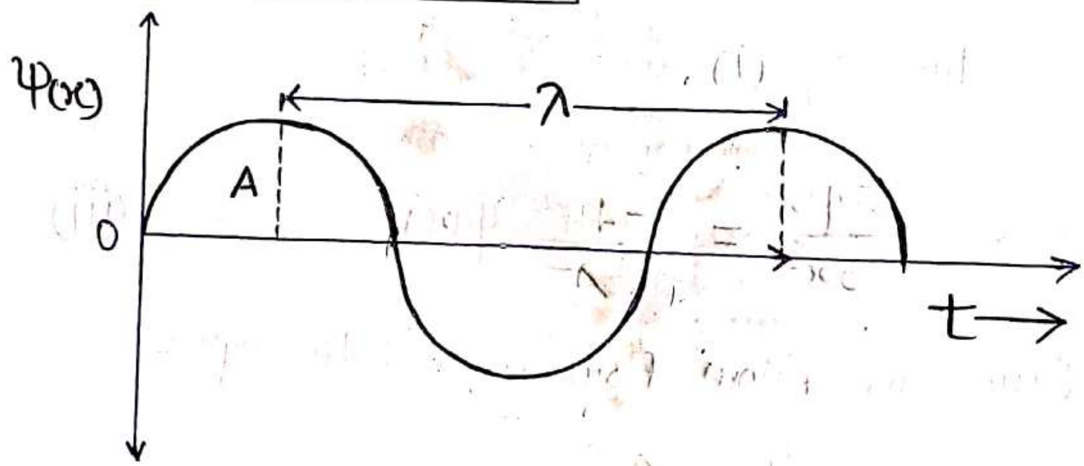
04/01/2020

Elementary Quantum Mechanics

Schrodinger wave eqn — Derivation

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

$$\boxed{\lambda=\frac{h}{mv}=\frac{h}{p}}$$ According to de-Broglie



Schrodinger derived a wave eqn for the e⁻-wave and is known as Schrodinger wave eqn.

The e⁻ wave can be represented as shown in above fig.

Here, in this fig., λ is wavelength, A is the amplitude and $\psi(x)$ is the displacement known as wave function.

Such a wave function ψ is used to represent the wave,

$$\psi(x)=A\sin\frac{2\pi x}{\lambda} \quad \text{— (i)}$$

$\psi(x)$ — spatial factor of amplitude, also known as spatial amplitude.

Differentiate this eqⁿ with respect to x.

$$\frac{\partial \psi(x)}{\partial x} = \left[A \cos \frac{2\pi}{\lambda} x\right] \frac{2\pi}{\lambda}$$

Again differentiating above eqⁿ with respect to x.

$$\frac{\partial^2 \psi(x)}{\partial x^2} = A\left[-\sin \frac{2\pi}{\lambda} x\right] \frac{2\pi}{\lambda} \times \frac{2\pi}{\lambda}$$

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \left(A \sin \frac{2\pi}{\lambda} x\right) \quad \text{—— (ii)}$$

from eqⁿ (i),

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi(x) \quad \text{—— (iii)}$$

Since we know from de-Broglie eqⁿ —

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

on squaring both sides

$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

Putting the value of λ^2 in the above eqⁿ (iii).

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{4\pi^2 m^2 v^2}{h^2} \psi(x) \quad \text{—— (iv)}$$

we know that total energy, E.

$$E = K.E. + P.E.$$

$$E = \frac{1}{2}mv^2 + V$$

$$[E-V] = \frac{1}{2}mv^2$$

$$2m(E-V) = (mv)^2 = m^2v^2$$

Putting this value of m^2v^2 in eq^n (iv).

$$\frac{\partial^2\psi(x)}{\partial x^2} = -\frac{4\pi^2\, 2m(E-V)}{h^2}\psi(x)$$

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

or

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

Above eq^n [v] is known as Schrodinger wave eq^n only in one direction [x].

Since the movement of the particle is always in three dimensional, hence eq^n (v) can be written in three dimensional as following—

$$\boxed{\frac{\partial^2\psi(x,y,z)}{\partial x^2} + \frac{\partial^2\psi(x,y,z)}{\partial y^2} + \frac{\partial^2\psi(x,y,z)}{\partial z^2} + \frac{8\pi^2 m}{h^2}[E-V]\psi(x,y,z) = 0} \qquad \text{— (vi)}$$

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

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

Laplacian Operator —

Eq^n (viii) can be written as,

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

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

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

∇ - Laplacian operator

Eq^n 8 is Schrodinger wave eq^n in the Laplacian operator form.

Hamiltonian Operator —

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

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

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

On multiplying above eq^n with $-\frac{h^2}{8\pi^2 m}$ on both sides,

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

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

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

Schrodinger wave eq^n in <u>Hamiltonian Operator form.</u>

where — $\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V$ = Hamiltonian operator

<u>Eigen values and Eigen functions — or Wave functions</u>

We know that Schrodinger wave equation is a second order differential eq^n and can have so many solutions for ψ [amplitude function]. But not all, only few values of ψ are acceptable which corresponds to total energy E, have definite values. Such values of the total energy E are called <u>eigen values</u>. These values are also called proper values or characteristic values. The corresponding values of the function ψ are called <u>eigen functions.</u> Only those wave-functions are acceptable in quantum mechanics, which are <u>**single valued**</u>, <u>continuous</u> and <u>finite</u> in the given Boundary conditions.

