow [E_T] = [E] + [ES]$$

$$[E] = [E_T] - [ES]$$

$$[ES] = \frac{[E_T][S]}{K_1 + K_2 + [S]}$$

$$\frac{d[E]}{dt} = \frac{K_m - [E_T][S]}{K_1 + K_2 + [S]}$$

$$\text{Let } \boxed{K_m = \frac{K_1 + K_2}{K_1}}$$

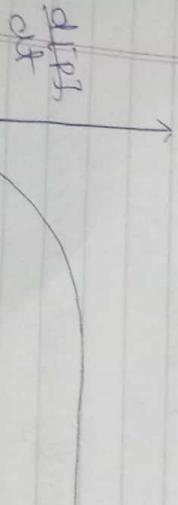
$$\frac{d[E]}{dt} = K_2 \frac{[E_T][S]}{K_m + [S]}$$

$$\frac{d[P]}{dt} = K_2 \frac{[E_T][S]}{K_m + [S]}$$

$$\frac{d[P]}{dt} = \frac{K_2 [E_T][S]}{K_m + [S]}$$

$$\cancel{\frac{d[S]}{dt} = K_2 [E_T]}$$

$$\frac{d[S]}{dt} = K_2 [E_T]$$

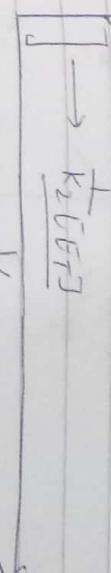
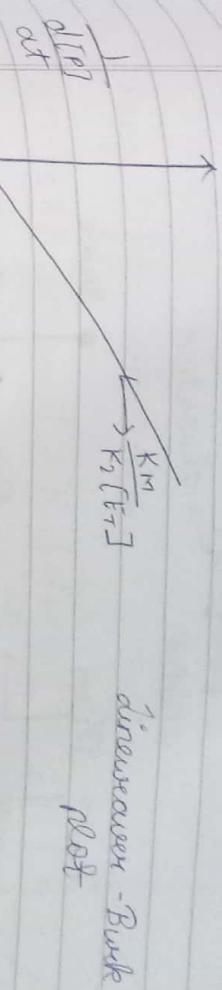


$$\cancel{\frac{d[S]}{dt} = K_2 [E_T]}$$

$$K_{cat} = K_2 = \frac{V_{max}}{[E_T]}$$

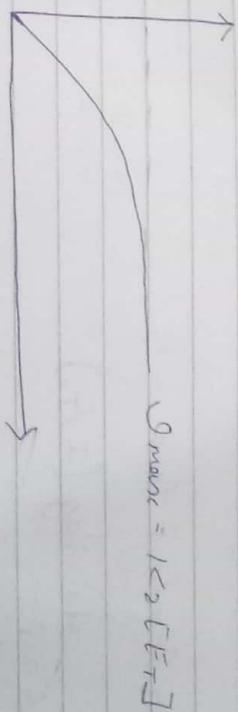
$$n = K_{cat} = \frac{K_2 K_1}{K_1 + K_2} = K_1$$

$$(K_1 \text{ is very small})$$



\Rightarrow turnover number (K_{cat})

$$\frac{d[P]}{dt} = K_2 [ES] = K_2 \frac{[E_T][S]}{K_m + [S]} = \frac{V_{max}[S]}{V_{max} + K_m}$$



$$V_{max} = K_2 [E_T]$$

$$K_{cat} = K_2 = \frac{V_{max}}{[E_T]}$$

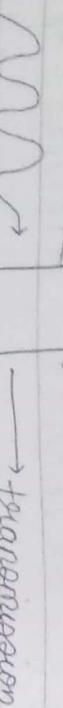
Spectroscopy

scattering (all direction)

$$\rightarrow h\nu$$

$$h\nu = E_2 - E_1$$

Resonance condition



absorbed
reflected

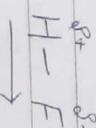
$$\lambda_{\text{max}} \Rightarrow 485 \text{ nm}$$

#

NMR	ESR	Microwave	IR	Visible	UV	X	γ
Nuclear magnetic resonance	Electronic spin resonance						

Rotational Spectroscopy [Microwave spectroscopy]

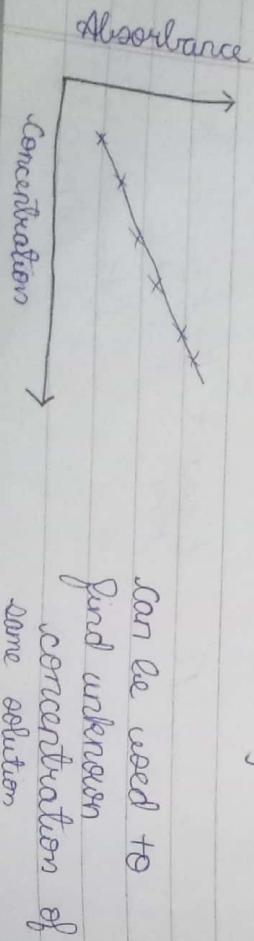
Vibole moment \Rightarrow



Magnitude same but directions different

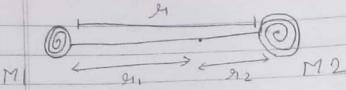
when frequency of rotation = frequency of light

