Module - III

Inadequencies of classical mechanics

Classical mechanics successfully explained the motion of the objects which are either observable directly or can be made observable by instruments like microscope.

When the classical concepts were applied to particles of atomic dimensions like electrons, they failed to describe the actual behaviour. Thus classical concept cannot be applied to atomic phenomenon. (Eg) Motion of electrons in an atom.

Failures

1) According to classical picture, the negatively charged electron experiences attractive electrostatic force due to positive charged nucleus. The energy of electrons should decrease continuously due to centripetal acceleration and it should come closer and closer until it collapses with nucleus

The above shows instability of an atom, but many atoms were and to more stable which is not clearly explained in classical mechanics

2) classical mechanics failed to explain the spectrum of hydrogen atom.

(ie) The excited atoms of hydrogen emit EM radiation of certain wavelength, while classical theory admits radiations of all wavelength continuously

3) Classical mechanics cannot explain black body radiation, Specific heat of solids at low temperatures

4) It cannot explain theory of atomic structure, Photo-electric effect and Compton effect.

In order to overcome above failures, Quantum theory was developed by Max plank and other scientist.

Black body radiation

Rayleigh and Jeans made a calculation of the energy density of cavity or blackbody radiation that points up a serious of conflict between classical physics and experimental results

A blackbody is one which absorbs all the heat radiation incident on it. Similarly during heating, it emits heat radiations with all possible wavelengths. As the temperature increases, the emitted radiation energy also increases. Further the wavelength corresponds to the maximum energy (λ_m) decreases with the increase of temperature

Thus $\lambda_m T$ = Constant = 2.897×10^{-3} mK

Plank's hypothesis

The classical theory failed to explain the experimentally observed distribution of energy in the spectrum of a black body. He discarded both the idea of radiation being a continuous stream as well as law of equipartion of energy.

Concept of photon

According to Max planck, radiation is not emitted in continuous fashion but in discrete bundles of energy equal to $h\nu$. These bundles (or) packets of radiations are called quanta (or) photons. It is obvious that quanta of radiation of different frequencies have different sizes (or) energies

The photon nature of radiation considers the radiation is still a wave phenomenon. But its energy contents are delivered to the atoms in quanta (ie) concentrated groups of waves. The photon structure of radiation also accounts for a number of phenomena such as Black body radiation, Photoelectric effect and Compton effect.

Properties of photons

1) Photon have no charge but can eject charged particles from matter when they impinge on atoms
2) Photon have wide range of energies and same velocity
3) If photon is considered as particle of radiation then mass, momentum and Energy are find as given below

(i) Its Energy $E = h\nu = hc/\lambda$

(ii) Its mass $E = h\nu = mc^2 = h\nu = \frac{h\nu}{c^2}$

(iii) Its momentum $(P) =$ mass $\times$ velocity

$$= \frac{h\nu}{c^2} \times c = \frac{h\nu}{c}$$

He suggested quantum theory of radiation. His assumption are: (4)

1) A black body radiation chamber is filled up not only with radiation but also particles which vibrate with all possible frequencies

2) The particle cannot radiate or absorb energy continuously. But particle of frequency (ν) can only radiate (or) absorb energy in units (or) quanta of magnitude ($h\nu$) [where h - Planck's Constant]

Therefore according to planck's hypothesis

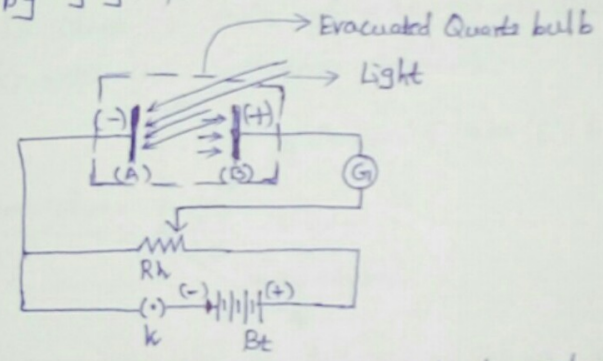
$$E = h\nu \quad \text{where } \nu = c/\lambda$$