Born Interpretation of the wave function :
[or Significance of the wave function ψ]
[or Physical interpretation of the wave function]

The Schrodinger wave eqn is the fundamental equation of quantum mechanics. The solutions to the schrodinger equation are called wave function, ψ. A wave function ψ, gives a complete description of any system.

ψ has only mathematical significance. It has no physical significance because ψ can have real as well as imaginary values. Imaginary value of ψ never explain any property of the wave.

Since we know that function ψ represents the amplitude of vibration at any point. In the classical theory of electromagnetic radiation, the square of the amplitude is proportional to the intensity of the light.

$$\text{intensity of light} \propto [\text{amplitude}]^2$$
$$\propto \psi^2$$

A very similar concept was suggested by Born in quantum mechanics according to which the square of the wave function ψ at any point is proportional to the probability of finding the system at the point.

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This definition of Probability is in agreement with the uncertainty principle as one can not talk about the precise position of a subatomic particle.

Now the function ψ may be real or imaginary. Since the probability of finding a material particle at a given point in space has to be real, the Term ψ^2 has to be replaced by $\psi^*\psi$, where ψ^* is the complex conjugate of ψ.

Suppose ψ is an imaginary wave function, $\psi = a+ib$

Then the complex conjugate of this $\psi^* = a-ib$.

The complex conjugate can be obtained by replacing i by $-i$, as in the above case. where $i=\sqrt{-1}$

The probability of finding the particular system in the small volume element $dx\,dy\,dz$ situated at a point in space is proportional to

$$\psi^*\psi\, dx\,dy\,dz \quad \text{or} \quad \psi^*\psi\, d\tau$$

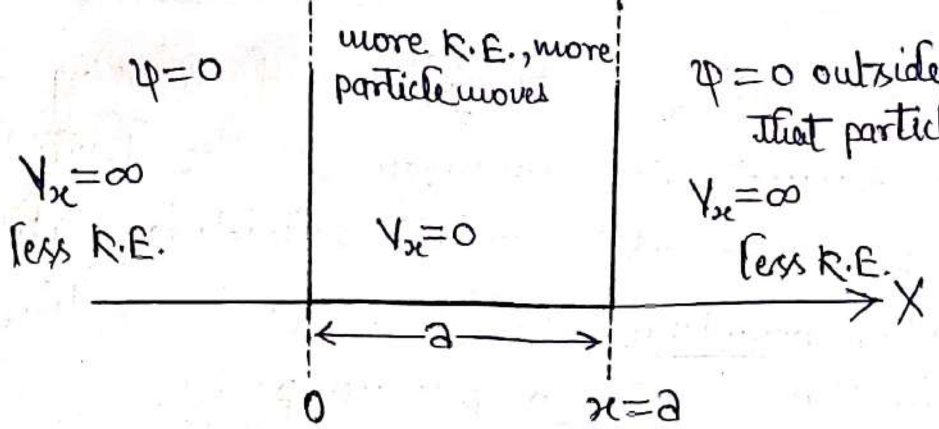
where $d\tau = dx\,dy\,dz$ and it represents the small element of the configuration space of the system or the whole of space where the system may occur.

Quantization of Translational Energy—

Introduction— A molecule may have three types of motions eg. Translation, rotational & vibrational. According to classical mechanics, the energy associated with each of the three motions can vary continuously, i.e. it can have any value. But according to wave mechanics, these energies are quantized, i.e. they vary in a discontinuous manner. We now consider the Translational motion from the wave-mechanical view point and show, taking a typical example of a particle in a box, how & why the quantization of energy takes place.

Particle in a one-dimensional box—

Let a free particle of mass m constrained to lie along the x axis between $x=0$ and $x=a$. This is called the problem of a particle in a 1-D box. Inside the box particle moving without experiencing any potential energy, i.e. $V=0$. The particle is not allowed to move outside this box. This can be achieved by setting a very high potential energy of infinity at the sides of the box, so that the moment the particle reaches the wall, it is reflected back instead of penetrating or crossing of the wall. This simple model has at least a crude application to the π-electrons in a linear conjugated hydrocarbon.



