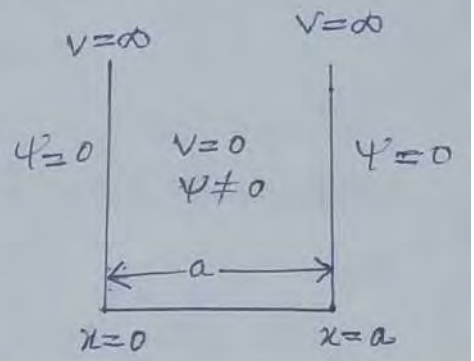
The Schrodinger equation — is used to find the allowed energy levels of quantum mechanical systems e.g. atoms. The wave function gives the probability of finding the particle at a certain position. The solution to this equation is a wave that describes the quantum aspects of a system.

Application of Schrödinger wave equation:—

Particle in a One Dimensional Box:

or

Particle on line Problem:



∵ The smallest particle is electron.

Let us consider an electron of mass m and it moves in x-direction from $x=0$ to $x=a$.

Outside this region the P.E., V is taken as ∞, and within the region is zero

$$V = 0 \quad \text{for} \quad 0 \le x \le a$$
$$V = \infty \quad \text{for} \quad x < 0;\ x > a$$

Outside the box, the Schrodinger wave equation is expressed as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m_e}{h^2}(E-\infty)\psi_{(x)} = 0 \qquad \text{---- 1)}$$

This equation is satisfied only if $\psi = 0$, at all points outside the box. i.e. the electron cannot be found outside the box at all.

Inside the box, the Schrodinger wave equation is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m_e}{h^2} E\,\psi_{(x)} = 0 \qquad \text{---- 2)}$$

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi_{(x)} = 0 \qquad \text{---- 3)}$$

$$\alpha^2 = \frac{8\pi^2 m_e}{h^2} E \qquad \text{---- 4)}$$

One of the solution of this differential equation is

$$\psi_{(x)} = A \sin \alpha x + B \cos \alpha x \qquad \text{---- 5)}$$

Since the particle must not exist outside the box, it is necessary for the wave function, $\psi(x)$, to go to zero at the walls of the 1-D box (fig 1)

Using this boundary conditions, $\psi = 0$ at $x = 0$

eqn 5) becomes

$$\psi(x) = 0 = A \sin \alpha 0 + B \cos \alpha 0$$

$$\text{or, } \quad 0 = A(0) + B(1) \qquad \text{---------- 6}$$

$$\text{or} \quad B = 0$$

Thus the wave function in eqn 5) reduces to

$$\psi(x) = A \sin \alpha x \qquad \text{---------- 7)}$$

At the other wall, the wave function must again go to zero

i.e. At point $x = a$; $\psi(x) = 0$

$\Rightarrow$ The wave function ψ is again zero

∴ For the point $x = a$, the wave function becomes

$$0 = A \sin \alpha a \qquad \text{---------- 8)}$$

there are two possible solutions in the right hand side of eqn 8)

i.e. either $A = 0$ or $\sin \alpha a = 0$

~ If $A = 0$, only identity will be maintained and no useful solution could be obtained.

~ If $\sin \alpha a = 0$ ---------- 9)

The sine of an angle is zero at any integral multiple of π i.e. $\alpha a = n\pi$ ---------- 10)

$$\text{or} \quad \alpha = \frac{n\pi}{a} \text{ ; } n \text{ is an integer}$$

Applying these boundary conditions, the wave equation for particle in one dimensional box becomes

$$\boxed{\psi(x) = A \sin \frac{n\pi x}{a}} \qquad \text{---------- 11)}$$

The coefficient A can be evaluated by normalizing the wave function. Since it is known that particle must be in the box, the probability of its finding in the box is unity.

$$\int_0^a \psi\psi^* dx = 1$$

$$\int_0^a A\sin\alpha x . A\sin\alpha x = 1$$

$$\text{or, } \int_0^a A^2 \sin^2 \alpha x \, dx = 1 \qquad \text{---------- 12)}$$

$$\text{or, } \frac{1}{A^2} = \int_0^a \sin^2 \alpha x \, dx$$

By solving eq^n 12) for A and sub-stituting the result into the wave equation, the complete normalized wave function for particle in a 1-Dimensional box

$$\boxed{\psi_{(x)} = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x} \qquad \text{---------- 13)}$$

