D.N.R.COLLEGE (AUTONOMOUS): BHIMAVARM
DEPARTMENT OF PG CHEMISTRY

GENERAL CHEMISTRY –I

I SEMESTER
Presented By
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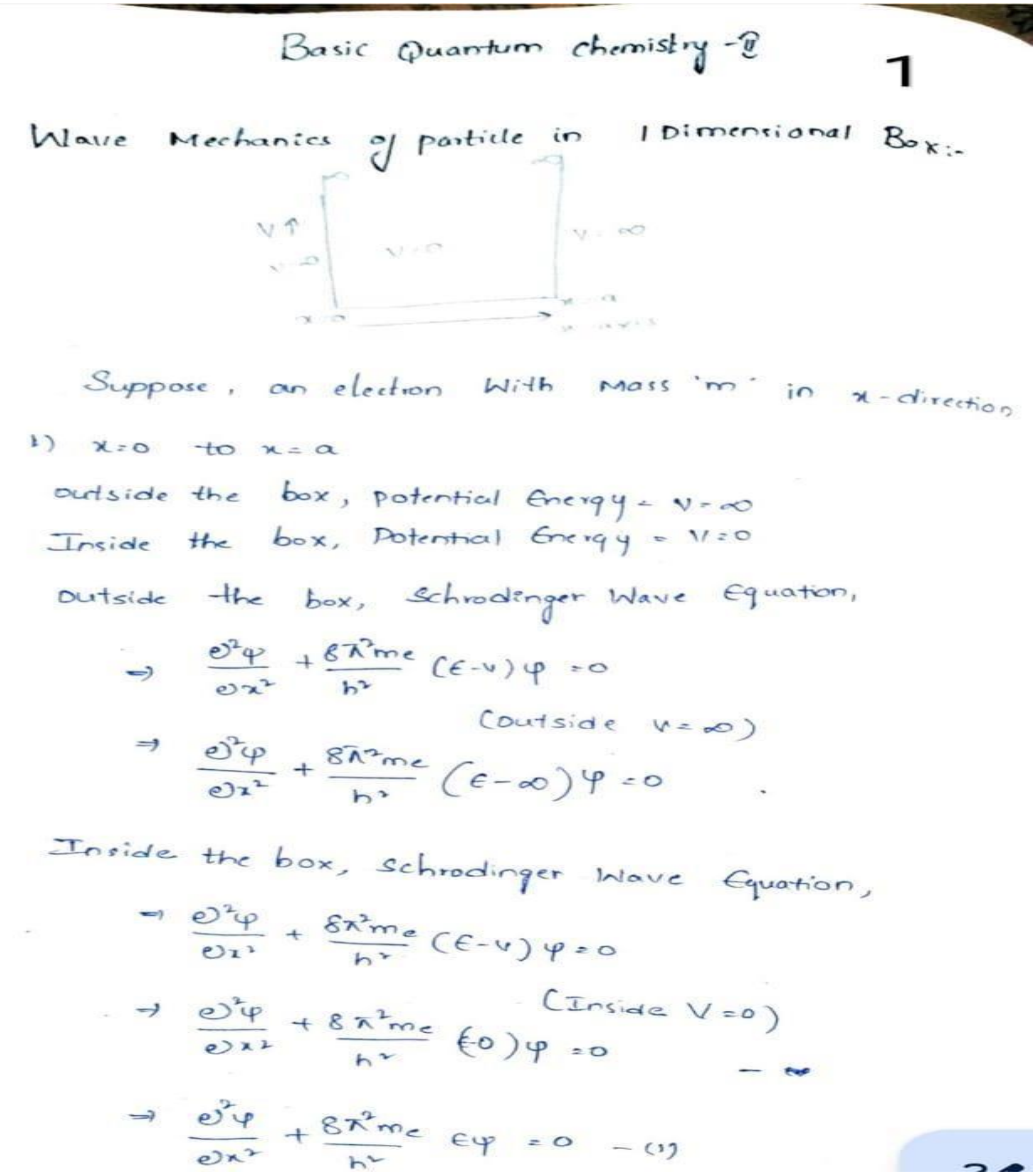
Unit 1



Basic Quantum chemistry -Ⅱ

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Wave Mechanics of particle in 1 Dimensional Box:-

Suppose, an election With Mass 'm' in x-direction

1) $x=0$ to $x=a$

outside the box, potential Energy = $V=\infty$

Inside the box, Potential Energy = $V=0$

Outside the box, Schrodinger Wave Equation,

$$\Rightarrow \frac{\partial^2\varphi}{\partial x^2} + \frac{8\pi^2 me}{h^2}(E-V)\varphi = 0$$

(Outside $V=\infty$)

$$\Rightarrow \frac{\partial^2\varphi}{\partial x^2} + \frac{8\pi^2 me}{h^2}(E-\infty)\varphi = 0$$

Inside the box, Schrodinger Wave Equation,

$$\Rightarrow \frac{\partial^2\varphi}{\partial x^2} + \frac{8\pi^2 me}{h^2}(E-V)\varphi = 0$$

(Inside $V=0$)

$$\rightarrow \frac{\partial^2\varphi}{\partial x^2} + \frac{8\pi^2 me}{h^2}(E-0)\varphi = 0$$

$$\Rightarrow \frac{\partial^2\varphi}{\partial x^2} + \frac{8\pi^2 me}{h^2}E\varphi = 0 \quad -(1)$$

$$\rightarrow \frac{\partial^2\psi}{\partial x^2} + K^2\psi = 0 \quad \left[K^2 = \frac{8\pi^2 m_e}{h^2}\epsilon\right] \quad -(2)$$

~~[illegible]~~

$$\psi(x) = C\sin Kx + D\cos Kx \quad \text{———} \quad (3)$$

C, D = orbitary Constants

According to law of Quantum Mechanics,

We can apply the boundary Condition and calculate the Values of C & D.

Condition-1:-

$\psi(x) = 0$ & at $x = 0$

$\psi(x) = C\sin Kx + D\cos Kx$

$0 = C\sin K(0) + D\cos K(0)$

$0 = 0 + D$ $(\because \cos 0 = 1, \sin 0 = 0)$

$\rightarrow \boxed{D = 0}$

Condition-2:-

$\psi(x) = 0$ at $x = a$

$\psi(x) = C\sin Kx + D\cos Kx$

$0 = C\sin K(a) + D\cos K(a)$

$0 = C\sin K(a) + 0$ (Condition - 1 D = 0)

$C\sin Ka = 0$

$$Ka = n\pi$$

$$\boxed{k = n\pi/a}$$

From equation (2),

$$k^2 = \frac{8\pi^2 m_e \epsilon}{h^2}$$

$$\Rightarrow \frac{n^2 \cancel{\pi^2}}{a^2} = \frac{8\cancel{\pi^2} m_e \epsilon}{h^2}$$

$$\Rightarrow \frac{n^2 h^2}{a^2} = 8 m_e \epsilon$$

$$\Rightarrow \boxed{\epsilon_n = \frac{n^2 h^2}{8a^2 m_e}}$$

If $n = 1$,

$$\epsilon_1 = \frac{h^2}{8a^2 m_e}$$

If $n = 2$,

$$\epsilon_2 = \frac{4h^2}{8a^2 m_e}$$

If $n = 3$,

$$\epsilon_3 = \frac{9h^2}{8a^2 m_e}$$

If $n = 4$,

$$\epsilon_4 = \frac{16h^2}{8a^2 m_e}$$

From equation (3),

$$\psi(x) = C \sin Kx + D \cos Kx$$

$$\psi(x) = C \sin Kx \quad (\because D = 0)$$

$$\psi_n(x) = C \sin Kx$$

Sub K value,

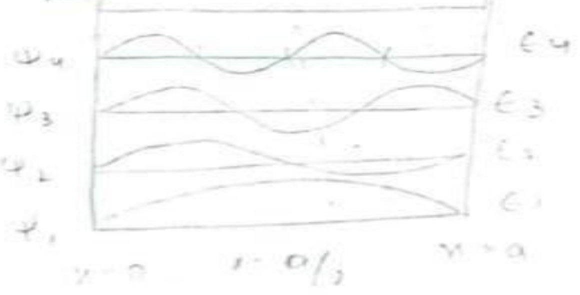
$$\psi_n(x) = C \sin \left[{}^{n\pi}/_{a} \right] x$$

If $n = 1$, $\psi_{1x} = C \sin {}^{\pi}/_{a}\, x$

If $n = 2$, $\psi_{2x} = C \sin {}^{2\pi}/_{a}\, x$

If $n = 3$,
$\psi_{3x} = C \sin {}^{3\pi}/_{a}\, x$

If $n = 4$,
$\psi_{4x} = C \sin {}^{4\pi}/_{a}\, x$



$\psi_n = n-1$ (The No. of Nodes depends on level of wave function)

If $n = 4$

$\psi_4 = 4-1$
$= 3$ Nodes.

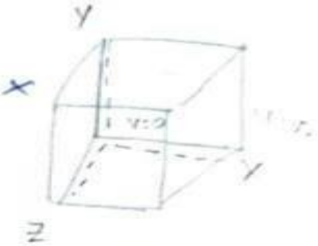
Increase in No. of Nodes the Wave length.

Wave mechanics of a Particle in 3D Box:-

1) Suppose an $e^{\ominus}$ moving in 3D box along X, Y, Z axis.

→ The Potential Energy of an $e^{\ominus}$ within the box is zero along X, Y, Z axis.

V = 0 → Inside the box



→ outside the box, V = ∞

→ The Schrodinger Wave Equation, along X, Y, Z axis is,

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

Outside the box,

the Schrodinger Wave Equation is given by,

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-\infty)\psi_{(x,y,z)}=0 \quad -($$

⇒ From this eqn it is clear that, the $e^{\ominus}$ is not fixed outside the box

Inside the box,

Schrodinger Wave Equation is given by.

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

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

The above equation is solved by,

let us consider,

$$\varphi = X(x), Y(y), Z(z) \quad - (3)$$

$$\boxed{\varphi = xyz - (4)}$$

sub Eq^n (4) in Eq^n (2), we get

$$\rightarrow \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2} + \frac{8\pi^2 m}{h^2} E\,\psi_{(x,y,z)} = 0$$

$$\rightarrow \frac{\partial^2 xyz}{\partial x^2} + \frac{\partial^2 xyz}{\partial y^2} + \frac{\partial^2 xyz}{\partial z^2} + \frac{8\pi^2 m}{h^2} E\,\psi_{(x,y,z)} = 0$$

$$\rightarrow yz\frac{\partial^2 x}{\partial x^2} + xz\frac{\partial^2 y}{\partial y^2} + xy\frac{\partial^2 z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E(x,y,z) = 0$$

dividing with xyz,

$$\rightarrow \frac{yz}{xyz}\frac{\partial^2 x}{\partial x^2} + \frac{xz}{xyz}\frac{\partial^2 y}{\partial y^2} + \frac{xy}{xyz}\frac{\partial^2 z}{\partial z^2} + \frac{8\pi^2 m}{h^2}\,\cancel{\frac{E(x,y,z)}{x,y,z}} = 0$$

$$\rightarrow \frac{1}{x}\frac{\partial^2 x}{\partial x^2} + \frac{1}{y}\frac{\partial^2 y}{\partial y^2} + \frac{1}{z}\frac{\partial^2 z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E = 0.$$

We know that,

$$\boxed{E = E_x + E_y + E_z}$$

Sub E value in above Eq^n,

$$\rightarrow \frac{1}{x}\frac{\partial^2 x}{\partial x^2} + \frac{1}{y}\frac{\partial^2 y}{\partial y^2} + \frac{1}{z}\frac{\partial^2 z}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E_x + E_y + E$$

$$\rightarrow {}^1/_x \frac{\partial^2 x}{\partial x^2} + {}^1/_y \frac{\partial^2 y}{\partial y^2} + {}^1/_z \frac{\partial^2 z}{\partial z^2} = -\frac{8\pi^2 m}{h^2}(E_x + E_y$$

$$\rightarrow {}^1/_x \frac{\partial^2 x}{\partial x^2} + {}^1/_y \frac{\partial^2 y}{\partial y^2} + {}^1/_z \frac{\partial^2 z}{\partial z^2} = -\frac{8\pi^2 m}{h^2}E_x - \frac{8\pi^2 m}{h^2}E_y$$

Compare the values in the above eqn,

$$\rightarrow {}^1/_x \frac{\partial^2 x}{\partial x^2} = -\frac{8\pi^2 m}{h^2} E_x$$

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$$\rightarrow \frac{\partial^2 x}{\partial x^2} = -\frac{8\pi^2 m}{h^2} E_x \cdot x$$

$$\Rightarrow \frac{\partial^2 x}{\partial x^2} + \frac{8\pi^2 m}{h^2} E_x \cdot x = 0.$$

Similarly,

$$\frac{\partial^2 y}{\partial y^2} + \frac{8\pi^2 m}{h^2} E_y \cdot y = 0$$

$$\frac{\partial^2 z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E_z \cdot z = 0$$

Considering, $A\sin({}^{n\pi}/_a)x$,

$$X(x) = A\sin\left(\frac{n_x\pi}{a_x}\right)x$$

$$Y(y) = A\sin\left(\frac{n_y\pi}{a_y}\right)y$$

$$Z(z) = A\sin\left(\frac{n_z\pi}{a_z}\right)z$$

From eqn (3),

$$\psi = X(x) \cdot Y(y) \cdot Z(z)$$

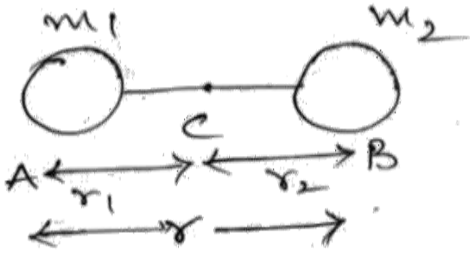
$$\Rightarrow \psi = A\sin\left(\frac{n_x\pi}{a_x}\right)x \cdot A\sin\left(\frac{n_y\pi}{a_y}\right)y \cdot$$

UNIT-II

BASIC QUANTUM CHEMISTRY-

→ Rigid rotator:-

- A mechanical model that is used to explain rotating systems.
- Consider a diatomic molecule which consists of two atoms A & B of mass m_1 and m_2.

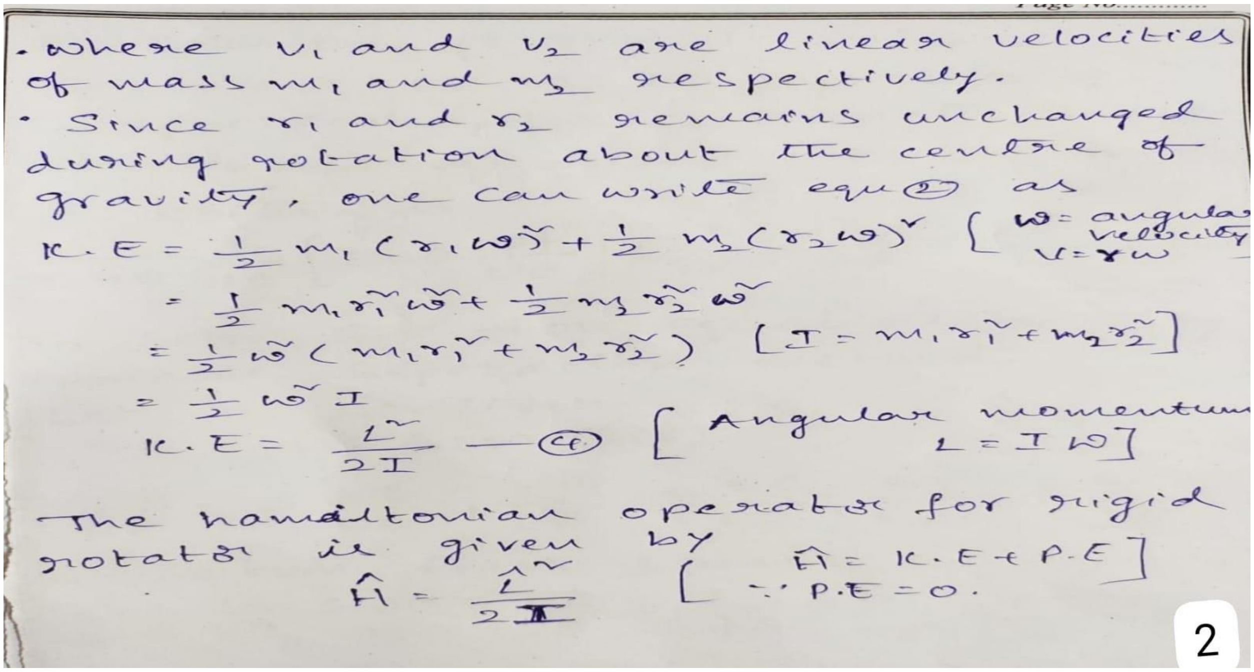


- The radius b/w A ~~to~~ C is "r_1" and C to B is "r_2".
- r is the distance b/w A and B.

$$m_1 r_1 = m_2 r_2 \qquad \text{——} \ ①$$
$$r = r_1 + r_2$$

The K.E of rigid rotator is

$$K.E = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \qquad \text{——} \ ②$$



• where v_1 and v_2 are linear velocities of mass m_1 and m_2 respectively.

• Since r_1 and r_2 remains unchanged during rotation about the centre of gravity, one can write equ ② as

$K.E = \frac{1}{2} m_1 (r_1\omega)^2 + \frac{1}{2} m_2 (r_2\omega)^2$ [ω = angular velocity $v = r\omega$

$= \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2$

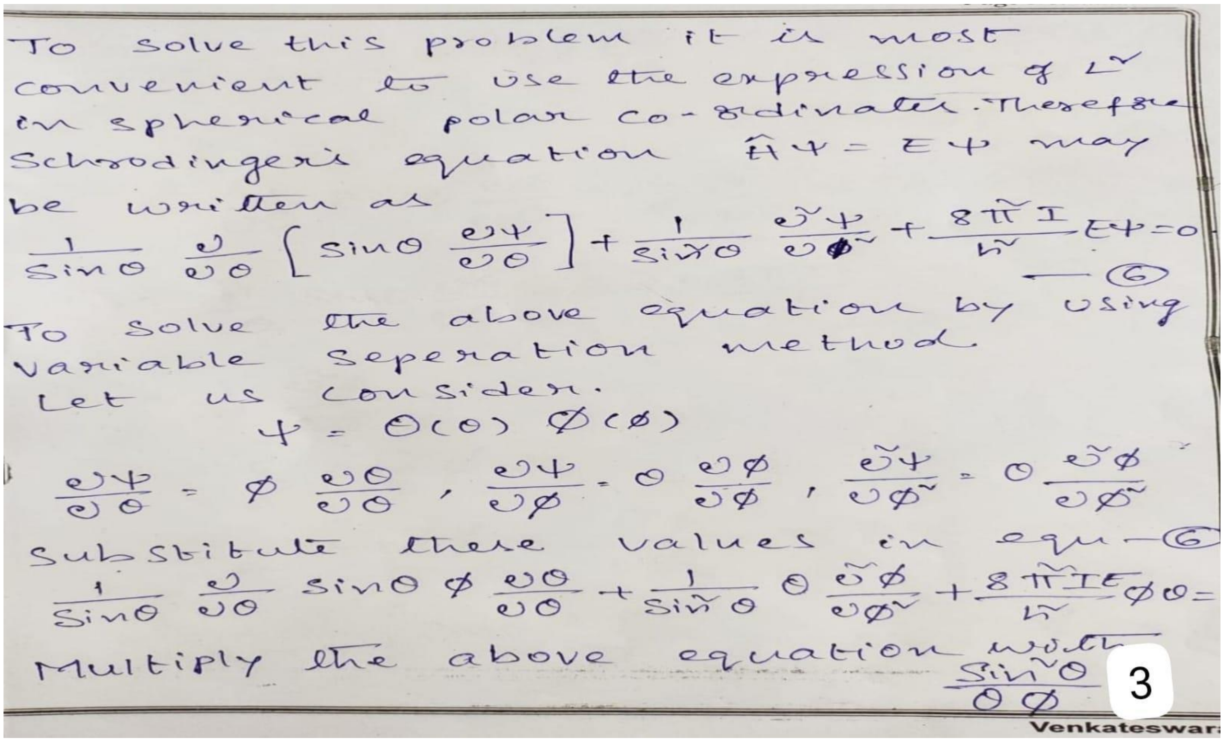
$= \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2)$ [$I = m_1 r_1^2 + m_2 r_2^2$]

$= \frac{1}{2} \omega^2 I$

$K.E = \frac{L^2}{2I}$ — ④ [Angular momentum $L = I\omega$]

The hamiltonian operator for rigid rotator is given by

$\hat{H} = \frac{\hat{L}^2}{2I}$ [$\hat{H} = K.E + P.E$]
∵ $P.E = 0$.