ψ = 0 outside the box, This means that particle can't exist outside the region $0<x<a$.

$$\because E = K.E. + P.E.$$

$$E = K.E. + V$$

inside the box, $V=0$, $\therefore E = K.E. + 0$

$$\boxed{E = K.E.}$$

Outside the box, $V=\infty$, $\therefore E = K.E. + \infty$

$$K.E. = E - \infty = -\infty$$

$$\boxed{K.E. = -\infty}$$

The Terminology "free particle" means that the particle experiences no potential energy i.e. $V=0$. If we set $V=0$ in SWE, we get,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0 \quad , \quad [0 \le x \le a] \text{ —— (i)}$$

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

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$
$\hbar$-reduced Planck const.

suppose, $\alpha^2 = \frac{8\pi^2 m E}{h^2}$

then above eqn (i) can be written as,

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \text{ —— (ii)}$$

Equation (ii) is the well known 2nd order differential eqn whose solution can be written or given as below—

$$\psi = A\sin\alpha x + B\cos\alpha x \text{ —— (iii)}$$

The particle is well with in the box and moving conti-
-nuously. To restrict the movement of the particle 10
with in the box, we apply certain restrictive conditions,
which are called boundary conditions. These conditions
are shown in the figure [on previous page].

According to the first boundary condition, when

$x=0$ & $\psi=0$

substituting these values in eq^n (iii)

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

$\because \sin 0 = 0$

& $\cos 0 = 1$

$\therefore$

$$0 = A \times 0 + B \times 1$$

$$B = 0.$$

putting this value in eq^n (iii)

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

$$\psi(x) = A \sin \alpha x \quad \text{—(iv)}$$

Applying IInd boundary conditions, when

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

putting this value in eq^n (iv)

$$0 = A \sin \alpha a$$

$\because$ A is an constant & $A \neq 0$

$\therefore \sin \alpha a = 0$

$\because \sin n\pi = 0$.
where, $n = 0, 1, 2, 3, 4 \ldots$

$\therefore \sin \alpha a = \sin n\pi$

$$\alpha a = n\pi$$

$$\boxed{\alpha = \frac{n\pi}{a}}$$

Putting this value of α in eq^n 4 -

$$\psi(x) = A \sin \frac{n\pi}{a} \cdot x \quad \text{—— (ii)}$$

Applying the condition of probability i.e. probability = 1 or the wavefunction should be normalised for which the condition is,

$$\int_{\text{lower limit}}^{\text{upper limit}} \psi^2(x)\, dx = 1$$

Applying the normalization condition in eq^n (ii)

$$\int_{x=0}^{x=a} \psi^2(x)\, dx = 1$$

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

$\because \cos 2x = 1 - 2\sin^2 x$

$\therefore 2\sin^2 x = 1 - \cos 2x$

$\sin^2 x = \frac{1-\cos 2x}{2}$

$$A^2 \int_0^a \sin^2 \frac{n\pi x}{a}\, dx = 1$$

or $A^2 \left[\frac{a}{2}\right] = 1$

$$A^2 = \frac{1}{a/2} = \frac{2}{a}$$

$$\boxed{A = \sqrt{\frac{2}{a}}}$$ Normalisation Constant

putting the value of A in eq^n 5.

$$\boxed{\psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x}$$

This is the solution of Schrodinger wave eq^n when particle in one dimensional box.

Total Energy of Particle in 1-D Box

we have assumed that,

$$\alpha^2 = \frac{8\pi^2 m}{h^2} \cdot E \quad \text{---(i)}$$

and we have also found out that,

$$\psi(x) = A \sin \alpha x$$

where $\alpha = \frac{n\pi}{a}$ ---(ii)

On squaring the eqn (ii) on both sides and equating it with eqn (i).

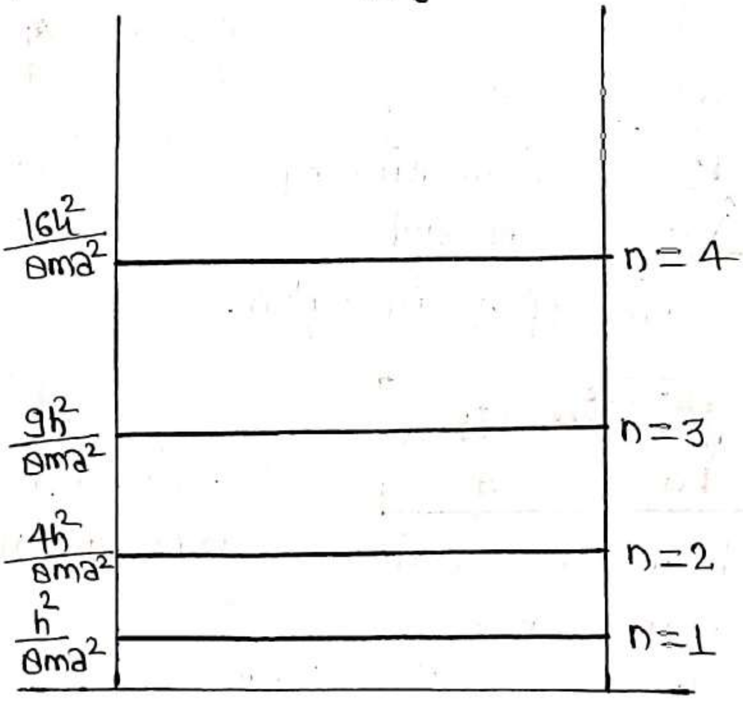
$$\alpha^2 = \frac{n^2\pi^2}{a^2}$$

$$\frac{n^2\cancel{\pi^2}}{a^2} = \frac{8\cancel{\pi^2} m}{h^2} \cdot E$$

$$\boxed{E = \frac{n^2 h^2}{8ma^2}}$$

where, $n = 1, 2, 3, \ldots$

This is the total energy in one dimensional box.



for 1D box – of 1 Å;
Energy of any state = $37.6 n^2$ eV

Factors at which the Energy, E depends—

(i) Energy has certain discrete value it is not continuous and called energy is quantized.