Evaluation of normalizing constant, A :-

$$\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$$

$$\frac{1}{A^2} = \int_0^a \left[\frac{1}{2}\left(1 - \cos 2\frac{n\pi}{a} x\right) dx\right]$$

$$= \frac{1}{2}\left[\int_0^a dx - \frac{1}{2}\int_0^a \cos 2\frac{n\pi}{a} x \, dx\right]$$

$$= \frac{1}{2}\left[(x)_0^a - \frac{1}{2}\underbrace{\left(\sin 2.\frac{n\pi}{a} x \, dx\right)_0^a}_{=0}\right] \quad \left| \because \sin 2\frac{n\pi}{a} = 0 \right|$$

$$= \frac{1}{2}\left[a - \frac{1}{2}(0)\right]$$

$$= \frac{1}{2} a$$

$$\text{or } A^2 = 2/a$$

$$\text{or } A = \sqrt{2/a}$$

Evaluation of Energy :-

From eq^{n} 4) $\alpha^2 = \frac{8\pi^2 m e}{h^2} E$

and from eq. 10) $\alpha^2 = \frac{n^2\pi^2}{a^2}$

Equating them, $\frac{n^2\pi^2}{a^2} = \frac{8\pi^2 m e}{h^2} E$

or $$\boxed{E = \frac{n^2 h^2}{8 m_e a^2}} \qquad \text{---------- 14)}$$

Equation 14) shows two main points:

1. Energy is quantized. Since the parameter, n, can have only integral values, the energy takes on the same type of discontinuous character that quantum theory demanded since its origin with Max Planck in 1900.

2. A relation b/w size of the box and energy of the particle is seen to exist. Smaller the size of Box, Greater is energy of particle.

~~If P.E. of the box is not zero but~~ of potential energy of the box is not zero but have some constant value V.

then $$E = \left[\frac{n^2 h^2}{8 m_e \alpha^2} + V\right] \qquad \text{---------- 15)}$$

Although the zero value of n is permissible but it is not acceptable b/c the function ψ_n becomes zero

Since an electron is assumed to be always present inside the box, ∴ the lowest K.E. (which is called as zero point energy) is given by putting $n = 1$

In eq^n (14) becomes

$$E_{\substack{\text{zero point} \\ \text{energy}}} = \frac{h^2}{8mL^2} \qquad \text{---------- 16)}$$

The existence of zero point energy indicates that electron inside the box is not at rest even at 0°K

Therefore the position of electron cannot be precisely known. Since only the mean value of K.E. is known, the momentum of electron is also not known precisely. The average of zero point energy is in accordance with the Heisenberg uncertainty principle.

If the walls are removed, an electron is free to move without any restriction in the field whose P.E may assumed to be zero, then the Schrodinger wave equation and its solutions are respectively given by the eq^n (3) and (5).

The arbitrary const. A & B and α^2 can now have any value which we choose to give them. Therefore the energy given by the eq^n

$$\boxed{E = \frac{\alpha^2 h^2}{8\pi^2 m}} \qquad \text{---------- 17)}$$

is not quantized.

Thus when a electron is bound in a system it has quantized energy level given by eq^n (14) and (15)

and it gives discrete spectrum. On the other hand, a free electron moving without any restriction has the continuous energy spectrum.

This qualitatively explains the occurrence of continuum in the atomic or molecular spectra b/c an electron lost by an atom or molecule is free to move without any restriction.

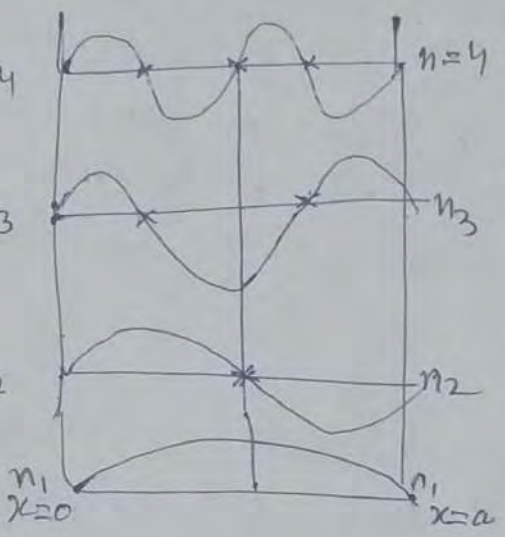


Fig. A few normalized wavefunctions for a particle in a one-dimensional box

$n=1 \Rightarrow E_1 = E_0 = \frac{h^2}{8m_e a^2}$

$n=2 \Rightarrow E_2 = \frac{4h^2}{8m_e a^2}$

$n=3 \Rightarrow E_3 = \frac{9h^2}{8m_e a^2}$

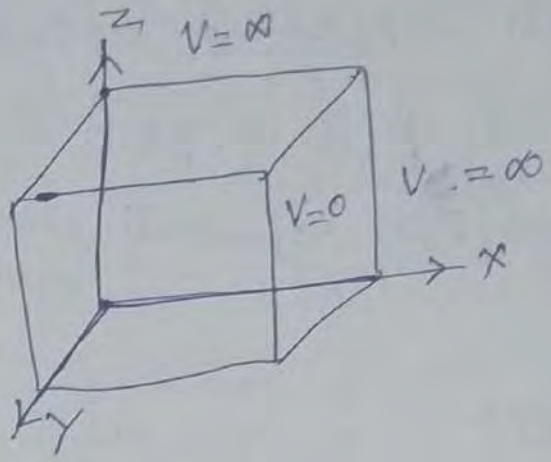
$n=4 \Rightarrow E_4 = \frac{16h^2}{8m_e a^2}$

If a one-dimensional mirror be placed at the centre of box and parallel to the walls of the box, it is seen that the wave functions are alternatively symmetrical and antisymmetrical w.r.t the reflection from such a mirror. Further besides the points on the walls of the box, there are points inside the box where the wavefunction is zero. These points are called Node.