To solve this problem it is most convenient to use the expression of L^2 in spherical polar co-ordinates. Therefore Schrodinger's equation $\hat{H}\psi = E\psi$ may be written as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 I}{h^2}E\psi = 0 \quad ⑥$$

To solve the above equation by using variable seperation method.

Let us consider.

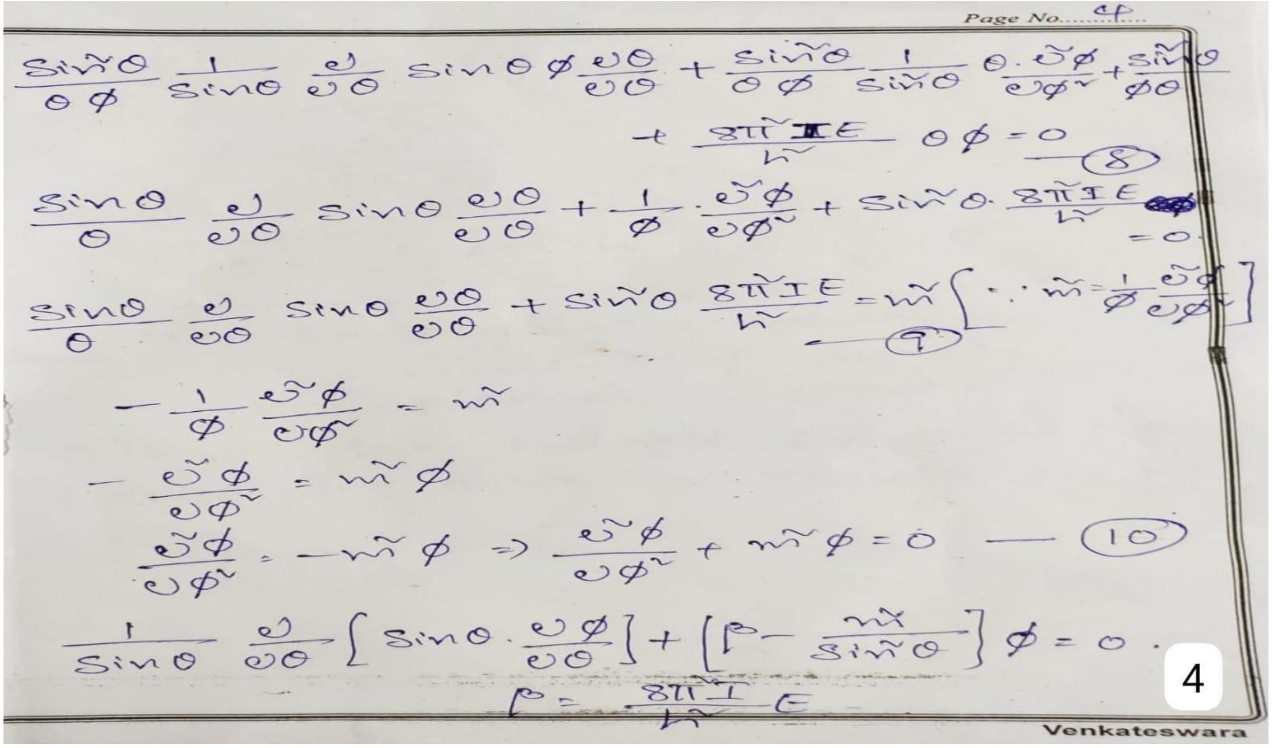
$$\psi = \Theta(\theta)\,\Phi(\phi)$$

$$\frac{\partial\psi}{\partial\theta} = \Phi\frac{\partial\Theta}{\partial\theta}, \quad \frac{\partial\psi}{\partial\phi} = \Theta\frac{\partial\Phi}{\partial\phi}, \quad \frac{\partial^2\psi}{\partial\phi^2} = \Theta\frac{\partial^2\Phi}{\partial\phi^2}$$

Substitute these values in equ-⑥

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\,\Phi\frac{\partial\Theta}{\partial\theta} + \frac{1}{\sin^2\theta}\Theta\frac{\partial^2\Phi}{\partial\phi^2} + \frac{8\pi^2 IE}{h^2}\Phi\Theta =$$

Multiply the above equation with $\frac{\sin^2\theta}{\Theta\Phi}$



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$$\frac{\sin^2\theta}{\Theta\phi}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\,\phi\frac{\partial\Theta}{\partial\theta}+\frac{\sin^2\theta}{\Theta\phi}\frac{1}{\sin^2\theta}\Theta\cdot\frac{\partial^2\phi}{\partial\phi^2}+\frac{\sin^2\theta}{\phi\Theta}$$

$$+\frac{8\pi^2 IE}{h^2}\Theta\phi=0 \quad —⑧$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}+\frac{1}{\phi}\cdot\frac{\partial^2\phi}{\partial\phi^2}+\sin^2\theta\cdot\frac{8\pi^2 IE}{h^2}=0$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}+\sin^2\theta\,\frac{8\pi^2 IE}{h^2}=m^2 \quad —⑨ \quad \left[\because m^2=\frac{1}{\phi}\frac{\partial^2\phi}{\partial\phi^2}\right]$$

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

$$-\frac{\partial^2\phi}{\partial\phi^2}=m^2\phi$$

$$\frac{\partial^2\phi}{\partial\phi^2}=-m^2\phi \Rightarrow \frac{\partial^2\phi}{\partial\phi^2}+m^2\phi=0 \quad —⑩$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\cdot\frac{\partial\phi}{\partial\theta}\right]+\left[\beta-\frac{m^2}{\sin^2\theta}\right]\phi=0.$$

$$\beta=\frac{8\pi^2 I}{h^2}E$$

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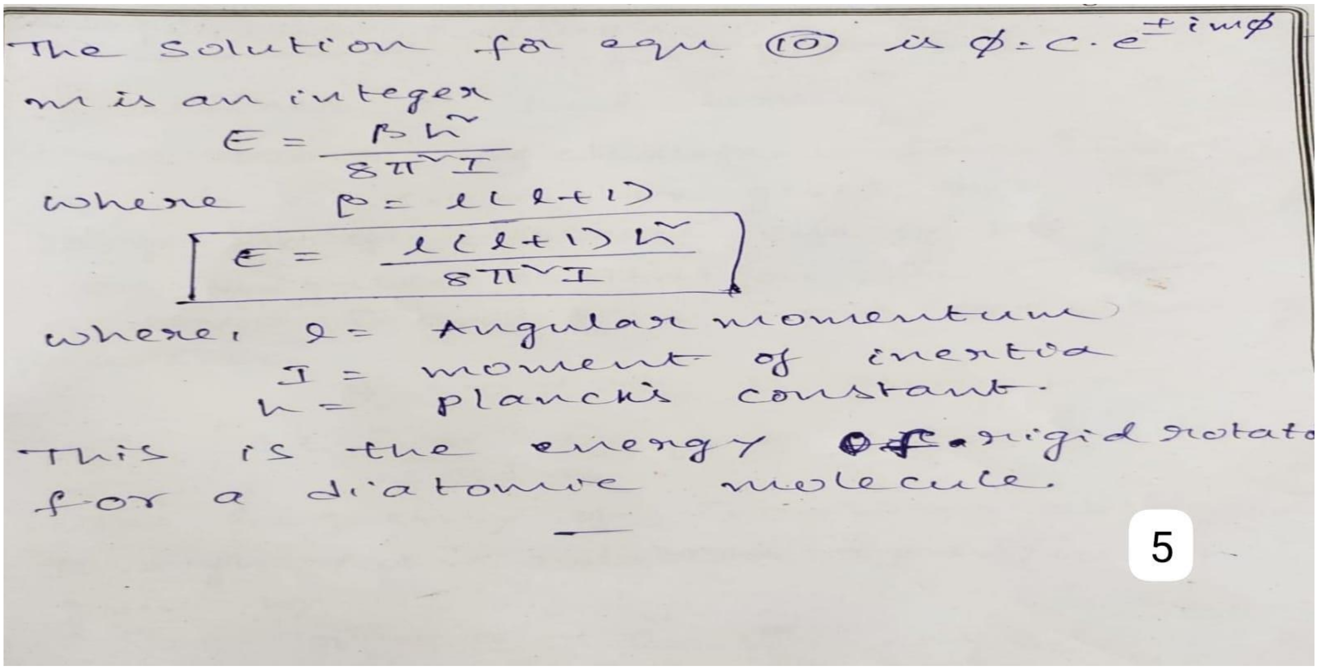

The solution for equ ⑩ is $\phi = C\cdot e^{\pm im\phi}$

m is an integer

$$E=\frac{\beta h^2}{8\pi^2 I}$$

where $\beta = l(l+1)$

$$\boxed{E=\frac{l(l+1)h^2}{8\pi^2 I}}$$

where, l = Angular momentum

I = moment of inertia

h = planck's constant.

This is the energy ~~Of~~ a rigid rotato

for a diatomic molecule.

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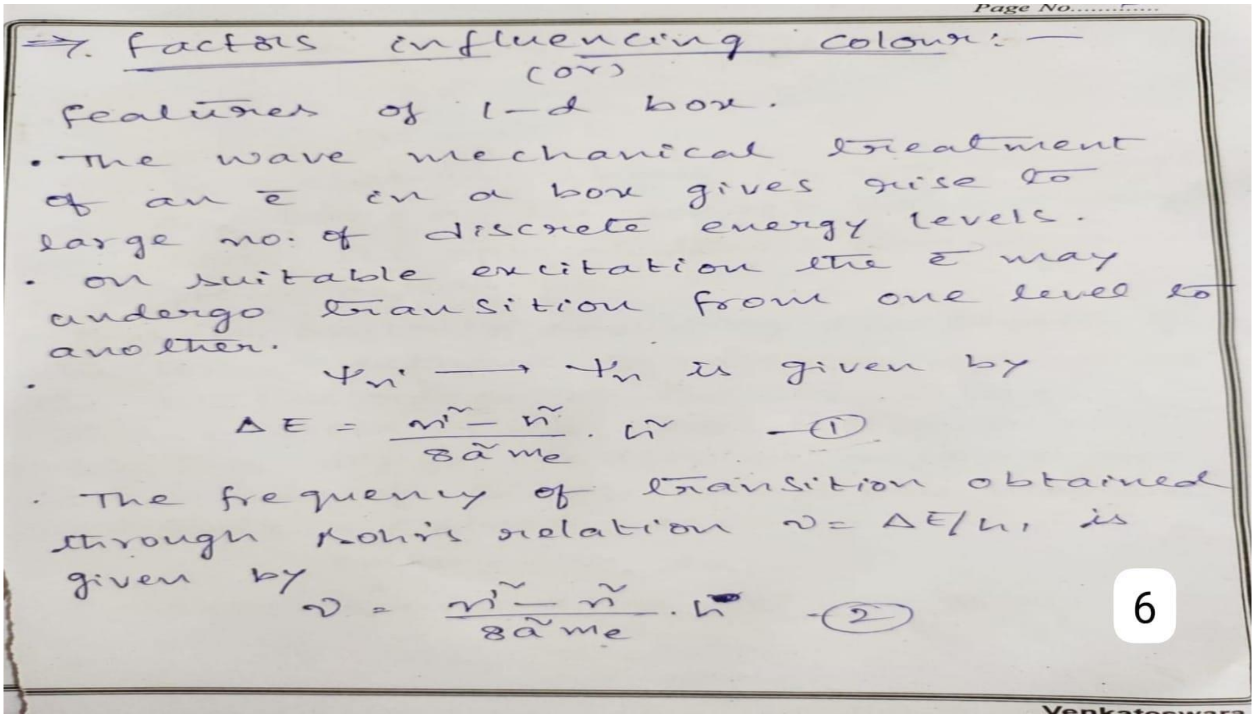

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⇒7. factors influencing colour: —

(or)

features of 1-d box.

- The wave mechanical treatment of an ē in a box gives rise to large no. of discrete energy levels.
- on suitable excitation the ē may undergo transition from one level to another.
- $\psi_{n'} \longrightarrow \psi_n$ is given by

$$\Delta E = \frac{n'^2 - n^2}{8a^2 m_e} \cdot h^2 \quad -①$$

- The frequency of transition obtained through Bohr's relation $\nu = \Delta E/h$, is given by

$$\nu = \frac{n'^2 - n^2}{8a^2 m_e} \cdot h \quad -②$$

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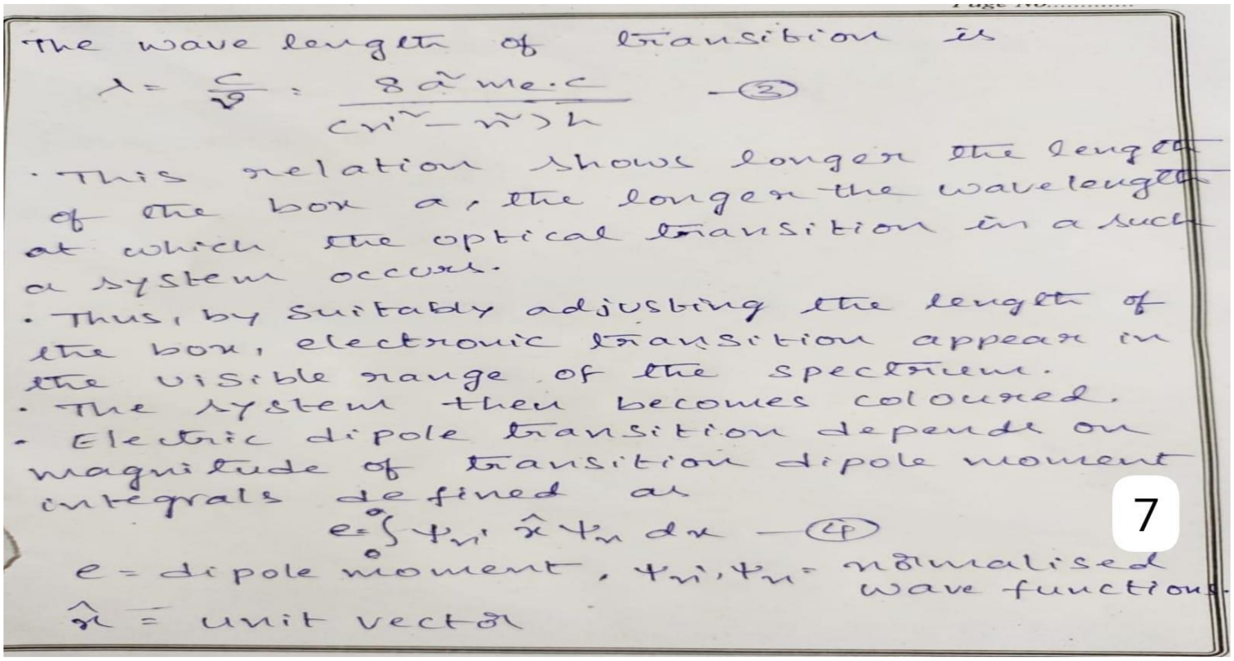

The wave length of transition is

$$\lambda = \frac{c}{\nu} = \frac{8a^2 m_e \cdot c}{(n'^2 - n^2)h} \quad -③$$

- This relation shows longer the length of the box a, the longer the wavelength at which the optical transition in a such a system occurs.
- Thus, by suitably adjusting the length of the box, electronic transition appear in the visible range of the spectrum.
- The system then becomes coloured.
- Electric dipole transition depends on magnitude of transition dipole moment integrals defined as

$$e = \int_0^a \psi_{n'} \hat{x} \psi_n \, dx \quad -④$$

e = dipole moment, $\psi_{n'}, \psi_n$ = normalised wave functions.

$\hat{x}$ = unit vector

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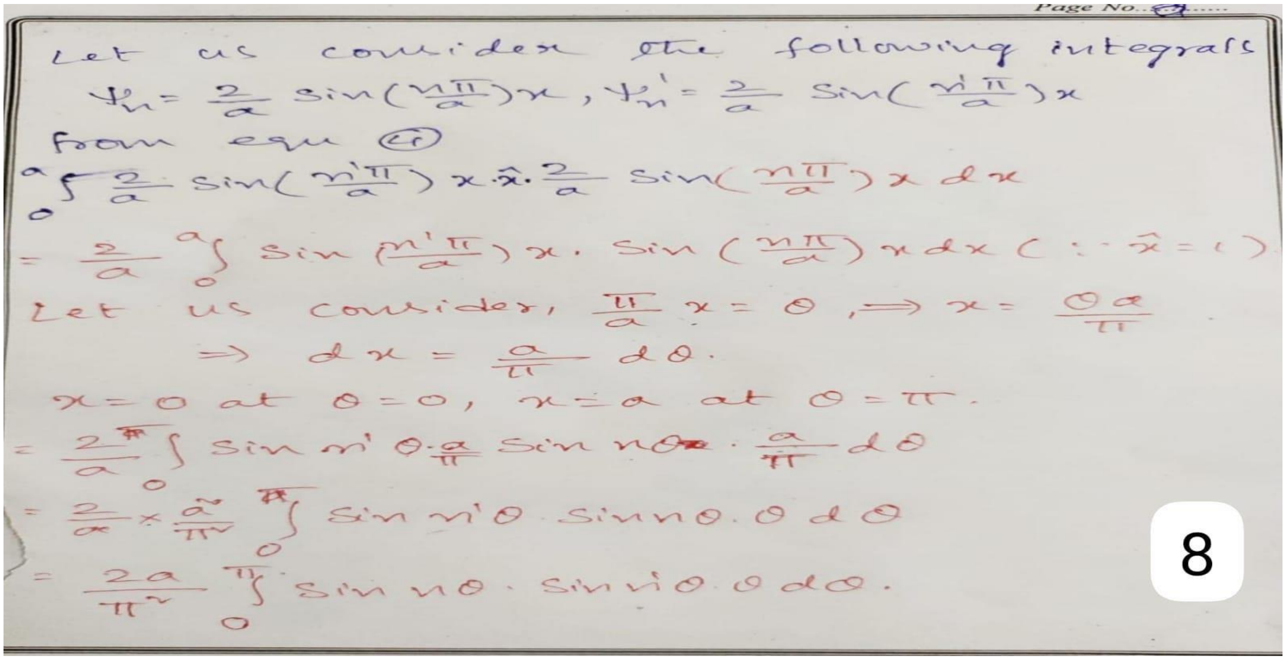


Let us consider the following integrals

$\psi_n = \frac{2}{a}\sin\left(\frac{n\pi}{a}\right)x$, $\psi_{n'} = \frac{2}{a}\sin\left(\frac{n'\pi}{a}\right)x$

from equ ④

$\int_0^a \frac{2}{a}\sin\left(\frac{n'\pi}{a}\right)x\cdot\hat{x}\cdot\frac{2}{a}\sin\left(\frac{n\pi}{a}\right)x\,dx$

$= \frac{2}{a}\int_0^a \sin\left(\frac{n'\pi}{a}\right)x\cdot\sin\left(\frac{n\pi}{a}\right)x\,dx \quad (\because \hat{x} = 1)$

Let us consider, $\frac{\pi}{a}x = \theta \Rightarrow x = \frac{\theta a}{\pi}$.