(ii) Total energy will increase by decreasing dimension of the box.

Probability Graph—

$n =$ Quantum Number

$(n-1) =$ Number of nodes

$\frac{x}{2n} =$ Maximum Probability.

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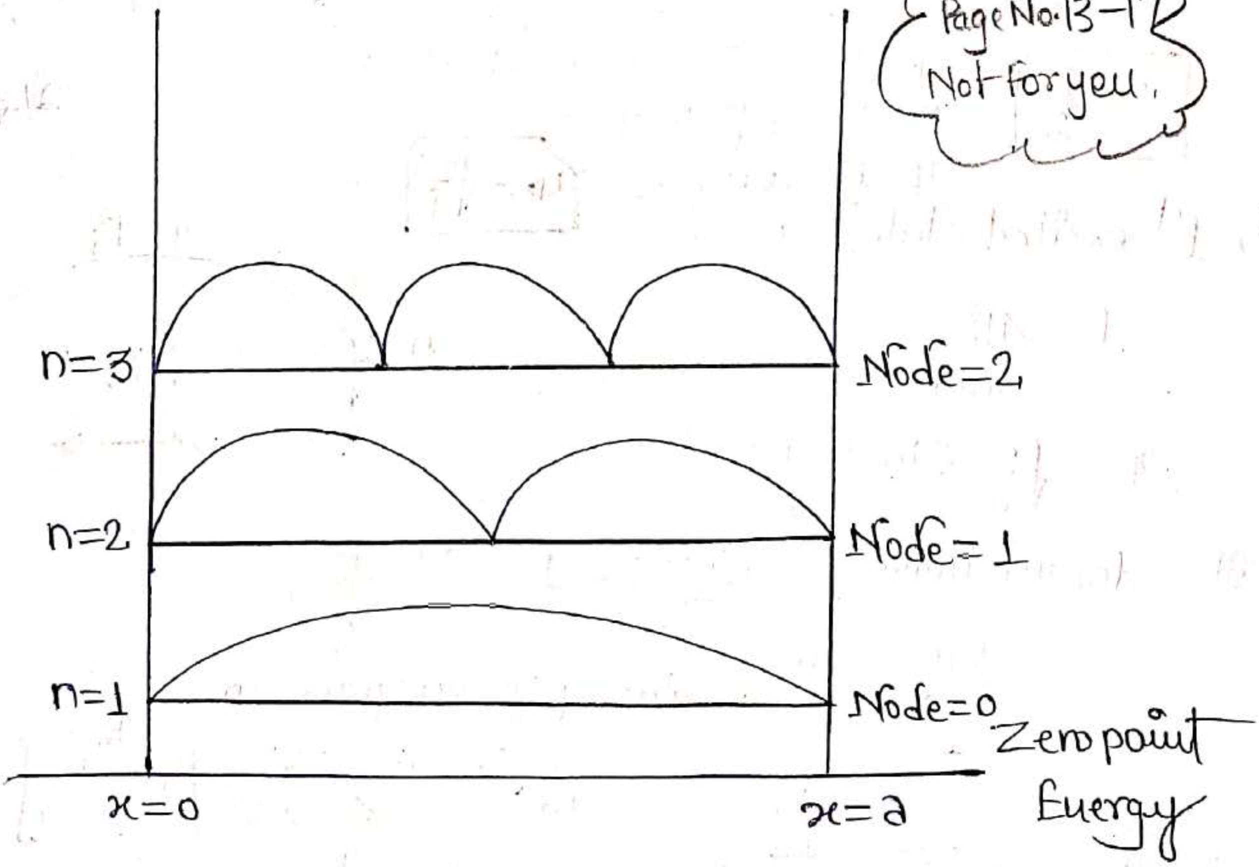


Fig. for particle in 1D box

Plot the graph of the wave function for the particle in a box —

Energy, $E = \frac{n^2 h^2}{8ma^2}$

Wave function, $\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$

(i) for ground state — $n = 1$

$$E = \frac{h^2}{8ma^2}$$

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$$

ψ is maximum when, $\sin \frac{\pi x}{a} = 1$

$$\sin \frac{\pi x}{a} = \sin \frac{\pi}{2} \Rightarrow \frac{\cancel{\pi} x}{a} = \frac{\cancel{\pi}}{2}$$

$\boxed{x = \frac{a}{2}} \Rightarrow \psi = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$ when $n = 1$; put $x = \frac{a}{2}$

we get $\psi = \sqrt{\frac{2}{a}} \sin \frac{\pi \times \cancel{a}}{\cancel{a} \times 2}$

$\psi = \sqrt{\frac{2}{a}} \sin \pi/2 \Rightarrow \boxed{\psi = \sqrt{\frac{2}{a}}}$

(ii) 1^{st} excited state — $n = 2$.