Further, it is observed from

figure, as the Quantum no, n increases, the no. of nodes also increases. For the state with wave function ψ_n there are (n-1) nodes inside the box. This type of behaviour is general for all system. Decreasing the no of nodes, decreases the wavelength and hence increases the K.E.

Particle in 3-dimensional Box:



Consider the motion of a particle of mass m (electron) in 3-D cubical box, with the edges of length a and volume a^3.

The potential is zero within the box and is infinite outside the box and at boundaries.

For the particle in 3-D box, the wave function will be a function of all the 3-coordinat

Let us consider a cartesian coordinate system with the origin at corner of the box and x, y, z are the edges, along the edges of length a

$V_x = 0$ for $0 < x < a$, $V_x = \infty$ otherwise

$V_y = 0$ for $0 < y < a$; $V_y = \infty$ otherwise

$V_z = 0$ for $0 < z < a$; $V_z = \infty$ otherwise

In b/w 0 to a, $V = 0$ and at the boundary and outside, $V = \infty$

The Schrödinger wave equation within the box is given by

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{8\pi^2 m_e E}{h^2} \cdot \psi(x, y, z) \quad \text{---} \quad 1)$$

For the particle in 3-D box, it is assumed that the wave function ψ is a product of three parts which separately depend on x, y and z,

$$\psi(x, y, z) = F(x) \cdot F(y) \cdot F(z) \quad \text{— 2)}$$

where $F(x)$ represents wavefunction that depends only on the variable x

$F(y)$ " " " " variable y

$F(z)$ " " " " " variable z

Differentiating equation 2) first w.r.t. x keeping y & z constant,

" " then w.r.t. y keeping x & z const.,

" " then w.r.t. z keeping x & y const.

$$\left.\begin{aligned} \frac{\partial^2\psi}{\partial x^2} &= F(y).F(z)\frac{\partial^2 F(x)}{\partial x^2} \quad \text{— 3a)} \\ \frac{\partial^2\psi}{\partial y^2} &= F(x).F(z)\frac{\partial^2 F(y)}{\partial y^2} \quad \text{— 3b)} \\ \frac{\partial^2\psi}{\partial z^2} &= F(x).F(y)\frac{\partial^2 F(z)}{\partial z^2} \quad \text{— 3c)} \end{aligned}\right] \text{— 3)}$$

Substituting equation 3) in equation 1) and dividing throughout by $-\frac{8\pi^2 m_e}{h^2} . F(x) F(y) F(z)$, we get

$$-\frac{h^2}{8\pi^2 m_e}\frac{1}{F(x)}\cdot\frac{\partial^2 F(x)}{\partial x^2} - \frac{h^2}{8\pi^2 m_e}\cdot\frac{1}{F(y)}\cdot\frac{\partial^2 F(y)}{\partial y^2} - \frac{h^2}{8\pi^2 m_e}\cdot\frac{1}{F(z)}\frac{\partial^2 F(z)}{\partial z^2} = E \quad \text{— 4)}$$

or, $$-\frac{h^2}{8\pi^2 m_e}\left[\frac{1}{F(x)}\cdot\frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{F(y)}\cdot\frac{\partial^2 F(y)}{\partial y^2} + \frac{1}{F(z)}\cdot\frac{\partial^2 F(z)}{\partial z^2}\right] = E \quad \text{— 4a)}$$

Energy is a function of 3- coordinates x, y and z. Equations 4) and 4a) shows that first term is a function of x only, independent of y and z. 2nd term is a function of y only, independent of x and z, and 3rd term is a function of z only, independent of y and x. Sum of three terms is equal to a constant amount, the energy E.

$\therefore$ E, total energy of the system is constant it is written as the sum of three contributions associated with the three coordinates x, y, z. Equation 4a) may be separated into 3 equation

One from contribution of x giving E_x

" " " " y " E_y

" " " " z " E_z

and sum of E_x, E_y and E_z gives total E.