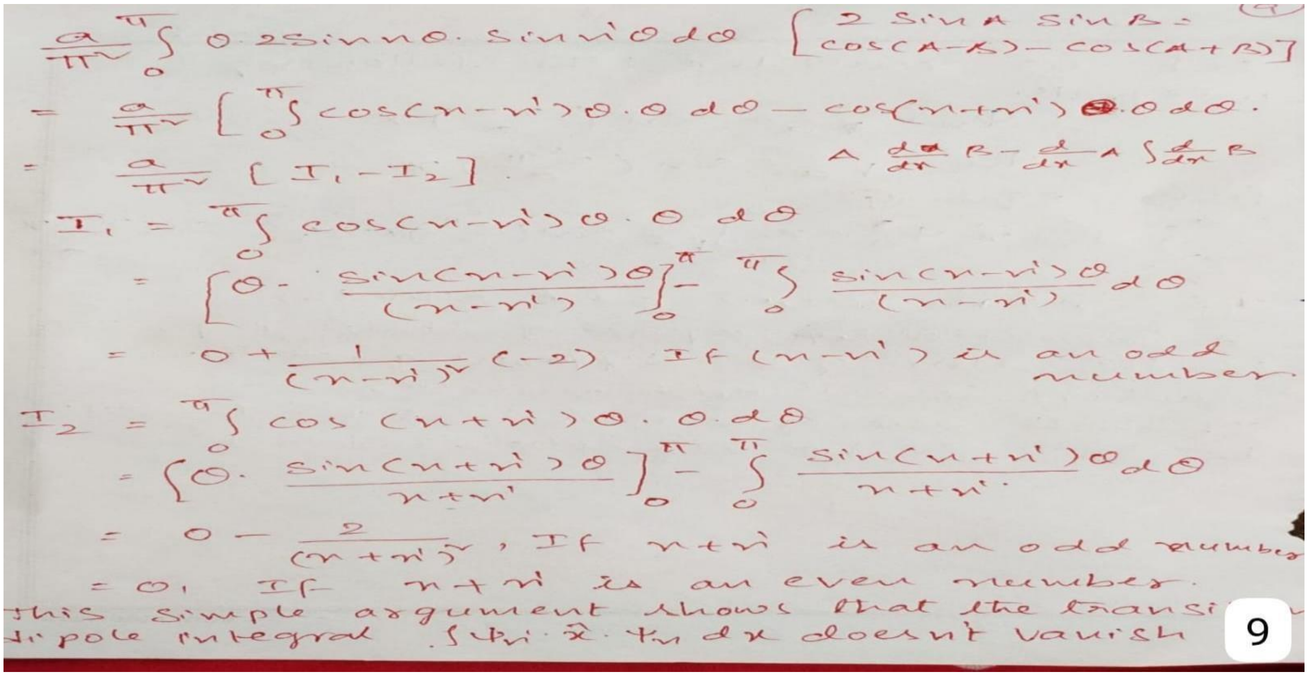
$\Rightarrow dx = \frac{a}{\pi}d\theta$.

$x = 0$ at $\theta = 0$, $x = a$ at $\theta = \pi$.

$= \frac{2}{a}\int_0^{\pi} \sin n'\theta\cdot\frac{a}{\pi}\sin n\theta\cdot\frac{a}{\pi}\,d\theta$

$= \frac{2}{\cancel{a}}\times\frac{a^2}{\pi^2}\int_0^{\pi}\sin n'\theta\cdot\sin n\theta\cdot\theta\,d\theta$

$= \frac{2a}{\pi^2}\int_0^{\pi}\sin n\theta\cdot\sin n'\theta\cdot\theta\,d\theta.$



$\frac{a}{\pi^2}\int_0^{\pi}\theta\cdot 2\sin n\theta\cdot\sin n'\theta\,d\theta \quad \left[\begin{array}{l}2\sin A\sin B = \\ \cos(A-B) - \cos(A+B)\end{array}\right]$

$= \frac{a}{\pi^2}\left[\int_0^{\pi}\cos(n-n')\theta\cdot\theta\,d\theta - \cos(n+n')\theta\cdot\theta\,d\theta.\right.$

$A\frac{d}{dx}B - \frac{d}{dx}A\int\frac{d}{dx}B$

$= \frac{a}{\pi^2}\left[I_1 - I_2\right].$

$I_1 = \int_0^{\pi}\cos(n-n')\theta\cdot\theta\,d\theta$

$= \left[\theta\cdot\frac{\sin(n-n')\theta}{(n-n')}\right]_0^{\pi} - \int_0^{\pi}\frac{\sin(n-n')\theta}{(n-n')}\,d\theta$

$= 0 + \frac{1}{(n-n')^2}(-2)$ If $(n-n')$ is an odd number.

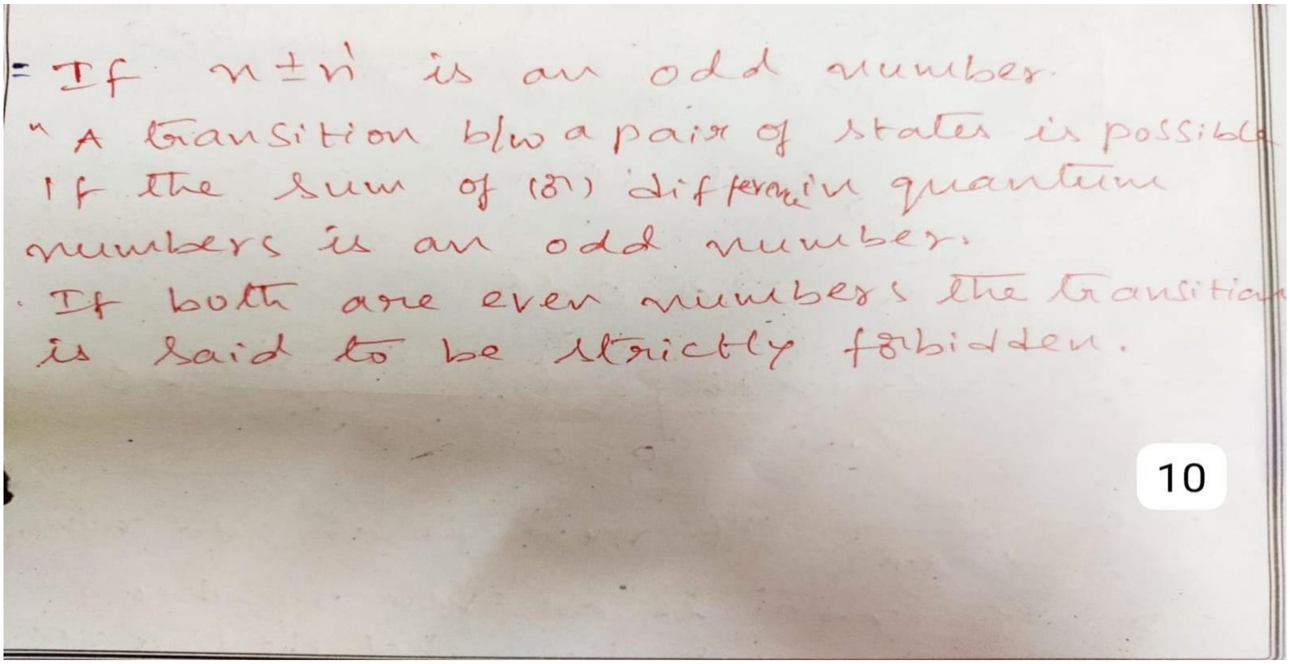
$I_2 = \int_0^{\pi}\cos(n+n')\theta\cdot\theta\cdot d\theta$

$= \left[\theta\cdot\frac{\sin(n+n')\theta}{n+n'}\right]_0^{\pi} - \int_0^{\pi}\frac{\sin(n+n')\theta}{n+n'}\,d\theta$

$= 0 - \frac{2}{(n+n')^2}$, If $n+n'$ is an odd number

$= 0$, If $n+n'$ is an even number.

This simple argument shows that the transi
dipole integral $\int\psi_{n'}^{*}\cdot\hat{x}\cdot\psi_n\,dx$ doesn't vanish



= If $n \pm n'$ is an odd number.

" A transition b/w a pair of states is possible If the sum of (or) difference in quantum numbers is an odd number.

. If both are even numbers the transition is said to be strictly forbidden.

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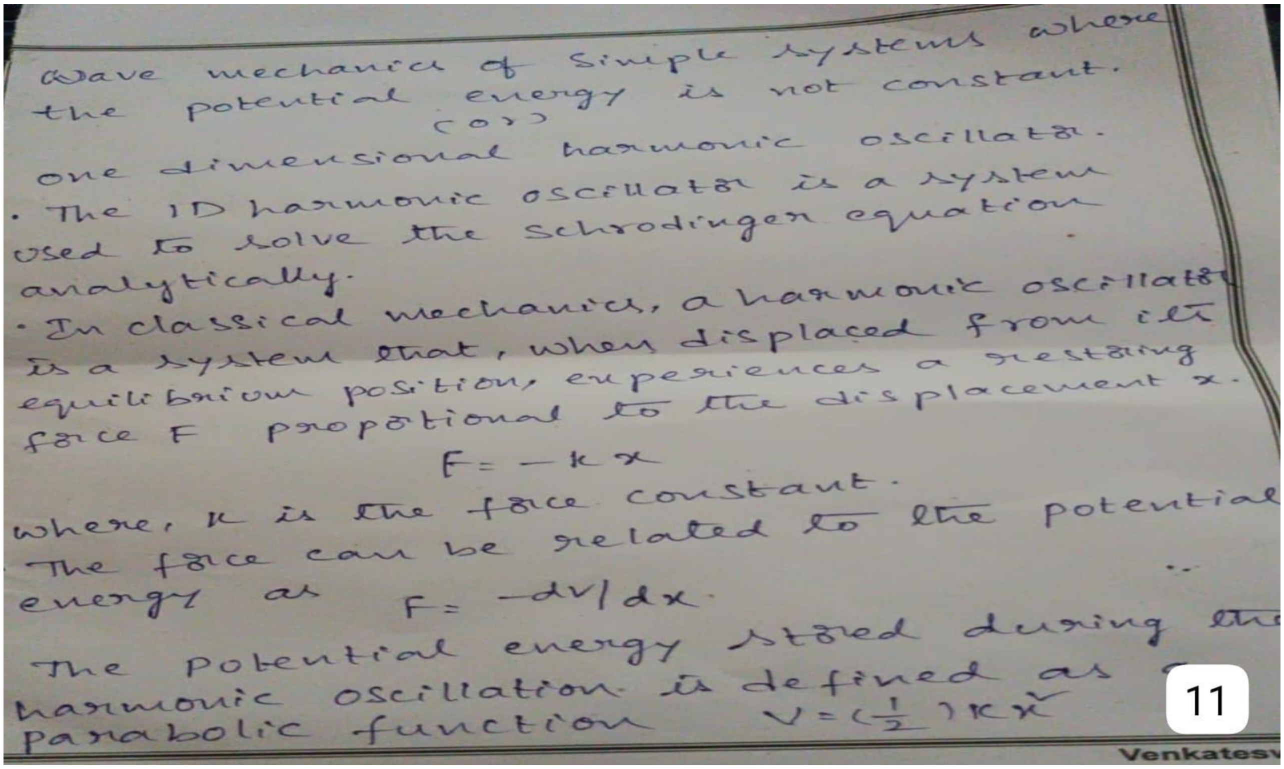

Wave mechanics of simple systems where the potential energy is not constant.

(or)

one dimensional harmonic oscillator.

. The 1D harmonic oscillator is a system used to solve the Schrodinger equation analytically.

. In classical mechanics, a harmonic oscillator is a system that, when displaced from its equilibrium position, experiences a restoring force F proportional to the displacement x.

$$F = -kx$$

where, k is the force constant.

. The force can be related to the potential energy as $F = -dV/dx$.

The potential energy stored during the harmonic oscillation is defined as a parabolic function $V = (\frac{1}{2})kx^2$

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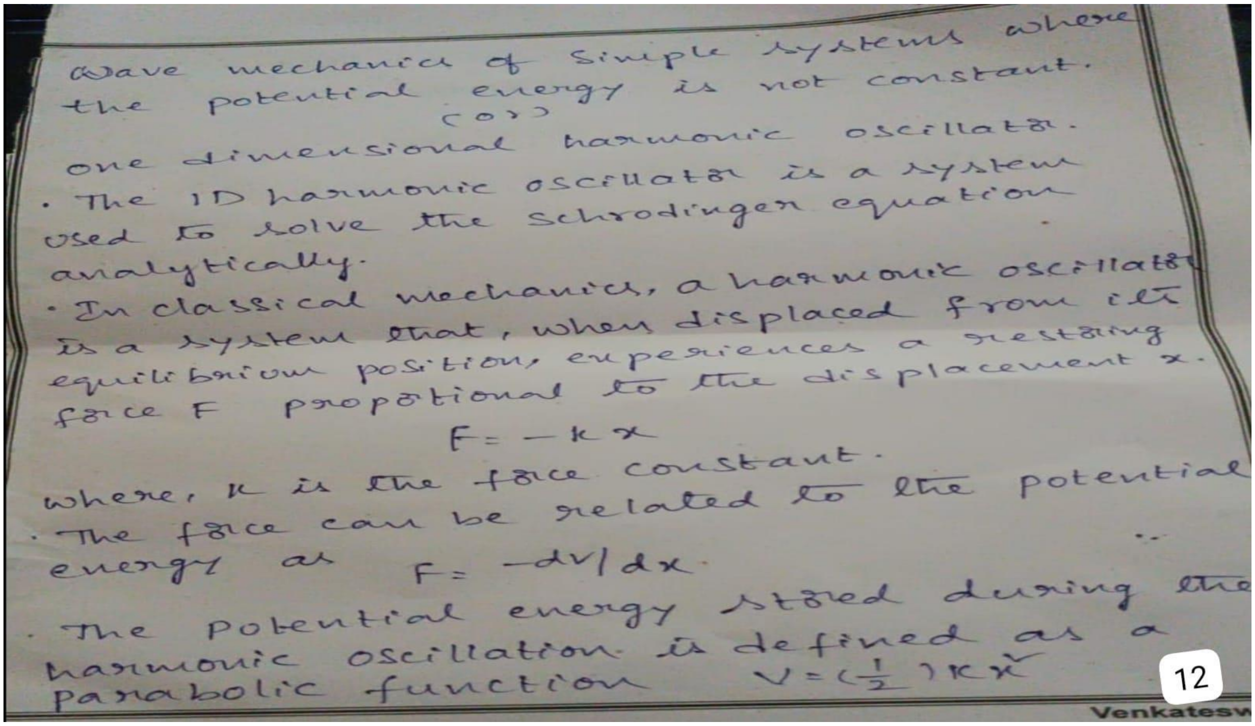
Venkatesv



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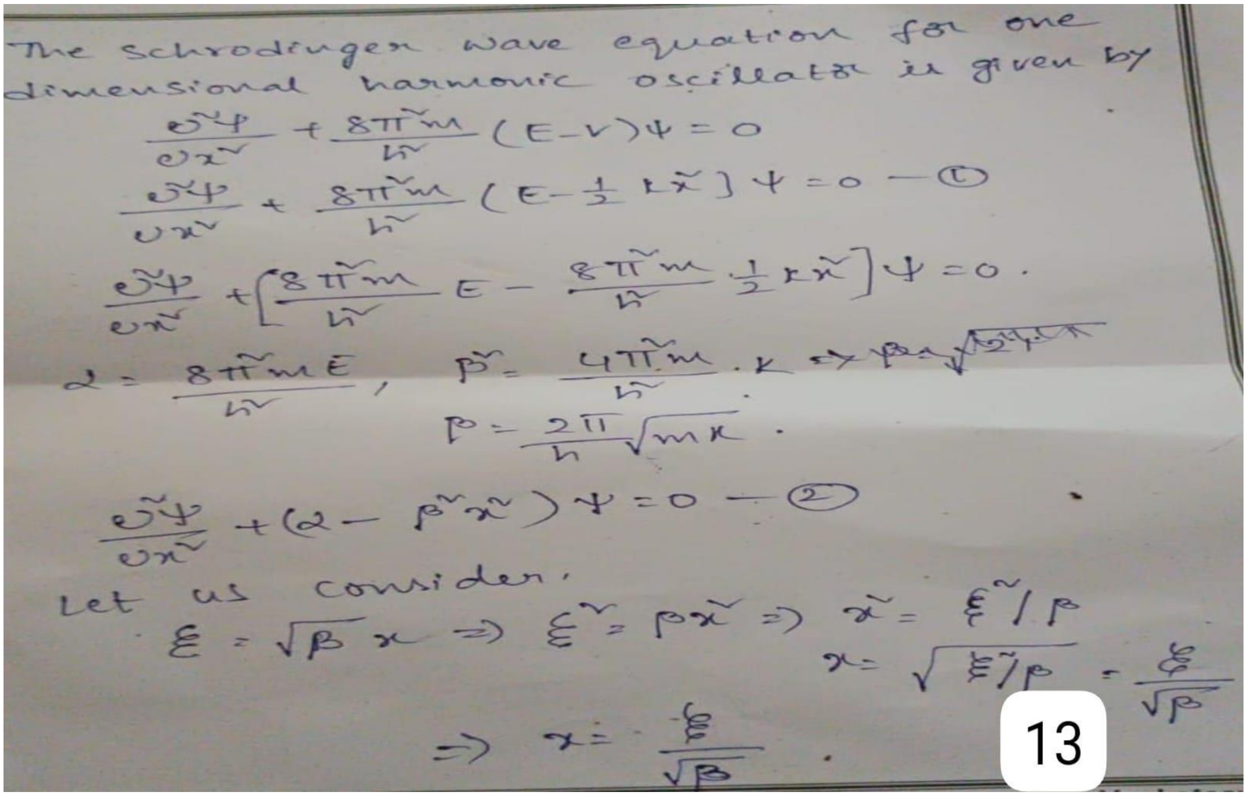


The schrodinger wave equation for one dimensional harmonic oscillator is given by