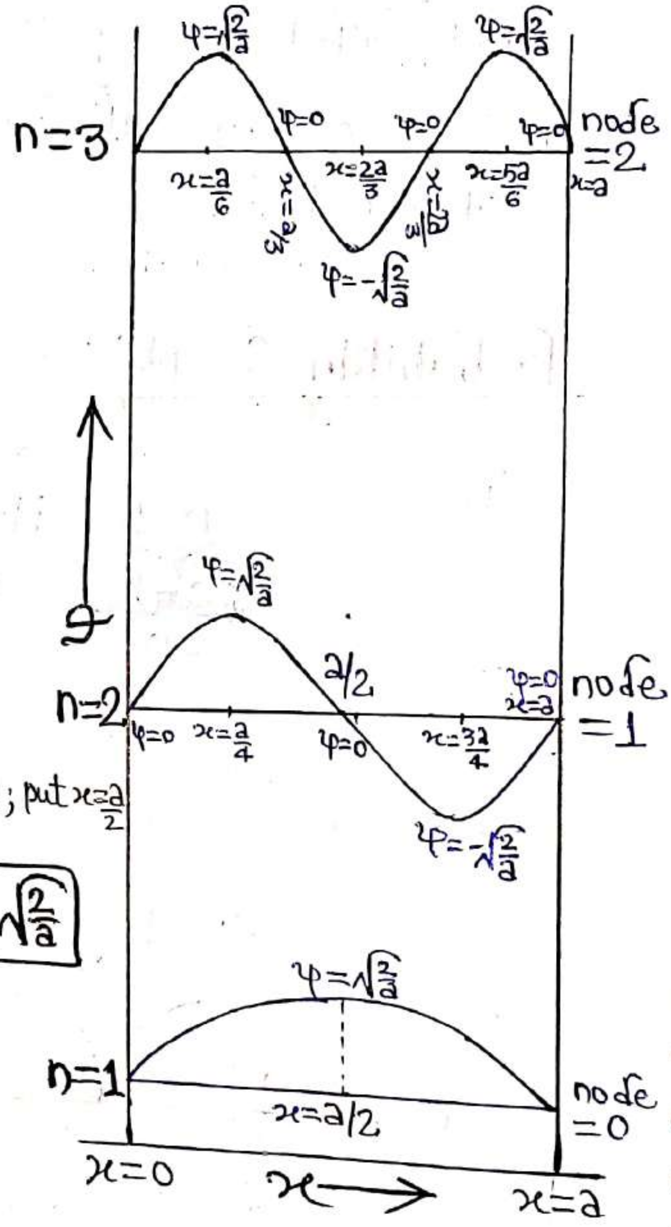
$$E = \frac{4h^2}{8ma^2}$$

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a}$$

a) for maximum, $\sin \frac{2\pi x}{a} = 1 = \sin \frac{\pi}{2}$

$\frac{2\cancel{\pi} x}{a} = \frac{\cancel{\pi}}{2}$; value of ψ corresponds to $x = \frac{a}{4}$

$\boxed{x = \frac{a}{4}}$; $\psi = \sqrt{\frac{2}{a}} \sin \frac{\cancel{2} \times \pi \times \cancel{a}}{\cancel{a} \times \cancel{4}_2} \Rightarrow \boxed{\psi' = \sqrt{\frac{2}{a}}}$



b) at $\frac{a}{4} + \frac{a}{4} = \frac{a}{2}$; value of ψ corresponds to $x = \frac{a}{2}$

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{2\pi}{a} x$$

On putting the value of $x = \frac{a}{2}$.

$$\psi = \sqrt{\frac{2}{a}}\ \sin \frac{2\pi}{\cancel{a}} \times \frac{\cancel{a}}{2}$$

$$\psi = \sqrt{\frac{2}{a}}\ \sin \pi$$

$$\boxed{\psi = 0}\ \&\ \boxed{x = \frac{a}{2}}$$

$\sin \pi = \sin 180°$

$\sin(90+90)$

$= \cos 90°$

$= 0$

$\sin, \operatorname{cosec}$ +ve | All +ve

$\tan, \cot$ +ve | $\sec, \operatorname{cosec}$ +ve

$\boxed{\pi = 180°}$

	$\sqrt{\frac{0}{4}}$	$\sqrt{\frac{1}{4}}$	$\sqrt{\frac{2}{4}}$	$\sqrt{\frac{3}{4}}$	$\sqrt{\frac{4}{4}}$
Angle	0°	30°	45°	60°	90°
Sin	0	$\frac{1}{2}$	$\sqrt{\frac{1}{2}}$	$\frac{\sqrt{3}}{2}$	1
Cos	1	$\frac{\sqrt{3}}{2}$	$\sqrt{\frac{1}{2}}$	$\frac{1}{2}$	0