For motion along x axis where x- varies, y, z remains constant, the 2nd and 3rd terms and R.H.S. remains constant. Hence

$$\boxed{-\frac{h^2}{8\pi^2 me}\cdot\frac{1}{F(x)}\cdot\frac{\partial^2 F(x)}{\partial x^2} = E_x} \qquad \text{---- 5a)}$$

Simy. for motion along y axis where y varies & x, z remain constt.

$$-\frac{h^2}{8\pi^2 me}\cdot\frac{1}{F(y)}\cdot\frac{\partial^2 F(y)}{\partial y^2} = E_y \qquad \text{---- 5b)}$$

For motion along z axis where z varies and y and x remains constant

$$-\frac{h^2}{8\pi^2 me}\cdot\frac{1}{F(z)}\frac{\partial^2 F(z)}{\partial z^2} = E_z \qquad \text{——— 5c)}$$

——— 6)

and $E = E_x + E_y + E_z$

Each of equation 5) is of the form,

$$\boxed{\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 me}{h^2} E\,\psi(x) = 0} \qquad \text{——— 7)}$$

{ble
From eq^n 5a) $\frac{\partial^2 F(x)}{\partial x^2} = -\frac{8\pi^2 me}{h^2} E_x F(x)$ } $\because F(x) = \psi$

Equation 7) can be written as,

$$\frac{\partial^2\psi}{\partial x^2} + k^2\psi(x) = 0 \qquad \text{——— 7a)}$$

where $\boxed{k^2 = \frac{8\pi^2 me}{h^2} E}$ ——— 7b)

comparing equations 7a) and 7b) with that of eq^n 3) and 4) of particle in one dimensional system and subjected to the boundary condition that

$\psi = 0$ at $x = 0$, $x = a$, $V = 0$

the wavefunction and energy term associated with eq^n 5a),

$$F(x) = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi}{a}x \qquad \text{——— 8)}$$

→ $\psi(x)$ value similar to eq^n (13) in 1-D

and $E_x = \frac{n_x^2 h^2}{8 me a^2}$ ——— (9)

→ Energy along x axis similar to eq^n 14) in 1-D

where n_x is an integer not including zero

There are similar solutions for the functions F(y) and F(z) which involve the quantum no., n_y and n_z respectively.

The Final form is :. given by the eqn

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

$$\psi(x,y,z) = \sqrt{\frac{8}{a^3}} \cdot \sin\frac{n_x\pi}{a}x \times \sin\frac{n_y\pi}{a}y \times \sin\frac{n_z\pi}{a}z \quad \text{— 10)}$$

Energy, $E = E_x + E_y + E_z$

$$E = \frac{h^2}{8m_e a^2}\left(n_x^2 + n_y^2 + n_z^2\right) \quad \text{— 11)}$$

where n_x, n_y, n_z are integers other than zero and may have value 1, 2, 3 →

If the dimensions of the box be a, b, c lying along x, y, z, then

wave function for particle in 3-dimensi box → 12)

$$\psi(xyz) = \sqrt{\frac{8}{abc}} \sin\frac{n_x\pi}{a}x \cdot \sin\frac{n_y\pi}{b}y \cdot \sin\frac{n_z\pi}{c}z$$

and $E = E_x + E_y + E_z$

$$E = \frac{h^2}{8m_e^2}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \quad \text{— 13)}$$

From the eqⁿ 11) and 13), it is again seen that energy of particle is quantized and requires the 3 quantum numbers (n_x, n_y, n_z) for the 3 degrees of freedom allowed.

Zero Point Energy

The zero point energy is three times that for 1 dimensional box

Ex Minimum value of n will be 1

$\therefore n_x = n_y = n_z = 1$

$$\therefore E_0 = \frac{h^2}{8 m_e a^2} (1^2 + 1^2 + 1^2)$$

$$\boxed{E_0 = \frac{3h^2}{8 m_e a^2}}$$

for 1-Dimensional box,

minimum $E_0 = \frac{h^2}{8 m_e a^2}$

$\therefore$ Minimum energy, E_0,

$$\boxed{E_{0\,(3d)} = 3 E_{0\,(1\text{-dim})}}$$

Degeneracy of Energy levels :-

$$E = \frac{h^2}{8m_e a^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Since total energy for particle in 3D box depends upon sum of the squares of the 3 quantum numbers hence it is possible that groups of different states, each specified by a unique set of quantum nos. can have the same energy. In such a case, the energy level and the corresponding independent states are said to be degenerate.

The lowest energy level, E_1, have $n_x = n_y = n_z = 1$ (and n cannot be zero, though it is allowed but not accepted)

$$E_1 = \frac{3h^2}{8m_e a^2} = 3E_0 \quad \text{where } E_0 = \frac{h^2}{8m_e a^2}$$

⇒ i.e. For the lowest quantum state (111), in which n_x, n_y and n_z equal to unity, there is only one set of quantum numbers that gives this energy state and this level is said to non-degenerate.

Second energy state :- There are three sets (112), (121), (211) of the quantum numbers n_x, n_y, and n_z that will give the same energy level,

$$E_2 = \frac{6h^2}{8m_e a^2} \text{ or } 6E_0$$

Such a level is said to be degenerate. In this case, it is triply degenerate

Simply, for third energy state, — there are 3 quantum states (122), (212), (221), of quantum nos n_x, n_y, n_z give the same energy level, $E = \frac{9h^2}{8ma^2} = 9E_0$

$\Rightarrow$ triply degenerate.