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

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - \tfrac{1}{2} kx^2]\psi = 0 \quad \text{— ①}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \left[\frac{8\pi^2 m}{h^2} E - \frac{8\pi^2 m}{h^2} \cdot \frac{1}{2} kx^2\right]\psi = 0.$$

$$\alpha = \frac{8\pi^2 mE}{h^2}, \quad \beta^2 = \frac{4\pi^2 m}{h^2} \cdot k \Rightarrow \beta = \sqrt{[illegible]}$$

$$\beta = \frac{2\pi}{h}\sqrt{mk}.$$

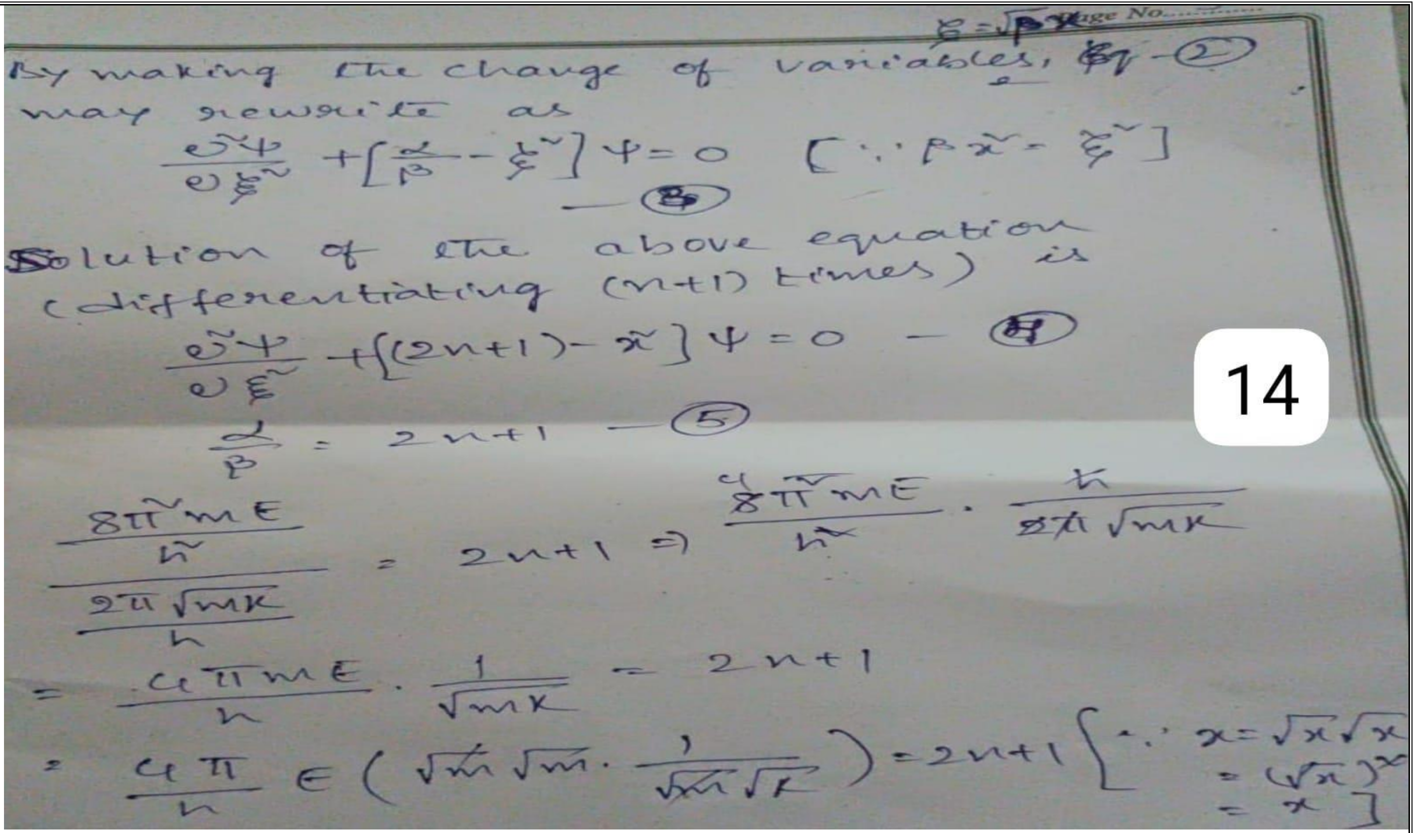
$$\frac{\partial^2 \psi}{\partial x^2} + (\alpha - \beta^2 x^2)\psi = 0 \quad \text{— ②}$$

Let us consider,

$$\xi = \sqrt{\beta}\, x \Rightarrow \xi^2 = \beta x^2 \Rightarrow x^2 = \xi^2/\beta$$

$$x = \sqrt{\xi^2/\beta} = \frac{\xi}{\sqrt{\beta}}$$

$$\Rightarrow x = \frac{\xi}{\sqrt{\beta}}.$$



$\xi = \sqrt{\beta}\, x$ Page No.

By making the change of variables, Eq-②
may rewrite as

$$\frac{\partial^2 \psi}{\partial \xi^2} + \left[\frac{\alpha}{\beta} - \xi^2\right]\psi = 0 \quad [\because \beta x^2 = \xi^2]$$

— ③

Solution of the above equation is
(differentiating (n+1) times)

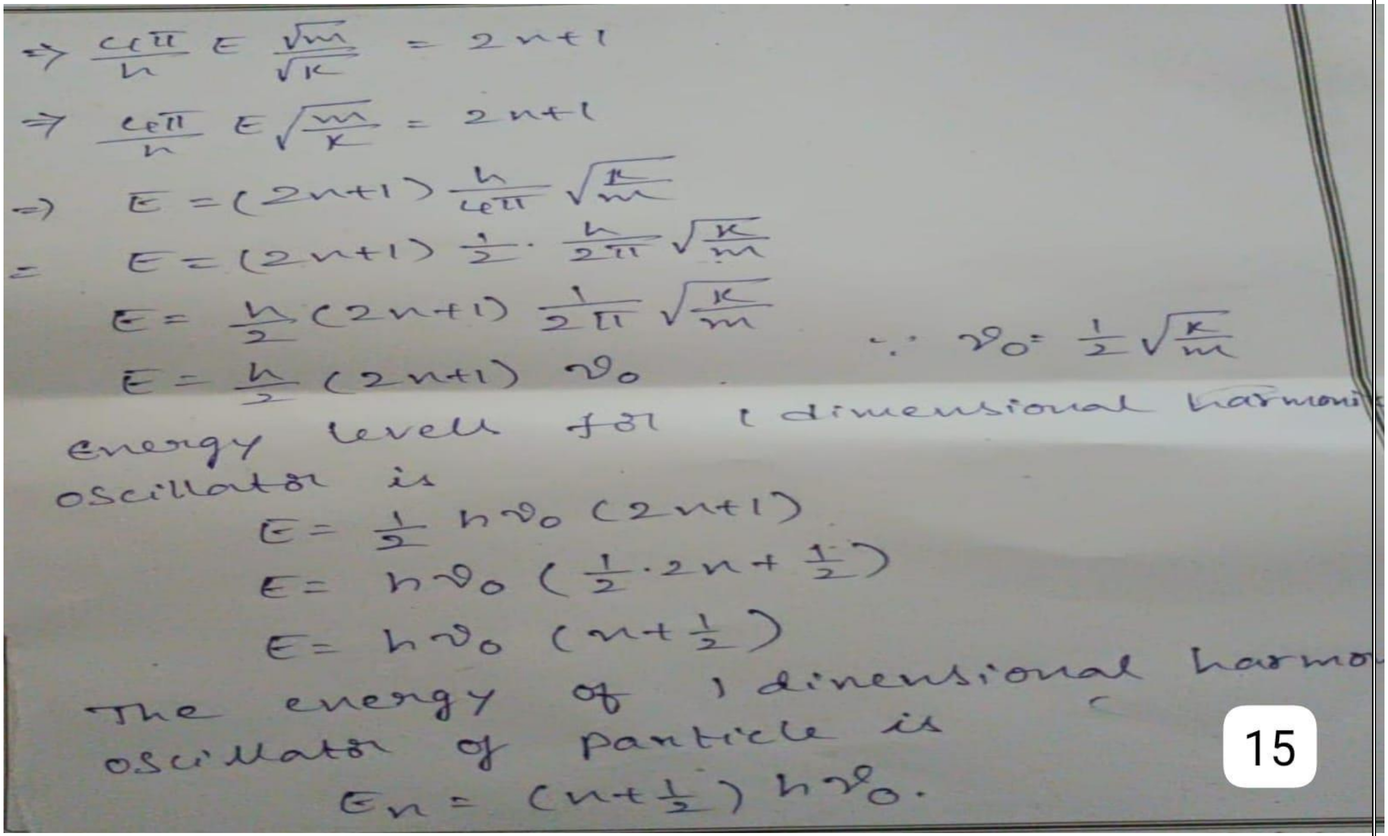
$$\frac{\partial^2 \psi}{\partial \xi^2} + \{(2n+1) - x^2]\psi = 0 \quad — ④$$

$$\frac{\alpha}{\beta} = 2n+1 \quad — ⑤$$

$$\frac{\frac{8\pi^2 mE}{h^2}}{\frac{2\pi\sqrt{mK}}{h}} = 2n+1 \Rightarrow \frac{\overset{4}{\cancel{8}}\pi^2 mE}{h^{\cancel{2}}} \cdot \frac{\cancel{h}}{\cancel{2}\cancel{\pi}\sqrt{mK}}$$

$$= \frac{4\pi mE}{h} \cdot \frac{1}{\sqrt{mK}} = 2n+1$$

$$= \frac{4\pi}{h} E\left(\sqrt{m}\sqrt{m} \cdot \frac{1}{\cancel{\sqrt{m}}\sqrt{K}}\right) = 2n+1 \left[\because x = \sqrt{x}\sqrt{x} = (\sqrt{x})^2 = x\right]$$



$$\Rightarrow \frac{4\pi}{h} E \frac{\sqrt{m}}{\sqrt{K}} = 2n+1$$

$$\Rightarrow \frac{4\pi}{h} E\sqrt{\frac{m}{K}} = 2n+1$$

$$\Rightarrow E = (2n+1)\frac{h}{4\pi}\sqrt{\frac{K}{m}}$$

$$= E = (2n+1)\frac{1}{2} \cdot \frac{h}{2\pi}\sqrt{\frac{K}{m}}$$

$$E = \frac{h}{2}(2n+1)\frac{1}{2\pi}\sqrt{\frac{K}{m}} \quad \because \nu_0 = \frac{1}{2}\sqrt{\frac{K}{m}}$$

$$E = \frac{h}{2}(2n+1)\,\nu_0$$

energy levels for 1 dimensional harmoni
oscillator is

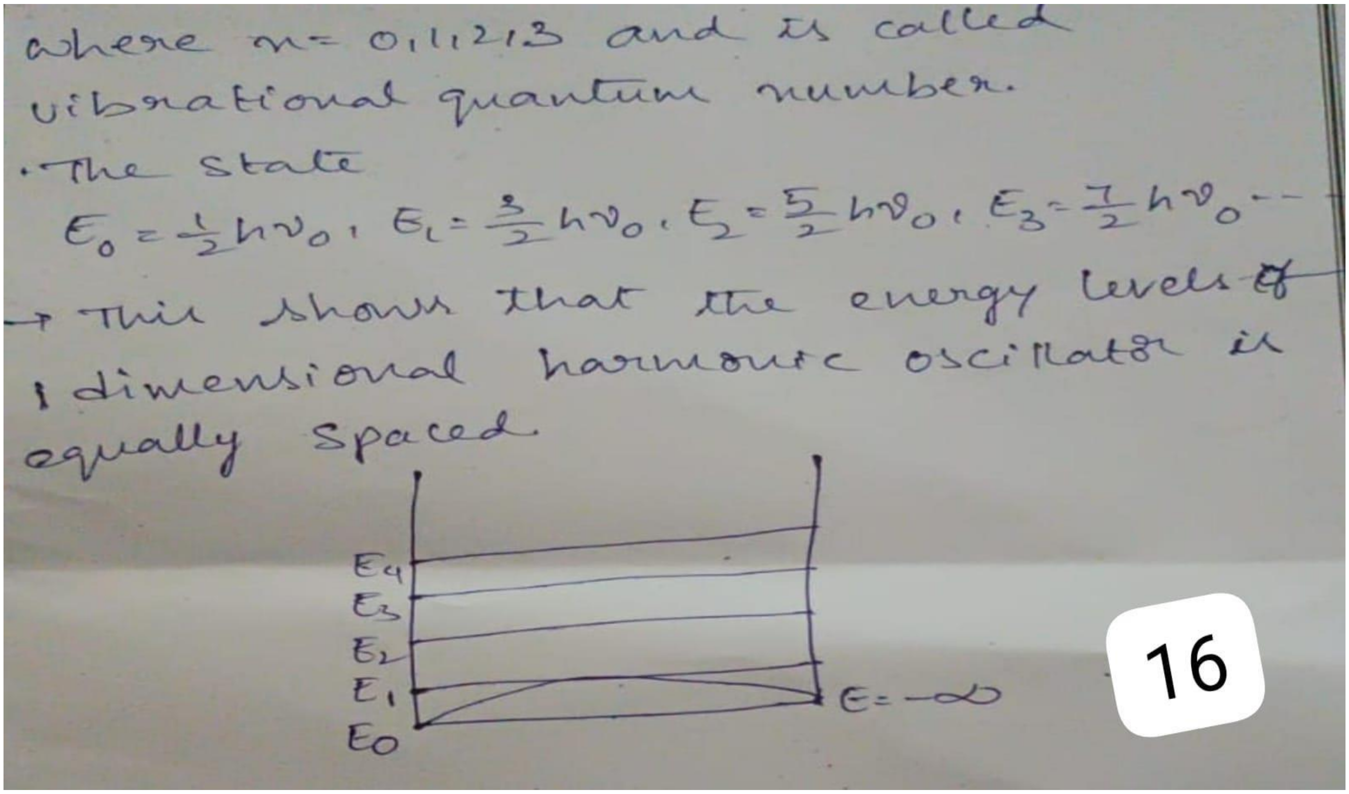
$$E = \frac{1}{2} h\nu_0 (2n+1)$$

$$E = h\nu_0\left(\frac{1}{2} \cdot 2n + \frac{1}{2}\right)$$

$$E = h\nu_0\left(n + \frac{1}{2}\right)$$

The energy of 1 dimensional harmo
oscillator of particle is

$$E_n = \left(n + \frac{1}{2}\right) h\nu_0.$$



where $n = 0, 1, 2, 3$ and is called vibrational quantum number.

- The state

$E_0 = \frac{1}{2}h\nu_0,\ E_1 = \frac{3}{2}h\nu_0,\ E_2 = \frac{5}{2}h\nu_0,\ E_3 = \frac{7}{2}h\nu_0 \cdots$

→ This shows that the energy levels of 1 dimensional harmonic oscillator is equally spaced.

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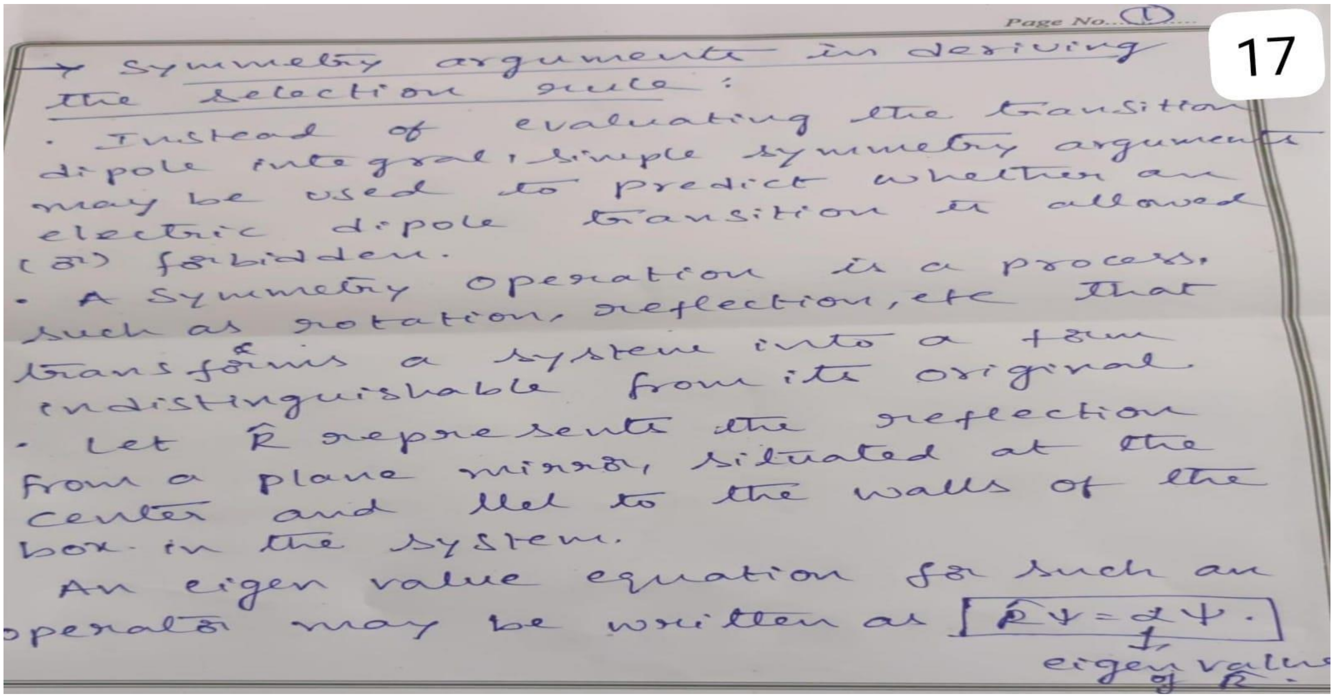

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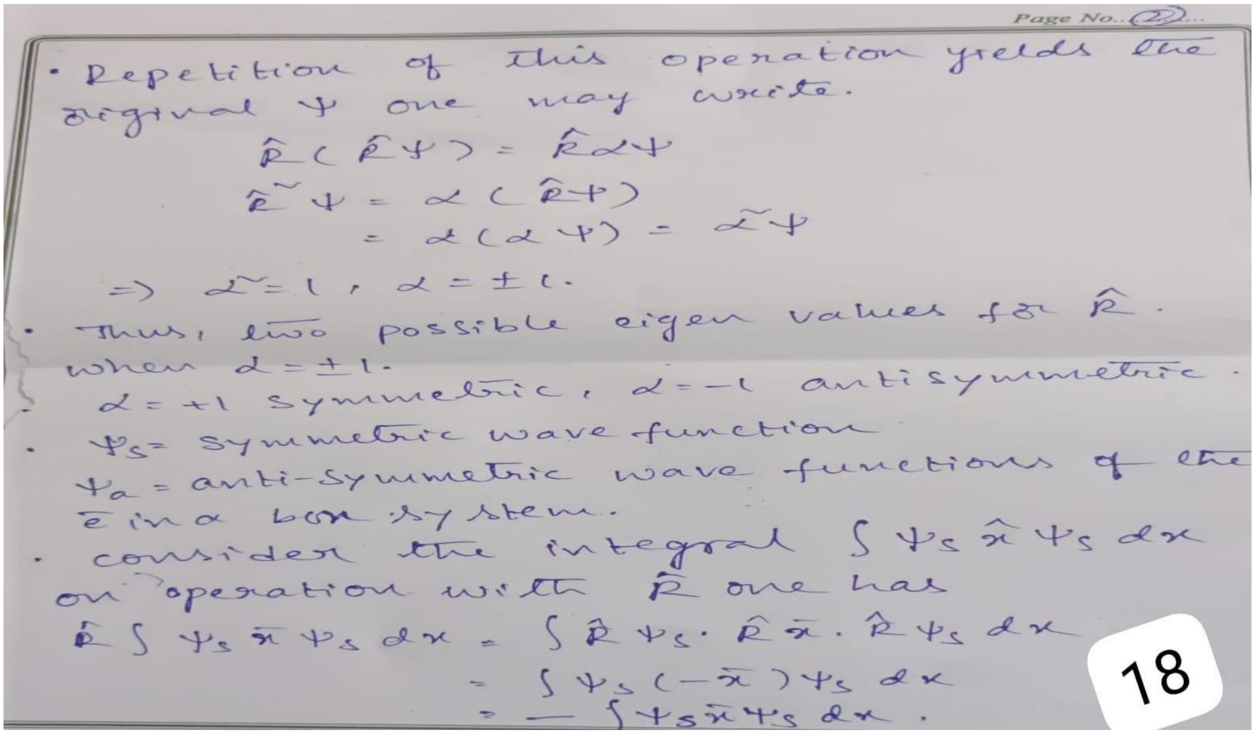
→ Symmetry arguments in deriving the selection rule:

- Instead of evaluating the transition dipole integral, simple symmetry arguments may be used to predict whether an electric dipole transition is allowed (or) forbidden.
- A symmetry operation is a process, such as rotation, reflection, etc that transforms a system into a form indistinguishable from its original.
- Let $\hat{R}$ represents the reflection from a plane mirror, situated at the center and ||el to the walls of the box in the system.

An eigen value equation for such an operator may be written as $\boxed{\hat{R}\psi = \underset{\uparrow}{\alpha}\psi.}$

eigen value of $\hat{R}$.