then Resonance condition



Can be used to

find unknown concentration of some solution



$$I = m_1\omega_1^2 + m_2\omega_2^2 \rightarrow \text{moment of inertia about COM}$$

$$m_1\omega_1 = m_2\omega_2 \rightarrow \text{COM at rest}$$

$$I = m_1\omega_1^2 + m_2\omega_2^2$$

$$= m_2\omega_2\omega_1 + m_1\omega_1\omega_2 = \omega_1\omega_2(m_1 + m_2)$$

$$m_1\omega_1 = m_2\omega_2$$

$$m_1\omega_1 = m_2(\omega_1 - \omega_2)$$

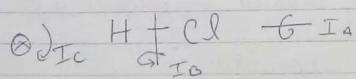
$$m_1\omega_1 = m_2\omega_1 - m_2\omega_1$$

$$\omega_1 = \frac{m_2\omega_1}{m_1 + m_2}$$

$$\omega_2 = \frac{m_1\omega_1}{m_1 + m_2}$$

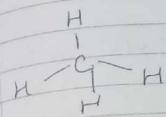
$$I = m_1\omega_1\omega_2(m_1 + m_2) = \frac{m_1m_2\omega_1^2(m_1 + m_2)}{(m_1 + m_2)} \\ = \underline{\underline{M\omega_1^2}}$$

Linear molecule



$$\therefore \underline{\underline{I_a = 0}} \quad \underline{\underline{I_b = I_c}}$$

Spherical Top



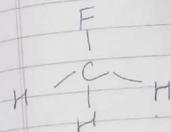
$$I_a = I_b = I_c \neq 0$$

Symmetric Top

$$I_b = I_c \neq I_a$$

$$I_a \neq 0$$

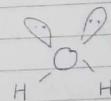
Cases :- $I_b = I_c > I_a$ (Prolate)



$$I_b = I_c < I_a$$
 (Oblate)

Asymmetric Top

$$I_a \neq I_b \neq I_c$$



Rigid Rotor

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1) \quad \text{Toules}$$

$J \rightarrow$ Rotation quantum number

The above is Energy but energy can also be written in wave number form

$$E_J = \frac{E_I}{hc} = \left[\frac{I^2}{8\pi^2 I C K} \right] J(J+1) \text{ cm}^{-1}$$

\Rightarrow But if doesn't consider it has rigid posture, the bond length would change

$$e_J = B(J)(J+1) \text{ cm}^{-1}$$

$$E_0 = 0$$

$$Rudle^{\circ} - \Delta T = \pm 1$$

$$F = -kx \rightarrow force_{constant\ (spring)}$$

Sentrifugal distortion constant

$$\frac{N_e}{N_g} = e^{-\left(\frac{E_J}{kT}\right)}$$

Population $\propto (2J+1) e^{-E_J/kT}$

It will be changed if isotopes are used

$$T = \sqrt{\frac{K_T}{2\hbar c B}} - \frac{1}{2}$$

If B is given how we can find bond length

$$B = \frac{h^2}{8\pi^2 IC} \quad . \quad I = \mu_0 A^2$$

Linear Rotation :-

$$\Rightarrow 3N - 5 \rightarrow \text{Vibrational}$$

$$E_J = B J(J+1) \text{ cm}^{-1}$$

$$\beta = \frac{h}{8\pi c} T = \alpha g c^2$$

Non-linear rotation \Rightarrow 3

vibrational $\Rightarrow 3N-3-3 \Rightarrow 3N-6$

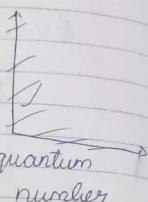
For vibrational Energy (IR) (Infrared radiation)
automatically microwave before
rotation automatically

$$E_v = \left(v + \frac{1}{2}\right) h\nu \quad \text{Joules}$$

$$E_v = \frac{E_e}{hc} = \left(v + \frac{1}{2}\right) \text{J cm}^{-1}$$

$$\left|_{\text{vibres}} \quad F=-Kx\right.$$

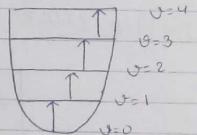
$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$



$$E_0 = \frac{1}{2} h\nu$$

$$E_1 = \frac{3}{2} h\nu$$

$$E_2 = \frac{5}{2} h\nu$$



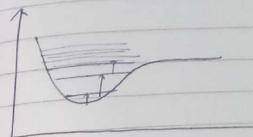
Assumption :- Bond will never broke even when large force is applied

$$E_v = \left(v + \frac{1}{2}\right) \bar{w}_e - \left(v + \frac{1}{2}\right)^2 \bar{w}_e \alpha_e$$

$$E_v = \bar{w}_e \left(1 - \alpha_e \left(v + \frac{1}{2}\right)\right) \left(v + \frac{1}{2}\right)$$

$$AHO \Rightarrow E_v = \bar{w}_e \left(1 - \alpha_e \left(v + \frac{1}{2}\right)\right) \left(v + \frac{1}{2}\right)$$

$$HO \Rightarrow E_v = \bar{w}_e \left(v + \frac{1}{2}\right)$$



0 \rightarrow 1 fundamental
1 \rightarrow 2 first overtone
2 \rightarrow 3 second overtone

Hot band : \rightarrow Transition from $v=1, 2, 3, \dots$ to higher