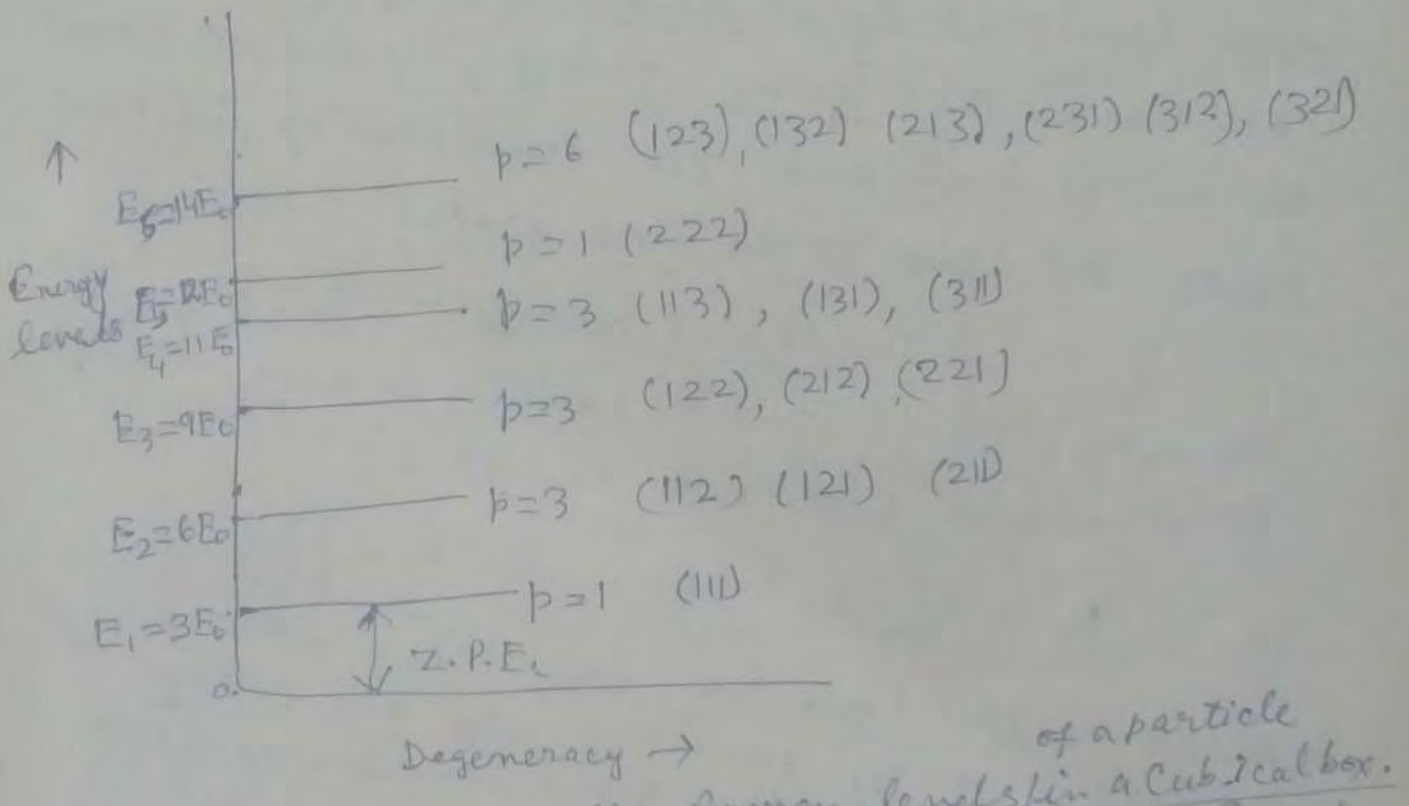
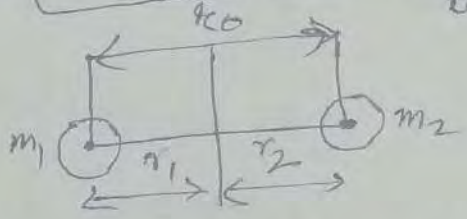


Fig- Degeneracy of the Energy levels of a particle in a Cubical box. The energy scale is in units of $h^2/8ma^2$ ($= E_0$)

Rigid Rotor

A diatomic molecule rotating about the axis perpendicular to the internuclear axis and passing through the centre of gravity of the molecule may be taken as an example of a Rigid Rotor.

r_0 = The distance b/w mass centre of the particles which is equal to the sum of r_1 and r_2



Let us assumed that the internuclear distance does not change during the rotation.

The term rigid being employed because of the ~~rotator means that~~ the fixed distance b/w the particle or molecule. The K.E. of the molecule is

$$I = \sum_i m_i r_i^2$$

$$K.E. = T = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$$

ω = Angular velocity, I = moment of Inertia of Rotating molecule

L = Angular momentum, $L = I\omega$.