- Repetition of this operation yields the original Ψ one may write.

$$\hat{R}(\hat{R}\Psi) = \hat{R}\alpha\Psi$$

$$\hat{R}^2\Psi = \alpha(\hat{R}\Psi)$$

$$= \alpha(\alpha\Psi) = \alpha^2\Psi$$

$\Rightarrow \alpha^2 = 1, \ \alpha = \pm 1.$

- Thus, two possible eigen values for $\hat{R}$. when $\alpha = \pm 1.$
- $\alpha = +1$ symmetric, $\alpha = -1$ antisymmetric.
- Ψ_S = symmetric wave function

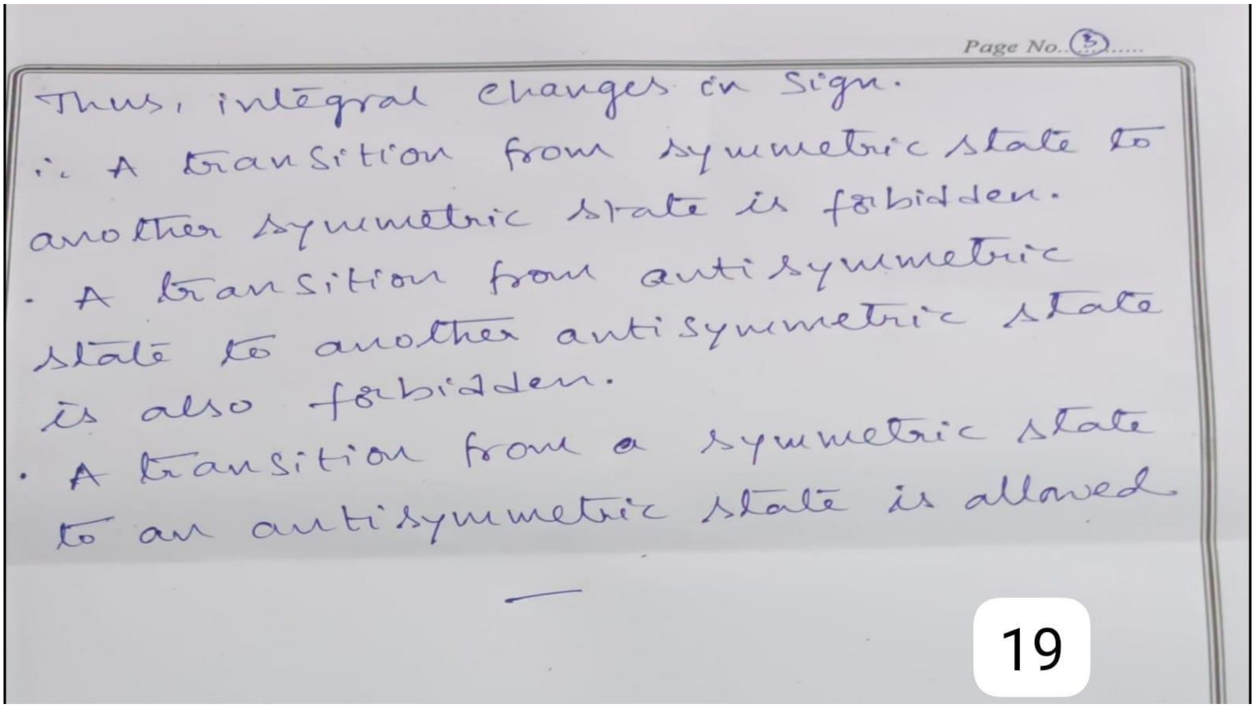
Ψ_a = anti-symmetric wave functions of the $\bar{e}$ in a box system.

- consider the integral $\int \Psi_s \hat{x} \Psi_s \, dx$ on operation with $\hat{R}$ one has

$$\hat{R} \int \Psi_s \bar{x} \Psi_s \, dx = \int \hat{R}\Psi_s \cdot \hat{R}\bar{x} \cdot \hat{R}\Psi_s \, dx$$

$$= \int \Psi_s (-\bar{x}) \Psi_s \, dx$$

$$= -\int \Psi_s \bar{x} \Psi_s \, dx.$$

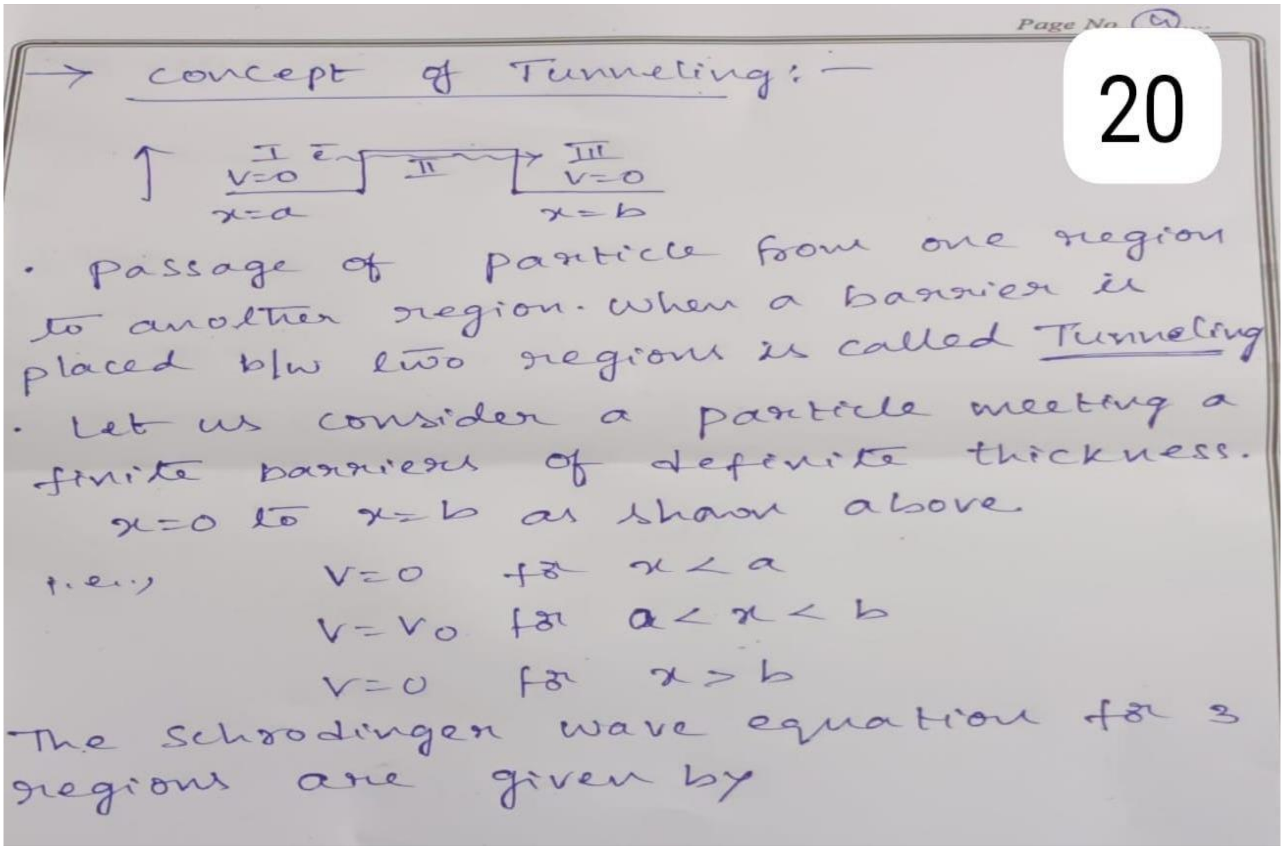


Thus, integral changes in sign.

∴ A transition from symmetric state to another symmetric state is forbidden.

- A transition from antisymmetric state to another antisymmetric state is also forbidden.
- A transition from a symmetric state to an antisymmetric state is allowed.

—



→ <u>concept of Tunneling:—</u>

- passage of particle from one region to another region. when a barrier is placed b/w two regions is called <u>Tunneling</u>
- Let us consider a particle meeting a finite barriers of definite thickness. $x=0$ to $x=b$ as shown above

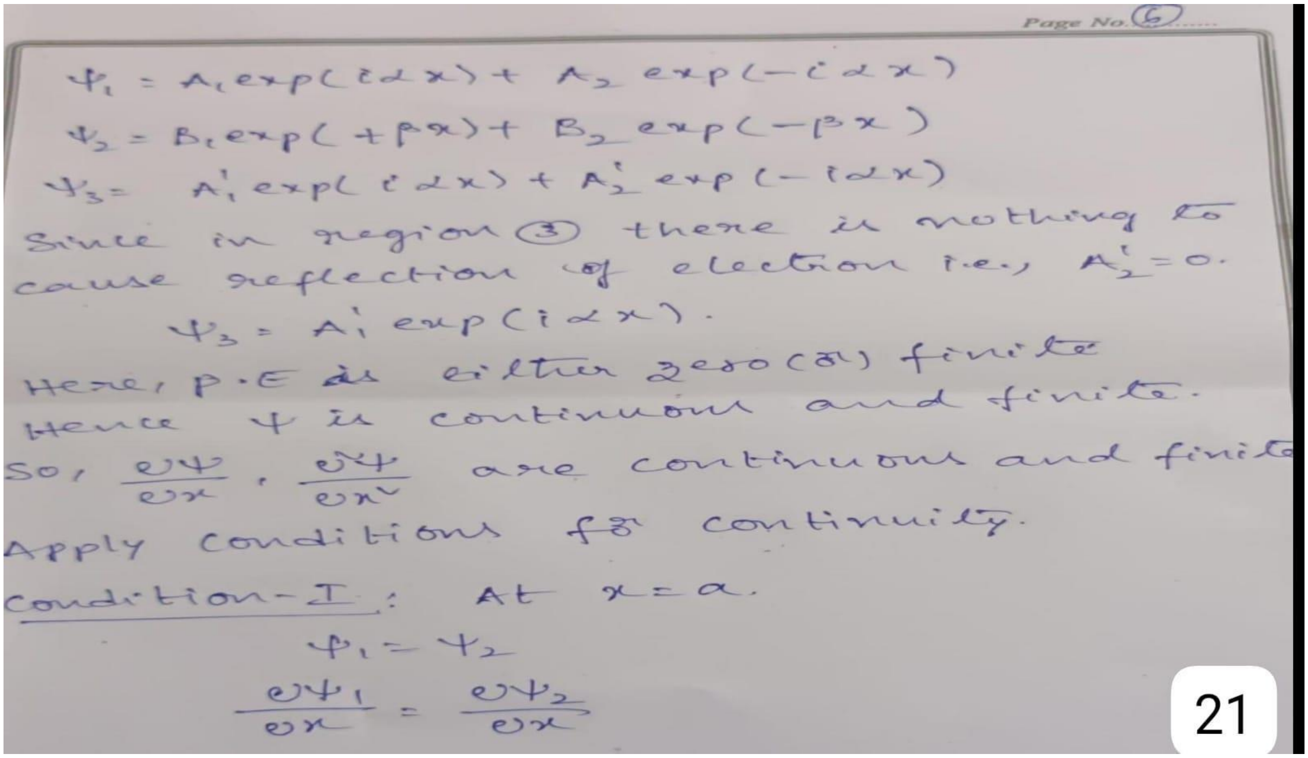
i.e.,

$V=0$ for $x<a$

$V=V_0$ for $a<x<b$

$V=0$ for $x>b$

The schrodinger wave equation for 3 regions are given by



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$\psi_1 = A_1 \exp(i\alpha x) + A_2 \exp(-i\alpha x)$

$\psi_2 = B_1 \exp(+\beta x) + B_2 \exp(-\beta x)$

$\psi_3 = A_1' \exp(i\alpha x) + A_2' \exp(-i\alpha x)$

Since in region ③ there is nothing to cause reflection of election i.e., $A_2' = 0$.

$\psi_3 = A_1' \exp(i\alpha x)$.

Here, P.E is either zero (or) finite

Hence ψ is continuous and finite.

So, $\frac{\partial \psi}{\partial x}$, $\frac{\partial^2 \psi}{\partial x^2}$ are continuous and finite

Apply conditions for continuity.

Condition-I: At $x = a$.

$$\psi_1 = \psi_2$$

$$\frac{\partial \psi_1}{\partial x} = \frac{\partial \psi_2}{\partial x}$$

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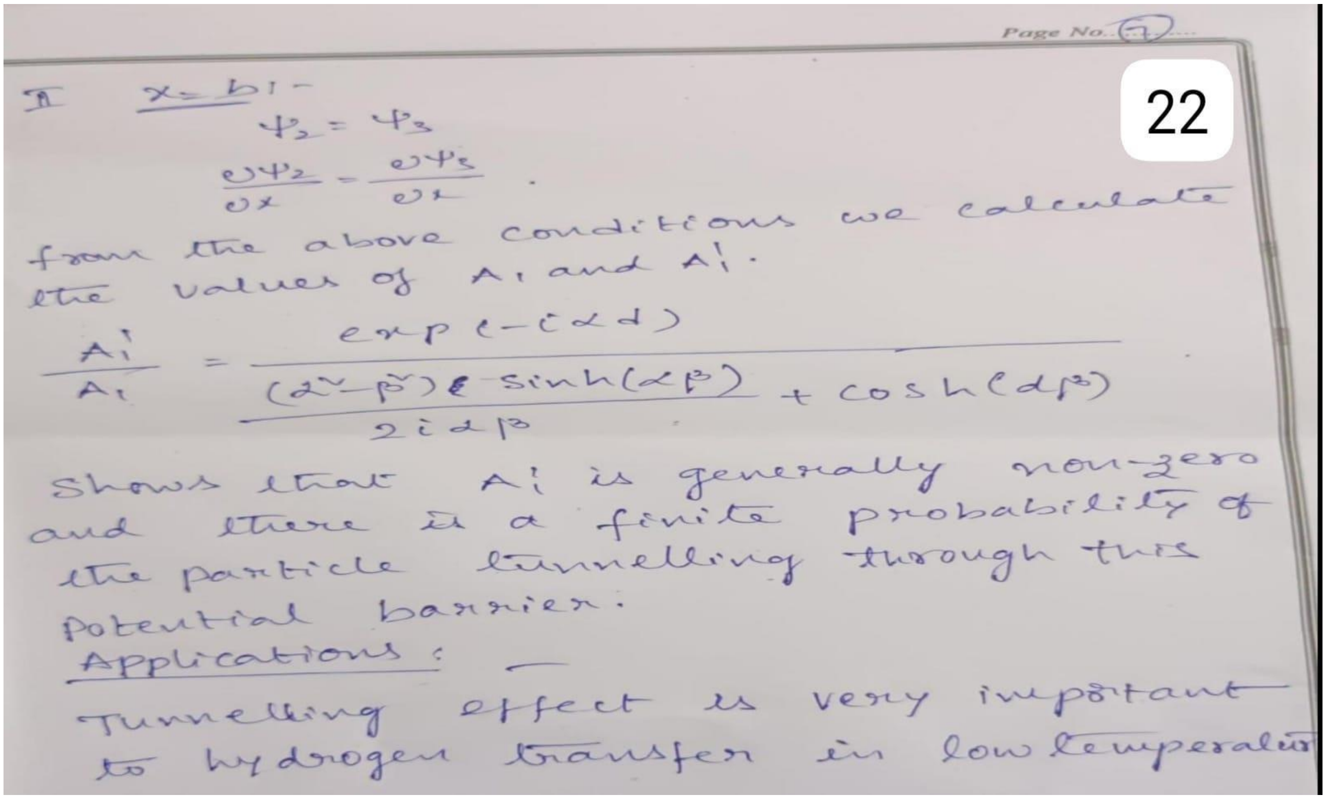

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II $x = b$:-

$$\psi_2 = \psi_3$$

$$\frac{\partial \psi_2}{\partial x} = \frac{\partial \psi_3}{\partial x}.$$

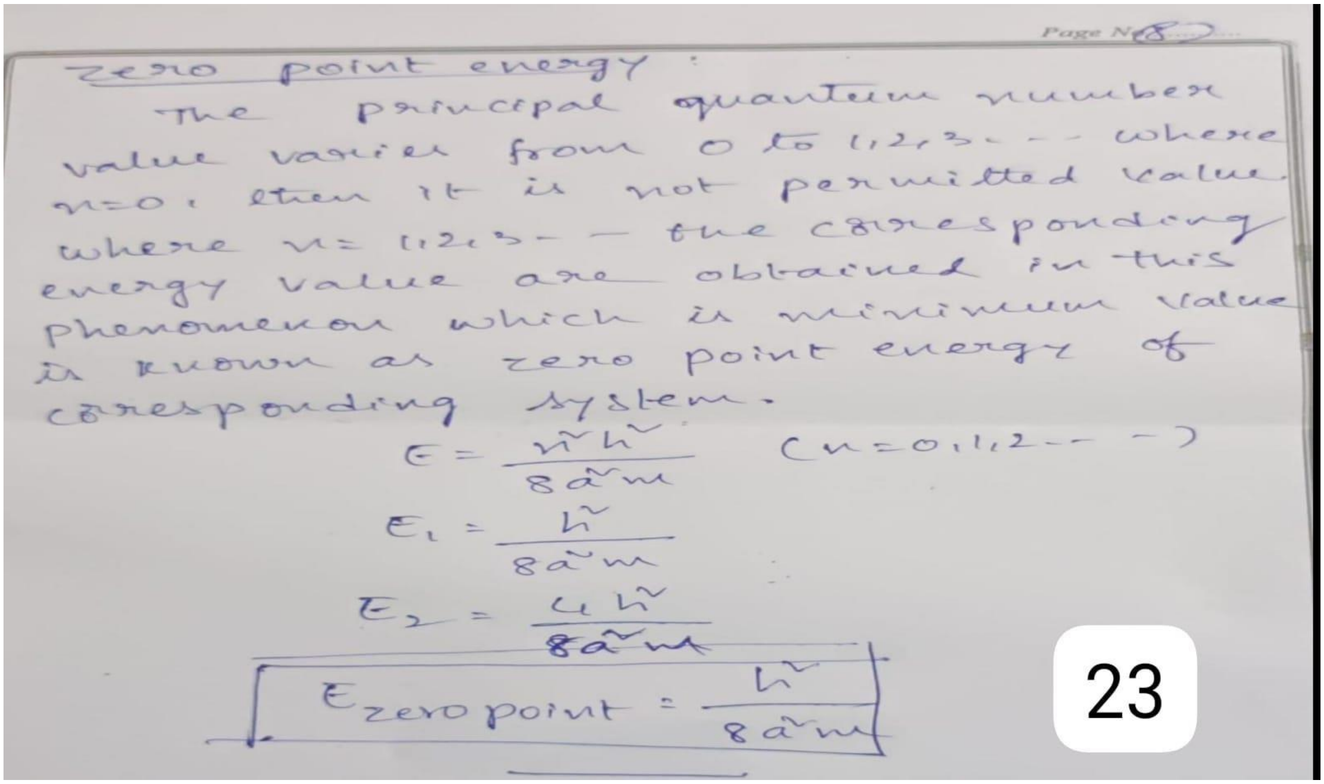
from the above conditions we calculate the values of A_1 and A_1'.

$$\frac{A_1'}{A_1} = \frac{\exp(-i\alpha d)}{\frac{(\alpha^2-\beta^2)\sinh(\alpha\beta)}{2i\alpha\beta} + \cosh(d\beta)}$$

Shows that A_1' is generally non-zero and there is a finite probability of the particle tunnelling through this potential barrier.

Applications: —

Tunnelling effect is very important to hydrogen transfer in low temperatur



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zero point energy :

The principal quantum number value varies from 0 to 1,2,3 --- where n=0, then it is not permitted value where n= 1,2,3 -- the corresponding energy value are obtained in this phenomenon which is minimum value is known as zero point energy of corresponding system.

$$E = \frac{n^2h^2}{8a^2m} \quad (n=0,1,2 \cdots)$$

$$E_1 = \frac{h^2}{8a^2m}$$

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

$$\boxed{E_{\text{zero point}} = \frac{h^2}{8a^2m}}$$

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UNT-III

FUNDAMENTALS OF MOLECULAR SPECTROSCOPY-I

Microwave spectroscopy and infrared (IR) spectroscopy are two distinct techniques used in the study of molecular structure and properties, albeit with different focuses and principles.