c) $\frac{a}{4} + \frac{a}{4} + \frac{a}{4} = \frac{3a}{4}$

for $n=2$; corresponding wave-function is $\psi = \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a}$

put $x = \frac{3a}{4}$ in above function, we get

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{\cancel{2}\pi}{\cancel{a}} \times \frac{3\cancel{a}}{\cancel{4}2} \Rightarrow \psi = \sqrt{\frac{2}{a}} \sin \frac{3\pi}{2}$$

$$\psi = \sqrt{\frac{2}{a}} \sin\left(\pi + \frac{\pi}{2}\right) \Rightarrow \psi = \sqrt{\frac{2}{a}}\left[-\sin \frac{\pi}{2}\right]$$

$$\psi = \sqrt{\frac{2}{a}}\ (-1) \Rightarrow \boxed{\psi = -\frac{\sqrt{2}}{\sqrt{a}}}\ \&\ \boxed{x = \frac{3a}{4}}$$

d) $\frac{a}{4} + \frac{a}{4} + \frac{a}{4} + \frac{a}{4} = \frac{4a}{4} \Rightarrow x = a$

On putting $x = a$, in corresponding wave function

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{2\pi}{\cancel{a}} \times \cancel{a}$$

$\because \sin 2\pi = 0$

$$\psi = \sqrt{\frac{2}{a}} \sin 2\pi$$

$$\boxed{\psi = 0}\ \&\ \boxed{x = a}$$

2nd Excited State — i.e. $n=3$.

for $n=3$; energy, $E = \frac{(3)^2 h^2}{8ma^2}$

$$\boxed{E = \frac{9h^2}{8ma^2}}$$

Then the corresponding wave function; for $n=3$.

General wave function $\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x.$

i.e. for $n=3$; $\psi = \sqrt{\frac{2}{a}} \sin \frac{3\pi x}{a}$

$\because \sin \frac{\pi}{2} = 1$

a) for maximum,

$$\sin \frac{3\pi x}{a} = 1$$

$$\therefore \sin \frac{3\pi x}{a} = \sin \frac{\pi}{2}$$

or $\frac{3\cancel{\pi}x}{a} = \frac{\cancel{\pi}}{2}$

$$x = \frac{a}{3\times 2} \Rightarrow \boxed{x = \frac{a}{6}}$$

and the value of ψ when $x = \frac{a}{6}$.

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{\cancel{3}\pi}{\cancel{a}} \times \frac{\cancel{a}}{\cancel{6}2} \Rightarrow \psi = \sqrt{\frac{2}{a}} \sin \frac{\pi}{2}$$

$\because \sin \frac{\pi}{2} = 1$

$$\psi = \sqrt{\frac{2}{a}}$$

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b] $x = \frac{a}{6} + \frac{a}{6} = \frac{2a}{6} = \frac{a}{3}$ Then $\psi = \sqrt{\frac{2}{a}} \sin \frac{3\pi}{\cancel{a}} \times \frac{\cancel{a}}{\cancel{3}}$

$\psi = \sqrt{\frac{2}{a}} \sin \pi$ $\quad \because \sin 180 = 0.$

$\psi = 0$

at $\boxed{x = \frac{a}{3}}$; $\boxed{\psi = 0}$

$\sin 0° = 0$
$\sin \frac{\pi}{2} = 1$
$\sin \pi = 0$
$\sin \frac{3\pi}{2} = -1$
$\sin 2\pi = 0$

c] $x = \frac{a}{6} + \frac{a}{6} + \frac{a}{6} = \frac{3a}{6} = \frac{a}{2}$, Then $\psi = \sqrt{\frac{2}{a}} \sin \frac{3\pi}{\cancel{a}} \times \frac{\cancel{a}}{2}$

$\psi = \sqrt{\frac{2}{a}} \sin \frac{3\pi}{2}$

$\psi = -\sqrt{\frac{2}{a}}$

at $x = \frac{a}{2}$; $\psi = -\sqrt{\frac{2}{a}}$

$\frac{5\pi}{2} = \pi + \frac{3\pi}{2}$
or $\left[2\pi + \frac{\pi}{2}\right]$
$\sin\left(2\pi + \frac{\pi}{2}\right)$
$\sin \frac{\pi}{2} = 1$

d] $x = \frac{a}{6} + \frac{a}{6} + \frac{a}{6} + \frac{a}{6} = \frac{4a}{6} = \frac{2a}{3}$ Then $\psi = \sqrt{\frac{2}{a}} \sin \frac{\cancel{3}\pi}{\cancel{a}} \times \frac{2\cancel{a}}{\cancel{3}}$

$\psi = \sqrt{\frac{2}{a}} \sin 2\pi = 0$

at $\boxed{x = \frac{2a}{3}}$; $\boxed{\psi = 0}$

e] $x = \frac{a}{6} + \frac{a}{6} + \frac{a}{6} + \frac{a}{6} + \frac{a}{6} = \frac{5a}{6}$; then $\psi = \sqrt{\frac{2}{a}} \sin \frac{\cancel{3}\pi}{\cancel{a}} \times \frac{5\cancel{a}}{\cancel{6}2}$