If no force act on rotor, P.E. may be taken as zero,

$V = 0$

Hence Hamiltonian is expressed as

$$H = T + V$$

$$\text{or } H = \frac{L^2}{2I} \quad \text{---------- 1)}$$

The Schrödinger equation

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

The expression for L^2 in spherical coordinate is (r, θ, ϕ) But here we leave the radial part so L^2 is a function of (θ, ϕ)

$$L^2 = \hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \quad \text{---- 2)}$$

$$\text{---- (3)}$$

$$H\psi = E\psi \quad \text{----}$$

$\hbar = h/2\pi$

$\hbar^2 = h^2/4\pi^2$

$\because \hat{H} = L^2/2I$

$$\text{or } \frac{1}{2I}\left[-\hbar^2 \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\psi}{\partial\theta}\right) \right\} + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} \right] = E\psi \quad \text{---- (4)}$$

eq^n 4) may be rearranged as

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} = \frac{8\pi^2 I}{h^2} E\psi \quad \text{---- 5)}$$

This eq^n (5) contains 2 variables ϕ and θ, it can be solved by the method of separation of variables

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi) \quad \text{---- 6)}$$

Differentiating eq^n 6) first w.r.t. θ keeping ϕ constant and then w.r.t. ϕ keeping θ constant.

$$\left.\begin{aligned} \frac{\partial\psi}{\partial\theta} &= \Phi \frac{d\Theta}{d\theta} \\ \frac{\partial\psi}{\partial\phi} &= \Theta \frac{d\Phi}{d\phi} \end{aligned}\right\} \quad \text{---- (7)}$$

Substituting eq. 6) and 7) in eq^n 5) and multiplying throughout by $\frac{\sin^2\theta}{\Theta\Phi}$, we get,

$$\frac{\sin\theta}{\Theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\Theta}{\partial\theta}\right) + \frac{8\pi^2 I E}{h^2} \sin^2\theta = -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} \quad \text{---- 8)}$$

Each side of eq^{n} 8) contain only one variable hence we can equate each side of eq^{n} 8) equal to a constant. Let this constant be m^2. Thus we can obtain two differential eq^{n} each having one

$$\text{i.e., } -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = m^2$$

$$\text{or } \frac{\partial^2\Phi}{\partial\phi^2} + m^2\Phi = 0 \quad \text{---------} \quad (9)$$

$$\text{and } \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \quad \text{---} \quad 10)$$

$$\text{where } \beta = 8\pi^2 IE/h^2$$

One of the solution of eq^{n} (9) is

$$\Phi = c\,e^{\pm im\phi} \quad \text{---------} \quad 11)$$

where c is the normalization const. and for evaluating c we apply the condition that at any point the function Φ must be single valued.

Applying Normalization ~~Constant~~ Condition

$$\int_0^{2\pi} \Phi\,\bar{\Phi}\,d\phi = 1$$

$$\text{i.e., } \int_0^{2\pi} c\,e^{\pm im\phi}\cdot c\,e^{\mp im\phi}\,d\phi = 1 \quad \text{---------} \quad 12)$$

$$\text{or } c^2\int_0^{2\pi} d\phi = 1 \quad \text{---------} \quad 13)$$

$$\text{or } c^2\,[\phi]_0^{2\pi} = 1$$

$$\text{or } c^2 \cdot 2\pi = 1$$

$$\boxed{c = \frac{1}{\sqrt{2\pi}}}$$

Hence normalized wave functions become

$$\Phi_{\pm m}(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i m \phi}$$

$$m = 0, 1, 2, 3, \cdots \qquad \text{---- 15}$$

Solution of equation 10) can be obtained by using Legendre polynomial,

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\Theta}{\partial\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\Theta = 0$$

of degree l and order m

The normalized solution for Θ is

$$\Theta(\theta) = \Theta_{l\pm m} = \left[\frac{(2l+1)(l-|m|)!}{2\,(l+|m|)!}\right]^{1/2} P_l^{|m|}\cos\theta \qquad (1)$$

One satisfactory solution occurs only if $\beta = l(l+1)$ where 'l' is a positive integer $l = 0, 1, 2, \cdots$ greater or equal to m ($l \geq |m|$)

The energy or eigen value for rigid rotor are obtained from eq^n 10) where β

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

$$\text{or } E = \frac{l(l+1)h^2}{8\pi^2 I} \; ; \; l = 0, 1, 2, 3, \cdots \qquad \text{---- 17}$$

In spectroscopy, above symbol J rather than l has been used for rotational quantum number, $\therefore$ the rotational energy level is

$$E_J = \frac{J(J+1)h^2}{8\pi^2 I} \; ; \; J = 0, 1, 2, 3, \cdots \qquad \text{---- 18}$$

Harmonic Oscillator

One-dimensional Simple Harmonic Oscillator

A diatomic vibrating molecule can be represented by a simple model, called simple harmonic oscillator (S.H.O).