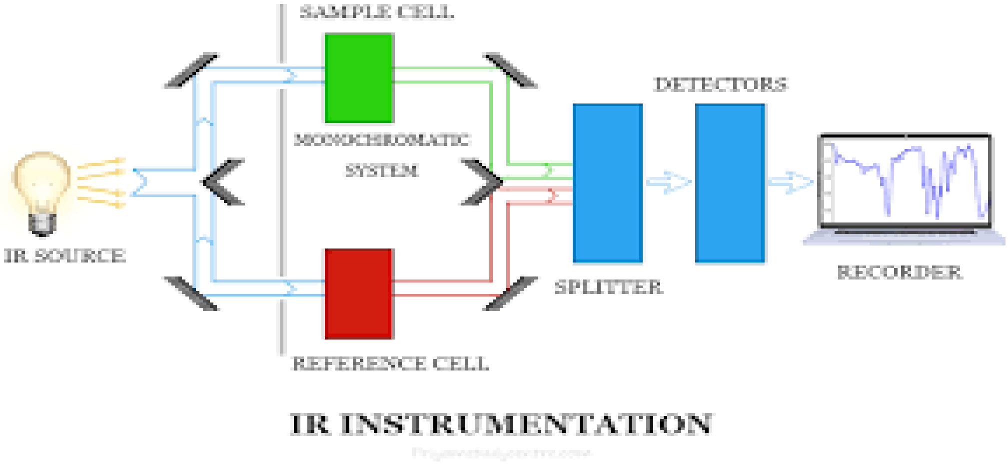
Microwave Spectroscopy:

- **Frequency Range:** Typically involves electromagnetic radiation in the microwave region (1 GHz to 1 THz).
- **Applications:** Primarily used to study the rotational transitions of molecules, providing detailed information about the rotational energy levels and moments of inertia.
- **Molecular Size:** Effective for studying larger molecules and complexes where rotational transitions occur at lower energies.
- **Instrumentation:** Requires specialized equipment such as microwave sources (like klystrons or Gunn diodes) and microwave detectors (like bolometers or superheterodyne receivers).

Infrared (IR) Spectroscopy:

- **Frequency Range:** Involves electromagnetic radiation in the infrared region (typically 3 THz to 400 THz).

- **Applications:** Used to study vibrational transitions within molecules, providing information about bond energies, molecular structure, and functional groups.
- **Molecular Size:** Effective for studying smaller molecules where vibrational transitions occur at higher energies corresponding to IR wavelengths.
- **Instrumentation:** Uses IR sources (like Nernst glowers or Globar) and detectors (like thermocouples or pyroelectric detectors).



Key Differences:

- **Energy Transitions:** Microwave spectroscopy probes rotational energy levels, while IR spectroscopy probes vibrational energy levels.
- **Molecular Complexity:** Microwave spectroscopy is typically used for simpler molecules or structural studies of larger molecules, while IR spectroscopy is more versatile and widely applicable to both organic and inorganic compounds.
- **Instrumentation and Technique:** Each technique requires specific instrumentation tailored to the respective frequency ranges and energy transitions.

Complementary Techniques:

- Together, microwave and IR spectroscopy provide a comprehensive toolkit for molecular analysis. Microwave spectroscopy gives insights into molecular structure through rotational constants and moments of inertia, which complement the detailed vibrational information obtained from IR spectroscopy.

ROTATIONAL SPECTRA OF DIATOMIC MOLECULES:

The rotational spectra of diatomic molecules refer to the set of discrete energy levels associated with the rotational motion of these molecules. Here are the key aspects and characteristics of rotational spectra for diatomic molecules:

1. Energy Levels:

- Diatomic molecules, such as H2, O2, or Cl2, can rotate around their center of mass.
- The rotational energy levels are quantized, meaning the molecule can only have certain specific rotational energies.
- The energy levels are given by $EJ=J(J+1)\hbar$, where J is the quantum number representing the rotational state (0, 1, 2, ...), is the reduced Planck's constant, and I is the moment of inertia of the molecule.

2. Spectroscopic Transitions:

- Rotational transitions occur when a molecule absorbs or emits radiation corresponding to the energy difference between two rotational states ($\Delta J=\pm 1$).
- The energy of these transitions in the microwave region corresponds to
- $E = 2B(J+1)$, where $B=\hbar 4\pi cI$ B is the rotational constant and c is the speed of light.

3. Spectral Lines:

- Rotational transitions produce spectral lines in the microwave region of the electromagnetic spectrum (typically in the range of 1 GHz to 1 THz).
- The spacing between rotational lines decreases with increasing J, resulting in a characteristic pattern of closely spaced lines at low J and more widely spaced lines at higher J.

4. Selection Rules:

- Selection rules govern which transitions are allowed based on changes in the rotational quantum number J.
- Allowed transitions occur when $\Delta J=\pm 1$.

5. Molecular Parameters:

- From the analysis of rotational spectra, important molecular parameters can be derived, such as the bond length RRR (from the moment of inertia $I=\mu R2$, where μ is the reduced mass of the molecule) and the rotational constant B.

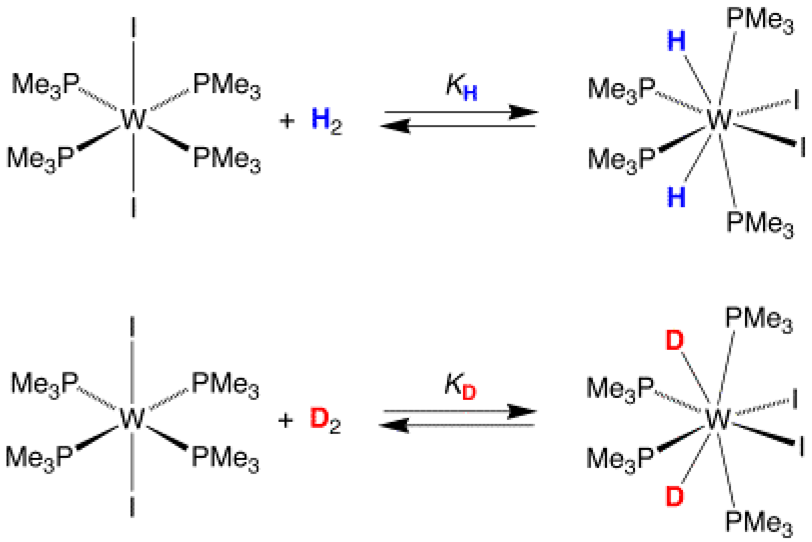
Applications:

- Rotational spectroscopy of diatomic molecules is crucial for determining molecular structure and fundamental properties such as bond length and rotational energy levels.
- It is widely used in atmospheric science, astrophysics (for studying interstellar molecules), and physical chemistry to study molecular dynamics and interactions.
- **Types of Isotopic Effects:**

1. **Mass Isotopic Effect:**

    - This effect occurs due to differences in mass between isotopes of the same element. The most common example is the substitution of hydrogen (with its isotopes deuterium or tritium) in organic molecules.
    - **Examples:**
        - **Deuterium Substitution:** Replacing hydrogen (1H) with deuterium (2H) affects bond strengths, vibrational frequencies in IR spectra, and reaction rates due to the higher mass of deuterium.

2. **Chemical Isotopic Effect:**
    - This effect arises from differences in chemical properties due to isotopic substitution, beyond just mass differences. It can affect reaction rates, equilibrium constants, and spectroscopic properties.
    - **Examples:**
        - **Kinetic Isotope Effect:** Different reaction rates observed for isotopically substituted molecules due to changes in bond vibrational frequencies affecting the activation energy.
        - **Equilibrium Isotope Effect:** Changes in equilibrium position or constant due to isotopic substitution affecting bond strengths or reaction energies.



$K_H/K_D = 0.63$ at 60˚C

Importance and Applications:

- **Molecular Structure:** Isotopic substitution can provide insights into molecular structure and dynamics by altering bond lengths, angles, and moments of inertia.
- **Reaction Mechanisms:** Kinetic isotopic effects are used to elucidate reaction mechanisms, especially in enzyme catalysis and organic chemistry.
- **Environmental Studies:** Isotopic analysis is crucial in environmental studies, such as tracing sources of pollutants or understanding nutrient cycling in ecosystems.

- **Astrophysics:** Isotopic ratios are essential in understanding the origin and evolution of elements in stars and planetary systems.

Experimental Techniques:

- **Mass Spectrometry:** Provides precise measurements of isotopic ratios, essential in geochemistry, archaeology, and biological research.
- **Nuclear Magnetic Resonance (NMR) Spectroscopy:** Can distinguish between isotopes based on their magnetic properties, aiding in structural elucidation.
- **IR and UV-Vis Spectroscopy:** Show differences in vibrational and electronic transitions for isotopically substituted molecules.

In summary, isotopic effects play a crucial role in various fields of science, providing valuable information about molecular structure, reaction mechanisms, and environmental processes. Their study relies on sophisticated analytical techniques to discern subtle differences in physical and chemical properties resulting from isotopic substitutions.

Second-Order Stark Effect:

The second-order Stark effect arises when the external electric field E becomes strong enough to induce a significant change in the molecular or atomic wavefunction beyond the linear perturbation considered in the first order. Here are key points about the second-order Stark effect:

H0 = p 2 2m − e 2 r and add a term arising from a uniform electric field along the z-axis

1. **Nonlinear Interaction:** At higher field strengths, the induced dipole moment p due to the external electric field can itself interact with E, leading to a nonlinear perturbation in the energy levels.
2. **Energy Shift (Second Order):** The second-order energy shift includes terms that depend on p is the induced dipole moment.
3. **Polarizability:** The second-order Stark effect is related to the molecular or atomic polarizability, which quantifies how much the induced dipole moment changes in response to the electric field.
4. **Experimental Observations:** The second-order Stark effect is typically observed under conditions of strong electric fields, such as in high-voltage electric fields or in the presence of intense laser fields. These conditions can induce significant changes in energy levels beyond what is predicted by the first-order Stark effect.

Applications and Significance:

- **Atomic and Molecular Spectroscopy:** Understanding the second-order Stark effect is crucial for accurately interpreting spectral lines in the presence of strong electric fields, which can affect energy level spacings and transition intensities.

- **Quantum Computing:** In the context of quantum systems and quantum information processing, precise control over energy levels influenced by electric fields is essential, making the study of Stark effects pertinent.

Infrared Absorption:

- **Selection Rules:** IR absorption occurs when there is a change in the molecule's dipole moment during the vibration (i.e., the vibration must induce a change in the molecular dipole moment, making the molecule temporarily an oscillating dipole).
- **Intensity of Absorption Bands:** The intensity of IR absorption bands is proportional to the change in dipole moment squared $\Delta\mu 2$ and the overlap of the vibrational wavefunction with the electric field of the IR radiation.

Spectral Features:

- **Fundamental Bands:** The fundamental vibrational transitions (like $v=0\rightarrow 1v = 0$ $2v=1\rightarrow 2$, etc.) appear as absorption bands in the IR spectrum. These bands correspond to the energy required to excite the molecule from one vibrational quantum state to the next.
- **Overtones and Combination Bands:** Higher-energy transitions (such as 2v bands) and combination bands (involving simultaneous excitations of different vibrational modes) can also be observed in the IR spectrum, especially under high-resolution conditions.

Molecular Parameters:

- **Bond Strength and Length:** The positions and intensities of IR absorption bands provide information about the strength of the chemical bond and the equilibrium bond length.
- **Isotopic Substitution:** Isotopic variants (like H2, D2) exhibit shifted absorption frequencies due to differences in reduced masses, providing additional structural information.

Experimental Techniques:

- **Fourier Transform Infrared (FTIR) Spectroscopy:** Most commonly used technique for obtaining IR spectra of diatomic molecules. FTIR spectroscopy provides high-resolution spectra and allows for the identification of vibrational transitions with high sensitivity.
- **Gas Phase Studies:** IR spectra are often recorded in the gas phase to avoid complications from intermolecular interactions, allowing for precise determination of vibrational frequencies.

Applications:

- **Chemical Identification:** IR spectroscopy is widely used for identifying diatomic molecules and determining their chemical structure, particularly in gas-phase studies and atmospheric chemistry.
- **Environmental Monitoring:** IR spectroscopy plays a role in monitoring atmospheric pollutants and greenhouse gases based on their characteristic absorption bands.

ZERO-POINT ENERGY:

Zero-point energy refers to the minimum energy that a quantum mechanical system possesses even at absolute zero temperature (0 Kelvin or -273.15 degrees Celsius). It arises from the fact that particles, such as atoms and molecules, cannot be perfectly at rest due to the principles of quantum mechanics, specifically the Heisenberg uncertainty principle.

Key Points about Zero-Point Energy:

1. **Quantum Mechanical Systems:**
   - According to quantum mechanics, particles like atoms and molecules cannot have zero energy even in their lowest possible vibrational or rotational states. This is because knowing the exact position (which would correspond to zero motion) would require knowing the exact momentum, violating the uncertainty principle.
2. **Vibrational and Rotational Systems:**
   - In molecules, zero-point energy primarily manifests in vibrational and rotational modes.
   - **Vibrational Zero-Point Energy:** Molecules vibrate around their equilibrium positions even at absolute zero, contributing to their zero-point energy. The zero-point vibrational energy depends on the vibrational frequency of the molecule.
   - **Rotational Zero-Point Energy:** Molecules also rotate around their center of mass, and even at absolute zero, they possess rotational motion contributing to the zero-point energy. The amount of rotational zero-point energy depends on the moment of inertia of the molecule.
3. **Calculation and Significance:**
   - The zero-point energy can be calculated using quantum mechanical principles and is typically a small fraction of the total energy of the molecule.
   - While the absolute value of zero-point energy is small, it has significant implications in certain physical phenomena, such as the stability of molecular structures and the behavior of materials at low temperatures.
4. **Experimental Observations:**
   - The effects of zero-point energy are observed in various spectroscopic techniques, where transitions between vibrational or rotational energy levels are observed. These transitions occur at energies corresponding to multiples of the zero-point energy plus the energy of the excited state.
5. **Applications:**
   - Understanding zero-point energy is crucial in fields such as quantum chemistry, molecular spectroscopy, and condensed matter physics.

- It influences the behavior of molecules in chemical reactions, the properties of materials at low temperatures (such as superfluidity and superconductivity), and the stability of molecular structures.

A significant role in the behavior and properties of atoms, molecules, and materials, influencing various aspects of physical and chemical processes.

FERMI RESONANCE:

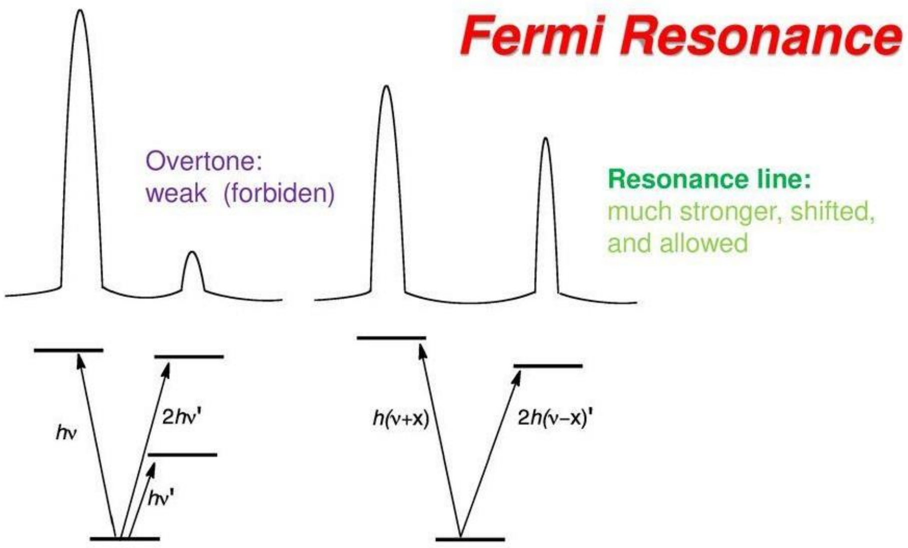
Fermi resonance is a phenomenon in molecular spectroscopy where two or more vibrational modes of a molecule interact to produce an apparent enhancement or splitting of vibrational bands in the infrared (IR) or Raman spectra. This interaction occurs when the energy difference between two vibrational modes is comparable to the energy of a quantum of near-infrared or visible light.

Key Features of Fermi Resonance:

1. **Vibrational Modes:**
    - Fermi resonance typically involves two vibrational modes: a fundamental mode (ν_1) and an overtone or combination mode (ν_2).
    - The fundamental mode (ν_1) is usually IR active, meaning it absorbs IR radiation directly.
    - The overtone or combination mode (ν_2) is often IR inactive in its pure form but can interact with the fundamental mode due to their proximity in energy.
2. **Energy Match:**
    - Fermi resonance occurs when the energy separation between the overtone or combination mode (ν_2) and twice the energy of the fundamental mode ($2\nu_1$) is close to the energy of a quantum of near-IR or visible light.
    - Mathematically, this condition can be expressed as $\nu 2$, where Δ is a small energy difference.
3. **Effects on Spectra:**
    - **Enhancement:** Fermi resonance can lead to an apparent increase in the intensity of certain vibrational bands in the IR or Raman spectra.
    - **Splitting:** It can also cause splitting of a single absorption or emission band into two closely spaced bands.
    - The observed positions and intensities of these bands depend on the nature and strength of the coupling between the vibrational modes involved.
4. **Mechanism:**
    - Fermi resonance arises from anharmonicity in molecular vibrations, where the potential energy surfaces for the vibrational modes are not purely harmonic.
    - The interaction between ν_1 and ν_2 can result in a mixing of their vibrational wavefunctions, altering the energy levels and transitions observed in the spectrum.
5. **Examples:**
    - A common example is the ν_1 and $2\nu_1$ overtone modes in molecules like carbon dioxide (CO_2). The fundamental stretching mode of CO_2 (ν_1) at 2349 cm^{-1}

interacts with its first overtone ($2\nu_1$) at $4698\ \text{cm}^{-1}$ due to their energy proximity, resulting in complex spectral patterns.

6. **Significance:**
    - Understanding Fermi resonance is important in molecular spectroscopy for accurate interpretation of vibrational spectra and determination of molecular structure.
    - It provides insights into the anharmonic nature of molecular vibrations and the coupling between different vibrational modes.



Two conditions must be satisfied for the occurrence of **Fermi Resonance**:
(1) the two vibrational states of a molecule transform according to the same **irreducible representation** of the molecular point group.
(2) The energies of the transitions (accidentally) have almost the **same energy.**

SIMULTANEOUS VIBRATIONAL-ROTATIONAL SPECTRA:

Simultaneous vibrational-rotational spectra of diatomic molecules refer to the combined analysis of both vibrational and rotational transitions within these molecules using spectroscopic techniques such as infrared (IR) spectroscopy. Here’s an overview of how vibrational and rotational spectra are interconnected and analyzed together:

Vibrational Transitions:

1. **Energy Levels and Spectra:**
    - Diatomic molecules can vibrate with various modes, such as stretching and bending of the bond between the two atoms.
    - Vibrational transitions occur when a molecule absorbs infrared radiation corresponding to the energy difference between two vibrational states.