$\psi = \sqrt{\frac{2}{a}} \sin \frac{5\pi}{2}$

$\sin \frac{5\pi}{2} = \sin \frac{\pi}{2} = 1$

$\psi = \sqrt{\frac{2}{a}} \times 1$

at $\boxed{x = \frac{5a}{6}}$; $\boxed{\psi = \sqrt{\frac{2}{a}}}$

f] $x = \frac{a}{6} + \frac{a}{6} + \frac{a}{6} + \frac{a}{6} + \frac{a}{6} + \frac{a}{6} = \frac{6a}{6}$; then $\psi = \sqrt{\frac{2}{a}} \sin \frac{3\pi}{\cancel{a}} \times \cancel{a}$

$x = a$

$\psi = \sqrt{\frac{2}{a}} \sin 3\pi \Rightarrow \psi = \sqrt{\frac{2}{a}} \times 0.$

at $\boxed{x = a}$; $\boxed{\psi = 0}$

$\sin 3\pi = \sin[\pi + 2\pi]$
$-\sin 2\pi = 0$
i.e. $\sin 3\pi = 0$
& $\sin \frac{5\pi}{2} = 1$

Postulates of Quantum Mechanics—

Postulate I— The Physical state of a system at time, t is completely described by a wave function ψ which is a function of co-ordinates $[x, y, z]$ and time.
The wave function ψ and its first derivative must be everywhere finite, continuous and single valued.
It may be real or complex.

Postulate II— To every observable in classical mechanics there corresponds an operator in quantum mechanics.

Postulates III— In any measurement of the observables associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a, which satisfy the eigenvalue equation.

$$\boxed{\hat{A}\psi = a\psi}$$

where ψ — Eigen state or Eigen function
a — Eigen value of $\hat{A}$.
$\hat{A}$ — an operator.

Postulates IV — The wave function or state function of a system evolves in time according to the Time-dependent Schrodinger equation.

$$\boxed{\hat{H}\psi = i\hbar . \frac{\partial \psi}{\partial t}}$$

We separate out the Time dependence by letting

$$\boxed{\psi(q,t) = \psi(q) \cdot e^{-2\pi i Et/h}}$$

or

$$\boxed{\psi(q,t) = \psi(q) \cdot e^{-iEt/\hbar}}$$

where E is the Energy. Hence the Time-independent wave equation is

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

Postulates V — If a system is in a state described by a normalized wave function ψ, Then The average value of the observable corresponding to $\hat{A}$ is given by—

$$\langle \hat{A} \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{A} \psi \, d\tau$$

where — $\langle \hat{A} \rangle$ — Expectation value or Average value.

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

where $\langle E \rangle$ — Expectation value for Energy

The expectation value of the operator $\hat{A}$ is a statistical average of The observed values of The quantity for which The operator $\hat{A}$ stands for — eg.

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

A postulates is a fundamental assumption or fundamental truth on which the theory is based and which does-not need a proof or support from anywhere.

The schrodinger wave equation was derived, use a wave and particle concept of e^-, this equation can also be derived without this concept & using the postulates of quantum mechanics.

The formulation of Quantum mechanics and wave mechanics for the wave mechanical treatment of structure of atom is also based upon these postulates. The postulates discussed above are for a system moving in any one direction.

Operator — Operator play an important role in quantum mechanics and any observable quantities in classical mechanics have an operator in Quantum Mechanics.

Observable Name	Observable Symbol	Operation
Position x	$\hat{x}$	multiplying by x
r	$\hat{R}$	multiplying by r
Momentum for 1-D p_x	$\hat{P}_x$	" $\frac{\hbar}{i}\frac{\partial}{\partial x}$
Momentum for 3-D $p=p_x+p_y+p_z$	$\hat{P}$	" $\frac{\hbar}{i}\nabla$
Kinetic Energy for 1-D K_x	$\hat{K}_x$	" $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
for 3-D K	$\hat{K}$	" $-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]$
Potential Energy for 1-D U_x	$\hat{U}_x$	multiplying by U_x
for 3-D U	$\hat{U}(x,y,z)$	multiplying by $U(x,y,z)$
Total Energy $E\,[K+U]$	$\hat{H}$	" $-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]+U(x,y,z)$
Angular Momentum		
$L_x = yp_z - zp_y$	$\hat{L}_x$	" $\frac{\hbar}{i}\left[y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right]$
$L_y = zp_x - xp_z$	$\hat{L}_y$	" $\frac{\hbar}{i}\left[z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right]$
$L_z = xp_y - yp_x$	$\hat{L}_z$	" $\frac{\hbar}{i}\left[x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right]$

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

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

∇ - Laplacian Operator

Acc. postulates 2nd.