The force acting on the molecule is

$$f = -kx$$

where x is the displacement from the equilibrium position and k is a constant, called the force constant

P.E. diag. for a S.H. oscillator

The P.E. $V(x)$ of this molecule is given by

$$V(x) = -\int_0^x f\,dx \qquad \text{---------- 1)}$$

$$= \int_0^x kx\,dx = \frac{1}{2}kx^2 \qquad \text{---------- 2)}$$

Eqn 2) is the equation of a parabola. Thus, if we plot potential energy of a particle executing simple harmonic oscillations as a function of displacement from the equilibrium position, we get a curve as shown in fig.

The vibrational frequency of the oscillator of mass m is given by

$$\nu = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{1/2} \qquad \text{---------- 3)}$$

The vibrational frequency may be defined more accurately as

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad \text{---- (4)}$$

where μ is the reduced mass of the diatomic molecule, defined as

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \text{---- (5)}$$

where m_1 and m_2 are the atomic masses of the two atoms.

∴ Schrödinger wave equation for a single particle

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

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

For a particle oscillating in one direction only, e.g. parallel to the x axis, the y and z remain constant, the wave equation for one dimensional system reduces to

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

or, $$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0 \quad \left(\because \hbar = \frac{h}{2\pi}\right) \qquad \text{---- (6)}$$

in which ψ is an appropriate eigenfunctions, and E is the corresponding eigen value of the total energy.

Inserting the value of P.E. from eq^n 2) into eq^n 6)

we get,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0 \quad \text{— 7)}$$

To simplify the form of this differential equation,

Let $\alpha = \frac{8\pi^2 mE}{h^2} = \frac{2mE}{\hbar^2}$ — 7a)

and $\beta = \frac{4\pi^2 \nu' m}{h}$ where $\nu' = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{1/2}$

$$= \frac{(mk)^{1/2}}{\hbar} \quad \text{— 7b)}$$

$$\sqrt{\beta} = \frac{(mk)^{1/2}}{\hbar}$$

The eq^n (7) can be expressed in terms of α and β

$$\frac{d^2\psi}{dx^2} + (\alpha - \beta^2 x^2)\psi = 0 \quad \text{— — — — 8)}$$

Introducing, in place of x, a new dimensionless variable ξ, ξ defined by

$$\xi = \beta^{1/2} x. \quad \text{— — — 9)}$$

$$\text{or } \frac{d}{dx} = \sqrt{\beta}\frac{d}{d\xi} \quad \text{— 9a)}$$

$$\text{or } \frac{d^2}{dx^2} = \beta\frac{d^2}{d\xi^2} \quad \text{— 9b)}$$

Hence eq^n 8) becomes $\beta\frac{d^2\psi}{d\xi^2} + (\alpha - \beta^2 x^2)\psi = 0$

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0 \quad \text{— — — 10)}$$

Eq^{n} 10) has a solution of the form

$$\psi(\xi) = \phi(\xi) e^{-\xi^2/2} \quad \text{---} \quad 11)$$

where $\phi(\xi)$ is a function of ξ, and series of ξ.

Differentiating eq^{n} (11)

$$\frac{d^2\psi}{d\xi^2} = e^{-\xi^2/2}\left\{ \frac{d^2\phi}{d\xi^2} - 2\xi \frac{d\phi}{d\xi} + (\xi^2 - 1)\phi \right\} \quad \text{---} \quad 11a)$$

in which ϕ is written for $\phi(\xi)$

Putting ψ and $\frac{d^2\psi}{d\xi^2}$ in equation 10), we get

$$e^{-\xi^2/2}\left\{ \frac{d^2\phi}{d\xi^2} - 2\xi \frac{d\phi}{d\xi} + (\xi^2 - 1)\phi \right\} + e^{-\xi^2/2}\left(\frac{\alpha}{\beta} - \xi^2\right)\phi = 0$$

$$\therefore e^{-\xi^2/2}\left\{ \frac{d^2\phi}{d\xi^2} - 2\xi \frac{d\phi}{d\xi} + \left(\frac{\alpha}{\beta} - 1\right)\right\}\phi = 0 \quad \text{---} \quad 11b)$$

$\because e^{-\xi^2/2}$ is not zero, except for $\xi = \pm\infty$ and hence the expression in the bracket must be zero, i.e.

$$\frac{d^2\phi}{d\xi^2} - 2\xi \frac{d\phi}{d\xi} + \left(\frac{\alpha}{\beta} - 1\right)\phi = 0 \quad \text{---} \quad 12)$$

Equation 12) is identical to a <u>second order differential equation</u>, called the <u>Hermite equation</u>

$$\frac{d^2\phi}{d\xi^2} - 2\xi \frac{d\phi}{d\xi} + 2n\phi = 0 \quad \text{---} \quad 13)$$

The Hermite equation has solutions which depend upon the value of n. These solutions are called <u>Hermite polynomials</u>, $H_n(\xi)$, i.e.

$$\phi(\xi) \equiv H_n(\xi)$$

The Hermite polynomial of degree n is defined as

$$H_n(\xi) = (-1)^n e^{\frac{\xi^2}{2}} \left[\frac{d^n (e^{-\frac{\xi^2}{2}})}{d\xi^n} \right] \quad \text{---- (14)}$$