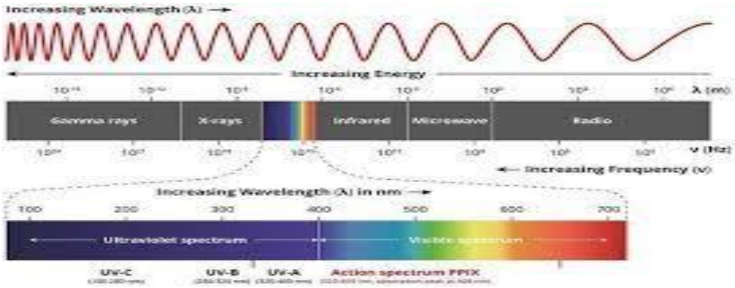
   - In IR spectra, each vibrational mode appears as absorption bands, where the energy of absorbed photons matches the energy gap between vibrational energy levels.
2. **Selection Rules:**
   - Vibrational transitions obey selection rules based on changes in the vibrational quantum number v. Typically, $\Delta v=\pm 1$ for fundamental transitions (direct vibrational excitations).
   - Overtones and combination bands (e.g., 2v, v+wv) are also observed, involving simultaneous excitations of multiple vibrational modes.

Rotational Transitions:

1. **Energy Levels and Spectra:**
   - Diatomic molecules can also rotate around their center of mass, with rotational energy levels quantized according to $EJ=J(J+1)2I\hbar 2$, where J is the rotational quantum number and I is the moment of inertia.
   - Rotational transitions occur when a molecule absorbs microwave radiation corresponding to the energy difference between rotational states.
   - In rotational spectra, transitions between rotational energy levels appear as distinct lines, typically in the microwave region of the electromagnetic spectrum.
2. **Selection Rules:**
   - Rotational transitions follow selection rules based on changes in the rotational quantum number J $\Delta J=\pm 1$.

Simultaneous Analysis and Interpretation:

1. **Combined Spectroscopic Techniques:**
   - Fourier Transform Infrared (FTIR) spectroscopy is commonly used to simultaneously observe vibrational and rotational transitions in diatomic molecules.
   - FTIR provides high-resolution spectra that allow for the identification of both vibrational bands (in the IR region) and rotational lines (in the microwave region).
2. **Energy Coupling and Analysis:**
   - Vibrational and rotational energy levels are coupled due to the dependence of the molecule's moment of inertia on its bond length.
   - The rotational constant B depends on the vibrational state v, leading to changes in rotational spectra with vibrational excitation.
3. **Applications and Insights:**
   - Simultaneous vibrational-rotational spectroscopy provides detailed information about molecular structure, bond strengths, and molecular dynamics.
   - It is used in atmospheric studies, physical chemistry, and astrophysics (e.g., studying molecular gases in space) to characterize molecules and their environments.



OVERTONES

overtones refer to higher frequencies present in the sound produced by a musical instrument or a voice, in addition to the fundamental frequency. These frequencies are integer multiples of the fundamental frequency and contribute to the timbre or tone color of the sound. Overtones are important in music and acoustics because they give different instruments and voices their distinct sound qualities, even when playing the same note at the same volume.

COMBINATION BANDS

Combination bands in spectroscopy refer to bands that arise from the combination of fundamental vibrational modes of molecules. In infrared spectroscopy, for example, combination bands occur when two or more vibrational modes are excited simultaneously. These bands appear at frequencies that are the sum or difference of the frequencies of the individual fundamental vibrations.

For instance, if a molecule has two vibrational modes with frequencies ν_1 and ν_2, combination bands could appear at frequencies $\nu_1 + \nu_2$ and $|\nu_1 - \nu_2|$, assuming they are within the detection range of the instrument.

In Raman spectroscopy, combination bands can also arise when a photon is absorbed or emitted in conjunction with one or more vibrational quanta, leading to a change in the vibrational state of the molecule.

Overall, combination bands provide additional information about the vibrational states of molecules and can be useful in analyzing complex spectra and identifying molecular structures.

HARMONIC OSCILLATOR

A harmonic oscillator is a fundamental concept in physics and refers to a system where the restoring force acting on a body is directly proportional to its displacement from the equilibrium position and acts towards that position. This results in a motion that is periodic and sinusoidal in nature.

Characteristics of Harmonic Oscillator:

1. **Restoring Force**: The force F acting on the oscillator is given by Hooke's Law:

$$F=-kx$$

   where k is the spring constant and x is the displacement from equilibrium.

2. **Equation of Motion**: For a mass m attached to a spring, the equation of motion is:

$$md^2x/ dt^2 +kx=0$$

   This second-order differential equation describes simple harmonic motion.

3. **Periodic Motion**: The oscillator moves back and forth around its equilibrium position with a periodic motion characterized by a specific frequency ω related to the mass m and spring constant k

$$\omega=\sqrt{}k/m$$

4. **Energy**: The total mechanical energy E of a harmonic oscillator is the sum of its kinetic and potential energies:

$$E=1/2\ m\omega 2A2$$

   where A is the amplitude of oscillation.

5. **Quantization**: In quantum mechanics, the harmonic oscillator is one of the few systems for which exact solutions to the Schrödinger equation can be found. The energy levels are quantized and given by:

$$En=\hbar\omega(n+1/2)$$

   where n=0,1,2,…n is the quantum number, and ℏ is the reduced Planck's constant.

Applications:

- **Mechanical Systems**: Many physical systems approximate simple harmonic motion, such as mass-spring systems, pendulums, and vibrating strings.
- **Quantum Mechanics**: The harmonic oscillator model is fundamental in quantum mechanics for describing vibrational modes of atoms and molecules, as well as in the context of quantum field theory.
- **Electrical Engineering**: Harmonic oscillators are used in electronics to generate stable frequencies, such as in oscillators for radio frequency (RF) applications.

ANHARMONIC OSCILLATOR

An anharmonic oscillator is a system where the restoring force acting on the oscillator is not directly proportional to its displacement from the equilibrium position, unlike in a harmonic oscillator where the force is linearly proportional to displacement (Hooke's law). This deviation from linearity introduces higher-order terms in the potential energy function, leading to more complex behavior compared to simple harmonic motion.

Characteristics of Anharmonic Oscillator:

1. **Restoring Force**: The restoring force F in an anharmonic oscillator is typically represented by a potential energy function V(x) that includes higher-order terms:

   $$F=-dV(x)/dx$$

   This results in a non-linear differential equation of motion.

2. **Equation of Motion**: The general equation of motion for an anharmonic oscillator can be expressed as:

   $$md^2x/dt^2+dV(x)dx=0$$

   Here, V(x) could include terms like x2, x3, x4 etc., beyond the linear term in a harmonic oscillator.

3. **Periodic and Non-Periodic Motion**: Anharmonic oscillators may exhibit periodic motion if the potential energy function V(x) still results in a periodic solution, but this is not guaranteed. In many cases, anharmonic oscillators exhibit non-periodic or irregular oscillations.
4. **Energy and Quantization**: Energy levels in an anharmonic oscillator are not equally spaced as in a harmonic oscillator. The quantization and exact solutions for anharmonic oscillators are generally more complex and may require numerical methods or approximations.
5. **Applications**:
   - **Molecular Vibrations**: Many molecular vibrations are anharmonic, especially for larger molecules or in the presence of strong bonds.
   - **Quantum Field Theory**: Anharmonic oscillators arise in theoretical physics, particularly in quantum field theory and condensed matter physics.
   - **Non-linear Dynamics**: Anharmonic oscillators are crucial in studying non-linear dynamics and chaotic systems.

Example of Anharmonic Oscillator:

An example of an anharmonic oscillator potential could be:

$$V(x)=1/2k_2x^2+1/3k_3x^3+1/4k_4x4$$

where k2,k3,k4 are constants determining the strength of each term. This potential introduces cubic and quartic terms beyond the quadratic term present in a harmonic oscillator.

In summary, anharmonic oscillators provide a more realistic model for many physical systems where the linear approximation of Hooke's law does not hold. They are essential for understanding complex oscillatory behaviours in both classical and quantum mechanical contexts.

UNIT-IV

FUNDAMENTALS OF MOLECULAR SPECTROSCOPY-II

Raman and electronic spectra are two distinct spectroscopic techniques used to study molecular structure, electronic transitions, and vibrational modes of molecules. Here's a comparison and overview of each:

Raman Spectra:

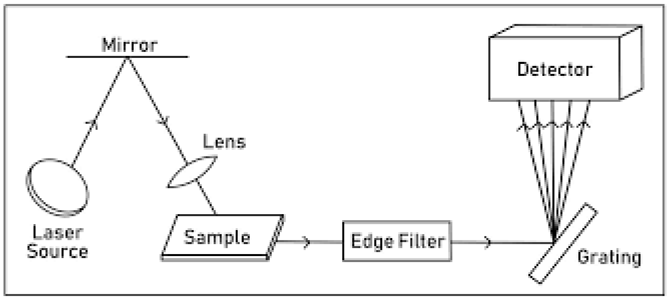
1. **Principle**: Raman spectroscopy measures the scattering of photons by molecules. When light interacts with a molecule, most of it is elastically scattered (Rayleigh scattering), but a small fraction undergoes inelastic scattering. This inelastic scattering results in Raman scattering, where the scattered photons have different energies (frequencies) compared to the incident photons due to the interaction with molecular vibrations.
2. **Information Obtained**:
   - **Vibrational Modes**: Raman spectra provide detailed information about molecular vibrations, including bond stretching, bending, and rotational transitions.
   - **Structural Information**: It can be used to identify functional groups and overall molecular structure based on characteristic vibrational frequencies.
   - **Symmetry Information**: Raman activity is sensitive to the symmetry of vibrational modes, providing insights into molecular symmetry.
3. **Instrumentation**: Raman spectroscopy typically involves using monochromatic laser light (commonly in the visible or near-infrared range) and detecting the scattered light. The frequency shifts (Raman shifts) between incident and scattered light correspond to vibrational energies.
4. **Applications**: Used in fields such as chemistry (analyzing molecular structure), materials science (identifying crystalline phases), biology (studying biomolecules), and pharmaceuticals (quality control and characterization).

Electronic Spectra (UV-Vis Spectra):

1. **Principle**: Electronic spectroscopy (UV-Vis spectroscopy) involves the absorption of light in the ultraviolet (UV) and visible (Vis) regions of the electromagnetic spectrum. It measures the transitions between electronic energy levels of molecules, typically involving promotion of electrons from lower to higher energy orbitals.
2. **Information Obtained**:
    - **Electronic Transitions**: UV-Vis spectra provide information about electronic transitions within molecules, such as from the ground state to excited states.
    - **Concentration and Purity**: It is used for quantitative analysis, determining concentrations of analytes, and assessing purity of substances.
    - **Structural Information**: Can give insights into conjugation and aromaticity in molecules.
3. **Instrumentation**: UV-Vis spectroscopy uses light sources covering the UV and visible regions, and measures the absorbance of light by the sample. The absorption spectrum shows the wavelengths at which the sample absorbs light.
4. **Applications**: Widely used in chemistry, biochemistry, environmental science, and materials science for analyzing substances, monitoring reactions, and studying electronic structure.

Comparison:

- **Nature of Information**: Raman spectroscopy primarily provides vibrational information (Raman-active modes), while UV-Vis spectroscopy provides electronic transition energies.
- **Sensitivity**: Raman spectroscopy is more sensitive to changes in molecular structure and symmetry, whereas UV-Vis spectroscopy is sensitive to the electronic environment and conjugation in molecules.
- **Complementary Techniques**: Both techniques are often used together to obtain a comprehensive understanding of molecular properties. For instance, Raman spectra can complement UV-Vis spectra by providing vibrational details that correlate with electronic transitions.



CLASSICAL EXPLANATION TO RAMAN SPECTRA

In classical theory, the explanation of Raman spectra can be understood in terms of the interaction of light with molecular vibrations, leading to the phenomenon of Raman scattering. Here's a classical explanation of Raman spectra:

Basics of Raman Scattering:

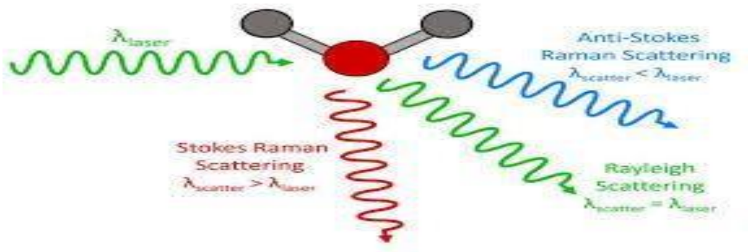
1. **Elastic and Inelastic Scattering**: When monochromatic light (typically from a laser) interacts with molecules, most of the incident photons undergo elastic scattering, known as Rayleigh scattering, where the scattered photons have the same energy (frequency) as the incident photons. However, a small fraction of photons undergo inelastic scattering, which is the basis of Raman scattering.
2. **Raman Effect**: In Raman scattering, a photon interacts with a molecule and temporarily excites it to a virtual energy state. During this interaction, the molecule undergoes a temporary deformation or vibration. The scattered photon can then lose or gain energy compared to the incident photon, corresponding to the energy of the molecular vibration.
3. **Stokes and Anti-Stokes Lines**:
    - **Stokes Lines**: These are Raman scattered photons that have less energy (longer wavelength) than the incident photons. They correspond to photons that have lost energy to the molecule during the vibration process.
    - **Anti-Stokes Lines**: These are Raman scattered photons that have more energy (shorter wavelength) than the incident photons. They correspond to photons that have gained energy from the molecule during the vibration process.

Classical Explanation Steps:

- **Polarizability and Molecular Vibration**: In the classical explanation, the key concept is that the electric field of the incident photon induces a temporary dipole moment in the molecule. This induced dipole interacts with the incident electric field, leading to the scattering process.
- **Vibrational Energy Exchange**: During the interaction, the molecule vibrates due to the induced dipole moment. The frequency of the scattered light can change because the energy of the incident photon can be either slightly increased (anti-Stokes) or decreased (Stokes) due to the energy exchange with the vibrational motion of the molecule.
- **Raman Scattering Cross-Section**: The intensity of Raman scattering depends on the polarizability of the molecule and the frequency of the incident light. The Raman scattering cross-section is proportional to the square of the change in polarizability induced by the vibration.

Limitations of Classical Explanation:

- The classical explanation of Raman scattering provides insights into the basic principles but does not fully account for quantum mechanical effects such as selection rules, detailed line shapes, and specific intensities observed in experimental spectra.
- Quantum mechanics is necessary to explain the full range of Raman scattering phenomena, including the selection rules that govern which vibrational modes are Raman-active and the exact energies and intensities of observed Raman lines.



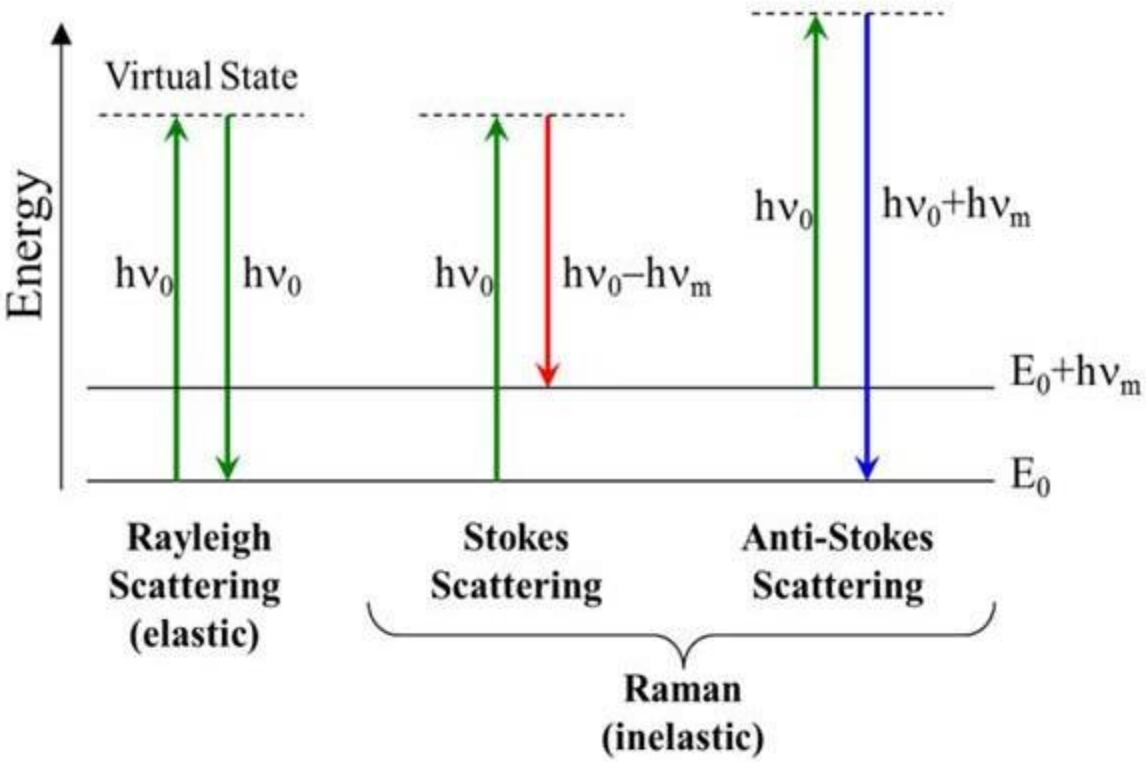
QUANTUM MECHANICAL EXPLANATION FOR RAMAN SPECTRA

In quantum mechanics, the explanation for Raman spectra involves the interaction of photons with molecules at a fundamental level, considering the quantum states of both light and matter. Here's a quantum mechanical explanation for Raman spectra:

Principles of Raman Scattering in Quantum Mechanics:

1. **Energy Levels and Transitions**: In quantum mechanics, molecules have discrete energy levels corresponding to electronic, vibrational, and rotational states. When a molecule interacts with photons (incident light), several processes can occur:
   - **Rayleigh Scattering**: Elastic scattering where the photon is scattered with the same energy (frequency) as the incident photon, indicating no change in the molecule's energy state.
   - **Raman Scattering**: Inelastic scattering where the photon interacts with the molecule, causing transitions between its energy levels.
2. **Virtual States and Vibrational Transitions**: During Raman scattering:
   - **Stokes Lines**: These correspond to photons that are scattered with less energy (longer wavelength) than the incident photon. This occurs when the molecule absorbs energy from the incident photon and transitions to a higher vibrational energy level.
   - **Anti-Stokes Lines**: These correspond to photons that are scattered with more energy (shorter wavelength) than the incident photon. This happens when the molecule loses energy to the incident photon and transitions to a lower vibrational energy level.
3. **Raman Effect Mechanism**: The Raman effect involves three main steps:
   - **Photon Absorption**: The incident photon is absorbed by the molecule, promoting it to a virtual energy state.

  - **Vibration Induced**: The molecule vibrates in this excited state, temporarily altering its dipole moment.
  - **Photon Emission**: The molecule returns to its ground state, emitting a photon with energy corresponding to the difference between the virtual state and the original state, resulting in Raman scattering.
4. **Selection Rules**: Quantum mechanics provides selection rules that govern which vibrational modes can be Raman-active. These rules are based on the symmetry of the molecule and the polarization of the incident and scattered photons.
5. **Quantum Mechanical Formulation**: The intensity of Raman scattering is related to the transition probability between initial and final vibrational states, which depends on the change in polarizability of the molecule induced by the vibrational motion.



Key Points:

- **Polarizability Change**: The Raman scattering cross-section is proportional to the square of the change in molecular polarizability induced by the vibration.
- **Detailed Spectral Features**: Quantum mechanics explains the detailed features of Raman spectra, such as line positions, intensities, and polarization characteristics, which arise from the quantum states of both the molecule and the photons involved.
- **Complementary to Infrared Spectroscopy**: Raman spectroscopy provides complementary information to infrared (IR) spectroscopy, as it can probe vibrational modes that are IR-inactive but Raman-active, and vice versa.