Application of Quantum Mechanics to Hydrogen and Hydrogen-like particles

A hydrogen-like atom means a system consisting of two particles, one of which is negatively charged e^- and the other is a positively charged nucleus eg. H, $He^{\oplus}$, Li^{2+}, Be^{3+}. This is the simplest example of a system in which energy is not constant.

The application of Schrodinger wave equation to the above system has not only proved the concept of quantization of electronic energy and solved many of the problems of Bohr's Theory but has also given a justification for quantum numbers which were intro-duced earlier simply as a requirement of the spectro-scopic studies.

Since we know that Schrodinger wave equation for the motion of a single particle is given by —

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

<u>where</u> — m — mass of the particle.
E — Total Energy.
V — Potential Energy.
x, y, z — are the co-ordinates of the particle.

for hydrogen like particles, the mass m is replaced by the reduced mass, μ of the system given by—

$$\mu = \frac{m_e \times m_n}{m_e + m_n} \quad \text{—(ii)}$$

and V, for hydrogen like particle, given by—

$$V = -\frac{Ze^2}{r} \quad \text{—(iii)}$$

where— $-e$ — charge on e^-
$+Ze$ — charge on nucleus.
r — distance b/w e^- & nucleus

force acting b/w the particles [According to Coulomb's law] is-

$$F = -\frac{e(Ze)}{r^2} = -\frac{Ze^2}{r^2}$$

$$\because V = \int_\infty^r F dr = \int_\infty^r -\frac{Ze^2}{r^2} dr$$

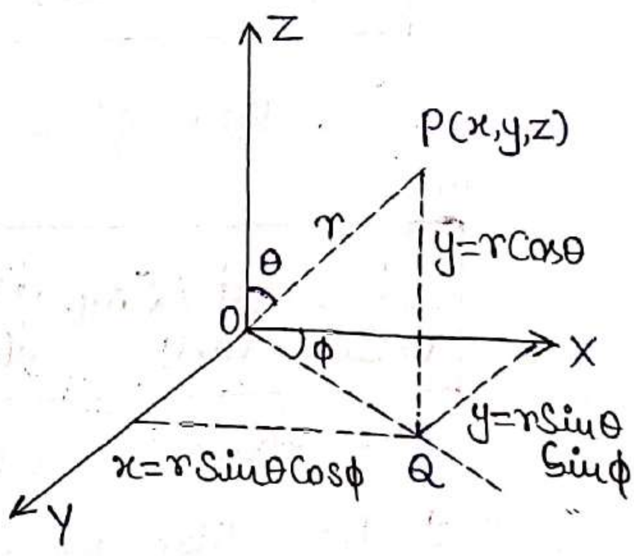
$$V = -\frac{Ze^2}{r}$$

On substituting values from eq^n (ii) & (iii) to eq^n (i), we get Schrodinger wave eq^n for H like particles in terms of cartesian co-ordinates—

$$\boxed{\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2\mu}{h^2}\left[E + \frac{Ze^2}{r}\right]\psi = 0}$$

in Polar-form,

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$



$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right]+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right]+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{r}\right]\psi=0.$$

Or

$$\boxed{\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{r}\right]\psi=0}$$

Above eq^n is the SWE in polar form, for H like particles.

Separation of variables—

ψ is a function of three variables r, θ & ϕ.
To separate the variables, first we assume that,

$$\psi(r,\theta,\phi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\phi) \quad \text{—— (i)}$$

we get,

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left[E+\frac{Ze^2}{r}\right]=\beta} \quad \text{—(ii)}$$

above eq^n is known as Radial equation.

and

$$\boxed{\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2}=-\beta} \quad \text{—(iii)}$$

above eq^n is known as Angular equation.

where— for H like particles— $\beta = l(l+1)$

where— $l = 0, 1, 2, 3, \ldots$

Again eqⁿ (iii) can be separated in Terms of θ & ϕ:—
we get—

$$\boxed{\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\beta\sin^2\theta = m^2} \quad \text{— (iv)}$$

and

$$\boxed{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2} \quad \text{— (v)}$$

Expression for the Angular spherical wave function—

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

where— $m = 0, \pm1, \pm2, \ldots$
— (vi)

Above eqⁿ (vi) is solution of eqⁿ (v) and following eqⁿ (vii) is the solution of eqⁿ (iv).

$$\boxed{\Theta^{|m|}_{l,m}\sqrt{\frac{2l+1}{2}\cdot\frac{\lfloor(l-|m|)}{\lfloor(l+|m|)}}\;P^{|m|}_l(\cos\theta)} \quad \text{— (vii)}$$

where $P^{|m|}_l$ represents Associated Legendre polynomial

The solutions of the angular equation, is given by $\Theta\Phi$, called spherical Harmonics.

Expression for the radial wave function—

The expression for the radial wave function [R] is obtained by solving the eqn – (ii). we get,

$$\boxed{R_{n,l} = N e^{-\rho/2} \rho^{l} L_{n+l}^{2l+1}(\rho)} \quad \text{— (viii)}$$

where— N - normalisation constant.
ρ - new variable in place of r
L_{n+l}^{2l+1} — is Associated Laguerre polynomial.