A few Hermite polynomials are given below

$$H_0(\xi) = 1$$

$$H_1(\xi) = 2\xi$$

$$H_2(\xi) = 4\xi^2 - 2$$

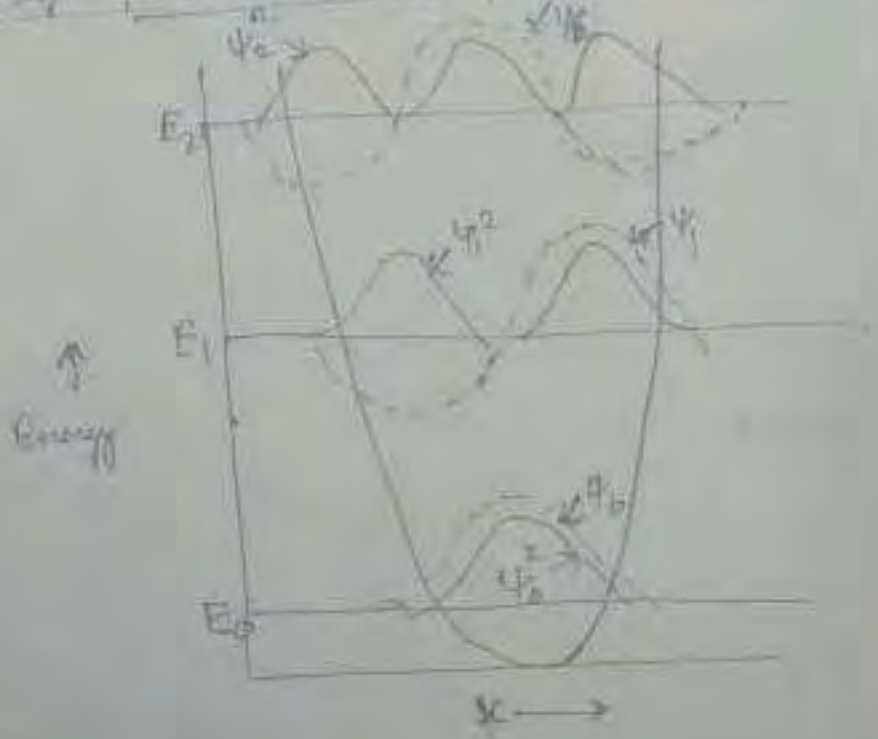
$$H_3(\xi) = 8\xi^3 - 12\xi$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$$

The normalized wave functions for the known of the one-dimensional S.H.O. are then written as

$$\psi_n(\xi) = \left[\frac{\beta^{1/2}}{2^n n! \sqrt{\pi}} \right]^{1/2} e^{-\xi^2/2} H_n(\xi) \quad \text{---- (15)}$$

where the first three wave functions (with $n = 0, 1, 2$), the corresponding energy levels and probability functions ψ_n^2 for the SHO are shown



Energy of S.H.O.:

The energy of the S.H.O. is obtained by comparing eq^{n} 12) and 13)

$$\alpha/\beta - 1 = 2n$$

$$\frac{\alpha}{\beta} = 2n + 1 \qquad \text{---------- 16)}$$

Substituting for α and β from eq^{n}s. 7a) and 7b)

$$\left(2mE/\hbar^2\right) \Big/ (mk)^{1/2}/k = 2n+1$$

$$= 2n+1$$

or, $$\frac{2mE}{\hbar} \times \frac{1}{(mk)^{1/2}}$$

$$E = \frac{1}{2m}(2n+1) \times \hbar (mk)^{1/2}$$

$$= \left(n + \tfrac{1}{2}\right) m^{1/2-1} \cdot k^{1/2}$$

$$= \left(n+\tfrac{1}{2}\right)(k/m)^{1/2}\hbar$$

$$\therefore E = \left(n+\tfrac{1}{2}\right)\hbar\,(k/m)^{1/2} \qquad \text{---------- 17)}$$

$\because$ eq^{n} 3) $\quad \nu = \frac{1}{2\pi}(k/m)^{1/2}$

$$\therefore (k/m)^{1/2} = 2\pi\nu \qquad \text{---------- 18)}$$

combining eq^{n}s 17) and 18)

$$E = E_n = \left(n+\tfrac{1}{2}\right)\hbar(2\pi\nu)$$

$$\boxed{E_n = \left(n+\tfrac{1}{2}\right)h\nu \;;\; n = 0, 1, 2, 3, \ldots} \qquad \text{--- 19)}$$

$\hbar = h/2\pi$

Zero point energy :-

The energy state with $n=0$ is the vibrational ground state with energy

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

This energy is called the zero point energy of the oscillator. classical mechanics predicts that the zero-point energy of the oscillator is zero whereas quantum mechanics predicts that the zero-point energy of the oscillator is non-zero.