ROTATIONAL RAMAN SPECTRA

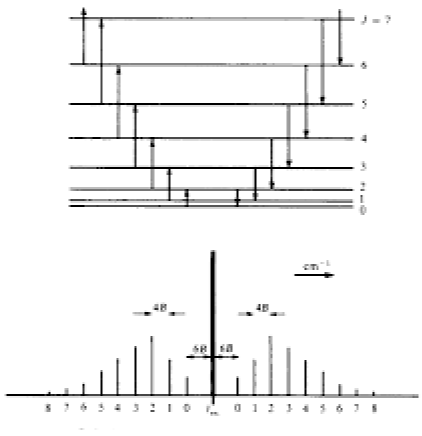
Rotational Raman spectra are a type of Raman spectroscopy that specifically probes the rotational transitions of molecules. Here's an explanation focusing on rotational Raman spectra:

Basics of Rotational Raman Spectroscopy:

1. **Principle**: Rotational Raman spectroscopy measures the inelastic scattering of photons by molecules due to rotational transitions. Unlike vibrational Raman spectra which probe vibrational energy levels, rotational Raman spectra involve changes in rotational energy levels of molecules.
2. **Energy Levels**: Molecules can rotate about their center of mass, and rotational energy levels are quantized. The rotational energy levels are determined by the moment of inertia of the molecule and are typically much smaller (on the order of a few cm^{-1} compared to vibrational energy levels (hundreds to thousands of cm^{-1}.
3. **Raman Effect in Rotational Spectroscopy**:
    - **Stokes and Anti-Stokes Lines**: Similar to vibrational Raman spectra, rotational Raman spectra also exhibit Stokes and Anti-Stokes lines.
        - **Stokes Lines**: These occur when the scattered photon has less energy (lower frequency, longer wavelength) than the incident photon. This corresponds to the molecule losing rotational energy and transitioning to a lower rotational state.
        - **Anti-Stokes Lines**: These occur when the scattered photon has more energy (higher frequency, shorter wavelength) than the incident photon. This corresponds to the molecule gaining rotational energy and transitioning to a higher rotational state.
4. **Selection Rules**: Rotational Raman spectra have selection rules based on changes in the rotational quantum number (ΔJ) of the molecule:

    $\Delta J=0$: Most intense lines because they involve no change in the rotational state of the molecule.

    - **$\Delta J=\pm 1$**: Weaker lines, occurring due to transitions where the molecule changes its rotational quantum number by ±1.
5. **Instrumentation**: Rotational Raman spectroscopy typically uses lasers in the visible or near-infrared range to excite the rotational transitions. The scattered light is analyzed to determine the frequencies of the scattered photons and thus the rotational energy differences.
6. **Applications**:
    - **Gas Phase Analysis**: Used for studying gases and their rotational dynamics.
    - **Thermodynamic Studies**: Provides information about rotational energies and thermal properties of molecules.
    - **Astrophysical Studies**: Helps in identifying and studying molecules in interstellar space based on their rotational Raman spectra.



Quantum Mechanical Explanation:

- **Energy Exchange**: In quantum terms, rotational Raman scattering involves the interaction of photons with molecules, causing transitions between rotational energy levels. The intensity of the Raman scattered lines depends on the change in the polarizability of the molecule induced by the rotational motion.
- **Detailed Spectral Features**: Quantum mechanics explains the positions and intensities of rotational Raman lines based on the rotational selection rules ($\Delta J=0,\pm1$) and the properties of the molecule's rotational energy levels.

VIBRATIONAL RAMAN SPECTRA

Vibrational Raman spectroscopy is a powerful technique used to study the vibrational modes of molecules. Here’s an overview of vibrational Raman spectra:

Principles of Vibrational Raman Spectroscopy:

1. **Principle**: Vibrational Raman spectroscopy measures the inelastic scattering of photons by molecules due to their vibrational transitions. When monochromatic light interacts with a molecule, some photons undergo Raman scattering where the energy (frequency) of the scattered photons differs from that of the incident photons due to energy exchange with the molecule's vibrational modes.
2. **Vibrational Energy Levels**: Molecules can vibrate in different ways, such as stretching and bending of chemical bonds. Each vibrational mode corresponds to specific energy levels that are quantized according to the molecule's potential energy surface.
3. **Raman Effect Mechanism**:
    - **Stokes and Anti-Stokes Lines**: These are the two types of Raman scattered photons observed in vibrational Raman spectra:
        - **Stokes Lines**: These occur when the scattered photon has less energy (lower frequency, longer wavelength) than the incident photon. This corresponds to the molecule losing vibrational energy and transitioning to a lower vibrational state.

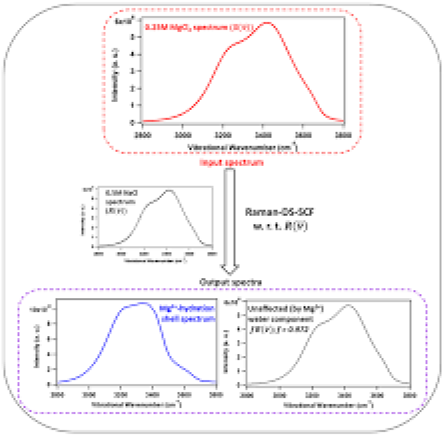
        - **Anti-Stokes Lines**: These occur when the scattered photon has more energy (higher frequency, shorter wavelength) than the incident photon. This corresponds to the molecule gaining vibrational energy and transitioning to a higher vibrational state.

4. **Selection Rules**: Vibrational Raman spectra obey selection rules that depend on the symmetry of the molecule and the polarization of the incident and scattered photons. Generally, only vibrational modes that cause a change in polarizability of the molecule are Raman-active.
5. **Instrumentation**: Vibrational Raman spectroscopy typically uses monochromatic laser light (commonly in the visible or near-infrared range) to excite the molecules. The scattered light is analyzed to detect the Raman shifts (frequency differences between incident and scattered light), which provide information about the vibrational energy levels of the molecule.
6. **Applications**:
    - **Chemical Analysis**: Used extensively in chemistry for identifying and characterizing molecules, determining molecular structures, and studying molecular interactions.
    - **Material Science**: Used in materials research to analyze crystalline structures, polymers, and surface chemistry.
    - **Biomedical Applications**: Applied in biology and medicine for analyzing biomolecules, pharmaceuticals, and tissues.

Quantum Mechanical Explanation:

- **Energy Exchange**: In quantum mechanics, vibrational Raman scattering involves the interaction of photons with the quantized vibrational states of molecules. The energy exchange between photons and molecules is quantized according to the energy levels of the vibrational modes.
- **Raman Scattering Cross-Section**: The intensity of Raman scattered light depends on the change in the polarizability of the molecule induced by the vibrational motion. This change in polarizability is related to the electric dipole moment of the molecule during vibration.
- **Detailed Spectral Features**: Quantum mechanics explains the positions, intensities, and line shapes of vibrational Raman bands based on the specific vibrational energies,

molecular symmetry, and the nature of the chemical bonds involved.



FRANCK CONDON PRINCIPLE

The Franck-Condon principle is a fundamental concept in spectroscopy that describes the intensity of vibronic transitions (electronic transitions accompanied by vibrational changes) between different electronic states of molecules. Here's an explanation of the Franck-Condon principle:

Basics of the Franck-Condon Principle:

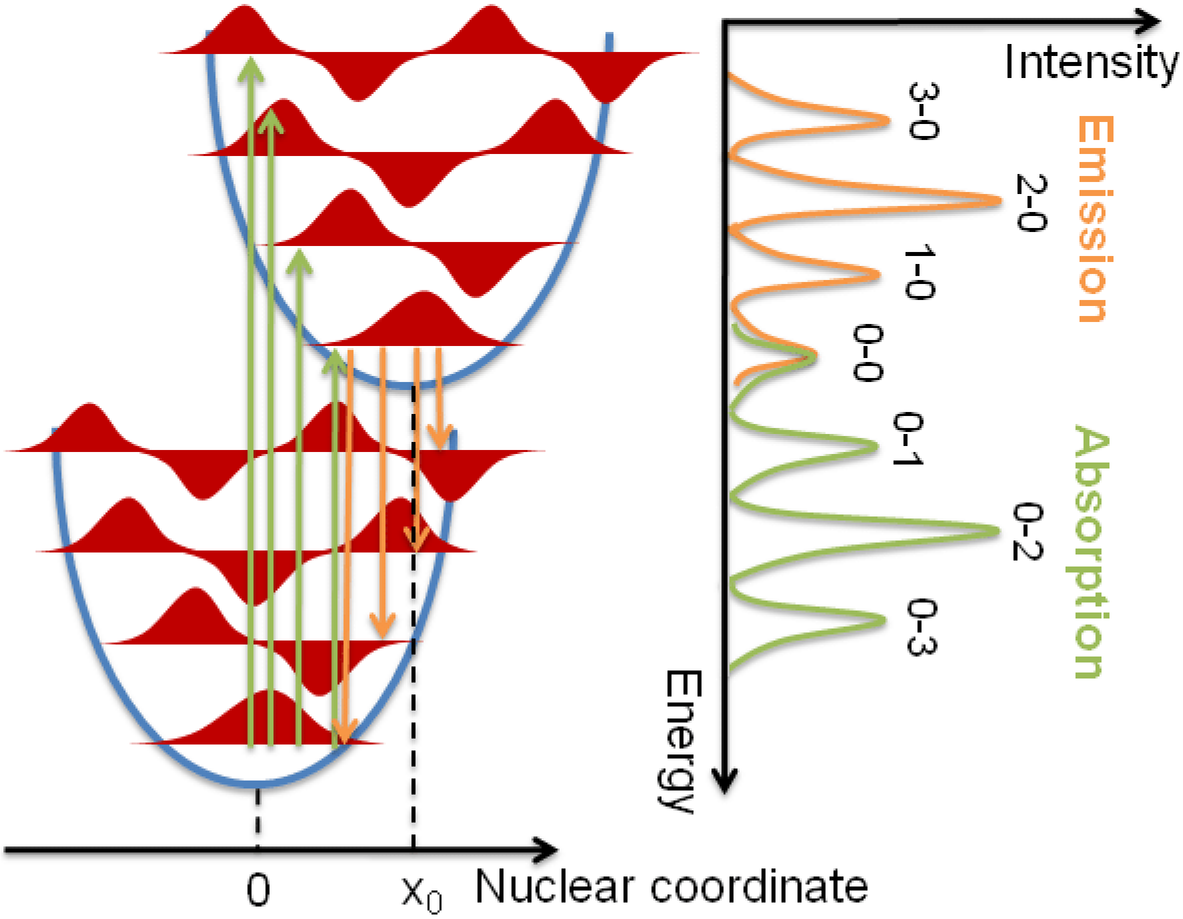
1. **Electronic and Vibrational States**: Molecules can exist in various electronic states with different energies. Each electronic state has associated vibrational energy levels due to molecular vibrations (stretching, bending of bonds, etc.).
2. **Transition Process**: When a molecule undergoes an electronic transition (such as absorption or emission of a photon), the molecule typically does not have enough time to change its vibrational state significantly during the electronic transition process. This is because electronic transitions occur much faster (on the order of femtoseconds) compared to vibrational relaxation (picoseconds to nanoseconds).
3. **Key Principle**: The Franck-Condon principle states that the intensity of a vibronic transition (transition involving both electronic and vibrational changes) is most intense when the overlap between the initial and final vibrational wavefunctions is maximized. In other words, the transition is most likely to occur without a significant change in the vibrational quantum number (Δv=0\Delta v = 0Δv=0).
4. **Implications**:
   - **Vibronic Bands**: The Franck-Condon principle explains the formation of vibronic bands in electronic spectra, where each electronic transition is accompanied by vibrational transitions between different vibrational levels.
   - **Spectral Features**: The principle helps to understand the relative intensities and positions of spectral lines in electronic spectra, as well as the vibrational fine structure within each electronic band.
5. **Experimental Observations**: Experimental techniques such as electronic spectroscopy and vibrational spectroscopy (including techniques like Raman and infrared

spectroscopy) confirm the Franck-Condon principle by showing distinct vibronic transitions with characteristic intensities and line shapes.

6. **Applications**:
    - **Spectroscopy**: Used extensively in spectroscopic studies to analyze electronic and vibrational states of molecules, determining molecular structure, and studying molecular dynamics.
    - **Chemical Reactions**: Provides insights into photochemical reactions and photophysical processes in molecules and molecular complexes.

Quantum Mechanical Interpretation:

- In quantum mechanics, the Franck-Condon principle arises from the consideration of wavefunctions and transition probabilities between different electronic and vibrational states. It involves calculating the overlap integral between initial and final vibrational wavefunctions to determine the transition probability.
- Quantum mechanically, the Franck-Condon factors are computed as integrals over the product of the vibrational wavefunctions in the initial and final electronic states. The magnitude of these factors determines the intensity of the vibronic transitions observed in electronic spectra.



ROTATIONAL FINE STRUCTURE

Rotational fine structure refers to the splitting of rotational energy levels in molecules due to factors such as centrifugal distortion and interactions between rotational and vibrational energy levels. Here’s an explanation of rotational fine structure in molecules:

Basics of Rotational Energy Levels:

1. **Quantization**: Molecules can rotate around their center of mass, and the rotational energy levels are quantized according to the molecule’s moment of inertia I and reduced mass μ. The rotational energy levels are given by:

   $$EJ=J(J+1)\hbar 2/2I$$

   where J is the rotational quantum number (integer values 0,1,2,…).

2. **Spectral Transitions**: Transitions between rotational energy levels occur when a molecule absorbs or emits a photon with energy corresponding to the energy difference between two rotational states

   $$\Delta E=EJ'-EJ$$

Rotational Fine Structure:

Rotational fine structure refers to the splitting and perturbations observed in the rotational energy levels of molecules beyond the simple J(J+1) rule. These deviations arise due to several factors:

1. **Centrifugal Distortion**: Molecules are not perfectly spherical, and centrifugal forces can cause a slight distortion in the bond lengths during rotation. This distortion alters the moment of inertia I and leads to slight differences in the rotational energy levels.
2. **Vibrational-Rotational Coupling**: In molecules, rotational and vibrational motions are coupled. Vibrational motion affects the moment of inertia of the molecule, leading to additional splitting of rotational energy levels. This coupling is described by the Watson's A and B coefficients.
3. **Interaction with Electronic States**: Rotational energy levels can be influenced by the electronic state of the molecule, particularly in electronically excited states where the potential energy surfaces change, affecting the rotational energy levels.

Experimental Observations:

- **Microwave Spectroscopy**: High-resolution microwave spectroscopy is used to observe rotational fine structure in molecules. The spectra show multiple closely spaced lines due to fine splitting, allowing for precise determination of rotational constants and other molecular parameters.
- **Infrared Spectroscopy**: Infrared spectra also show rotational transitions, though the resolution is typically lower compared to microwave spectroscopy. Rotational fine structure can be observed in high-resolution infrared spectra, especially for low-mass molecules.

Applications:

- **Structural Determination**: Analysis of rotational fine structure helps in determining molecular structures and geometries, as different isotopes and structural isomers exhibit distinct rotational spectra.
- **Astrophysics**: Rotational fine structure in molecular spectra is crucial for identifying molecules in space and studying physical conditions in interstellar environments.

CHARGE TRANSFER SPECTRA

Charge transfer spectra refer to a type of electronic spectroscopy that occurs when electrons are transferred between two molecular entities, resulting in characteristic absorption bands in the UV-Vis (Ultraviolet-Visible) region of the electromagnetic spectrum. Here's an explanation of charge transfer spectra:

Basics of Charge Transfer Spectra:

1. **Principle**: Charge transfer (CT) spectra occur when there is a transfer of electronic charge from one molecular entity (donor) to another (acceptor) within a molecule or between molecules. This transfer often involves a significant reorganization of electronic density and can lead to distinct electronic transitions that are observable in the UV-Vis spectrum.
2. **Types of Charge Transfer**:

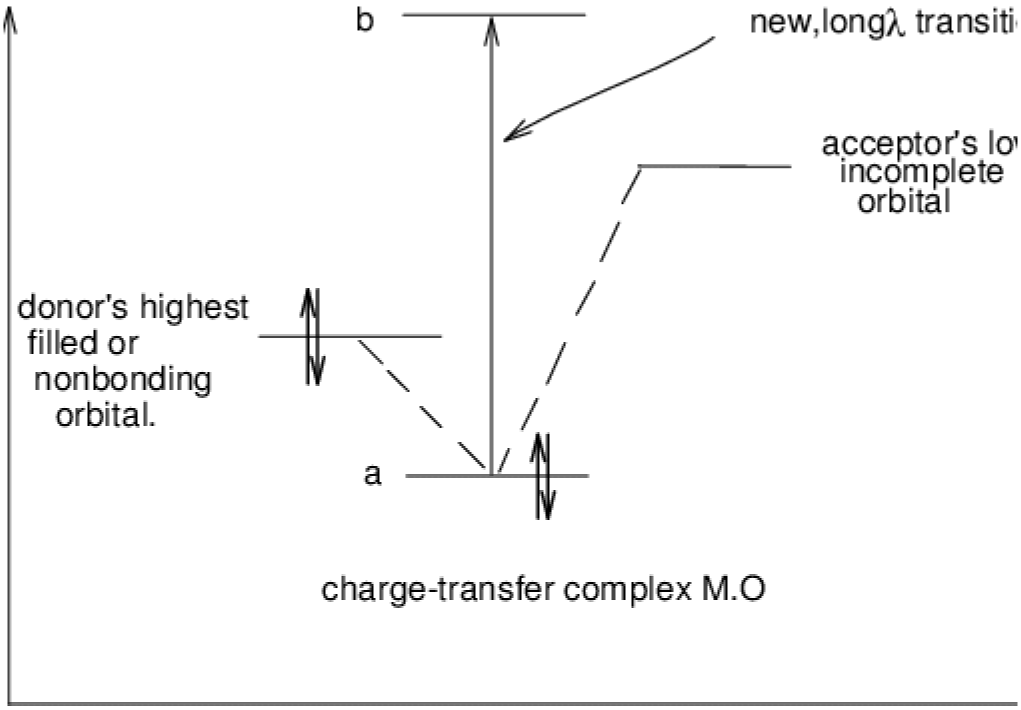
   - **Intramolecular Charge Transfer (ICT)**: This occurs within a single molecule where an electron moves from one part (site) of the molecule (the donor) to another part (the acceptor), resulting in a change in the electronic structure and observable absorption bands.
   - **Intermolecular Charge Transfer**: This involves electron transfer between different molecules, typically in complexes or aggregates where the donor and acceptor are separate molecular entities.
3. **Electronic Transitions**: Charge transfer spectra manifest as broad absorption bands in the UV-Vis spectrum, typically at longer wavelengths (lower energies). The position and intensity of these bands depend on:
   - **Nature of Donor and Acceptor**: The electronic energy levels and the extent of overlap between the donor and acceptor orbitals.
   - **Environment**: Solvent polarity and intermolecular interactions can influence the energy and intensity of charge transfer transitions.
4. **Characteristics**:
   - **Red-Shifted Absorption Bands**: Charge transfer bands are usually red-shifted compared to typical electronic transitions, often extending into the visible region.
   - **Intensity**: The intensity of charge transfer bands can be quite strong, especially in cases where the donor and acceptor have strong electronic coupling.
5. **Applications**:
   - **Organic Electronics**: Studying charge transfer spectra is crucial for developing organic electronic materials and understanding their electronic properties.
   - **Photochemistry**: Charge transfer processes are fundamental in photochemical reactions, such as photocatalysis and photovoltaic devices.
   - **Biochemistry**: Charge transfer spectra are observed in biomolecules and are important in understanding biological electron transfer processes.

Example:

An example of charge transfer spectra is seen in transition metal complexes where a metal ion acts as an electron acceptor and an organic ligand acts as a donor. The absorption spectrum of such complexes often exhibits intense charge transfer bands due to the transfer of an electron from the ligand to the metal ion.

Quantum Mechanical Explanation:

- **Transition Probabilities**: In quantum mechanics, the intensity of charge transfer bands is determined by the transition probability between initial and final electronic states, which is influenced by the overlap of donor and acceptor wavefunctions and the nature of the electronic coupling.
- **Electron Density Redistribution**: Charge transfer transitions involve a redistribution of electron density, leading to changes in the molecular orbital energies and resulting in observable absorption bands.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