Then $\boxed{E = \frac{hc}{\lambda}}$

Photoelectric effect

The emission of electrons from a metal plate when illuminated by light or any other radiation of suitable wave length or frequency is called photo electric effect. The emitted electrons are called photoelectrons

Discovered by Hertz when he allowed UV light to fall on zinc plate. Experimentally verified by J.J. Thomson, R.A. Mullikan and others



In the given experimental setup to study photoelectric effect, two photosensitive surfaces (A & B) are enclosed in a evacuated quartz bulb.

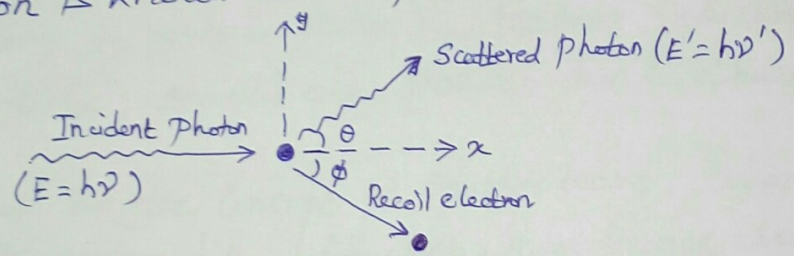
Plate (A) is connected to negative terminal of potential divider while plate B is connected to positive terminal through galvanometer (G). In absence of light, no current flow is observed and so galvanometer shows zero deflection. But when monochromatic light falls on plate (A), a current flows in circuit and galvanometer shows deflection. The current observed is called photo-current. This shows that when light falls on metallic surface, electrons are ejected.

The ejected electron depends on 1) potential difference between plate (A) and (B), 2) Intensity of incident radiation, (3) Frequency of incident radiation and (4) photo metal used

Compton effect

When X-rays of sharply defined frequency were incident on a material of low atomic number like Carbon, they suffered a change in frequency on Scattering.

(ie) The scattered beam contains two wavelengths. In addition to the expected incident wavelength, there exists a line of larger wavelength. The change of wavelength is due to loss of energy of the incident X-rays. This elastic interaction is known as Compton effect.



This effect was explained on the basis of quantum theory. The whole process is treated as a particle collision event between X-ray Photon and a loosely bound electron of the scatterer

In the photon - electron collision, a portion of the energy of the photon is transferred to the electron. As a result, the X-ray photon moves with less energy than the original energy and therefore it has a higher wavelength (or) lower frequency

Thus Loss of energy is $\propto \left[\frac{Z}{A}\right] \times \left[\frac{1}{E_n}\right]$

where Z and A are Atomic and mass number

$E_n \rightarrow$ Energy of incident Photon

De-broglie Hypothesis for matter wave

In 1924 - Louis de-Broglie proposed that matter (electrons, protons and other particles) has dual characteristic just like radiation. His concept about dual nature of matter was based on following observation

(i) The whole universe is composed of matter and EM radiation. Since both are forms of energy so can be transformed into each other

(ii) The nature loves symmetry. As the radiation has dual nature (wave inaddition to particle nature), matter (electrons or other atomic dimension particle) should also posses dual character.

According to de-Broglie concept of matter wave, when matter is moving it shows wave properties like diffraction, interference etc, and when matter is at rest it shows particle properties. The wave associated is called de-Broglie wave.

Wavelength of de-Broglie wave

Consider photon whose energy is given by $E = h\nu = \frac{hc}{\lambda} \rightarrow (1)$

If photon posses mass, then according to theory of relativity its energy

$E = mc^2 \rightarrow (2)$

From (1) & (2), mass of photon $\Rightarrow m = \frac{h}{c\lambda}$

Then momentum of photon $p = mc = \frac{h}{\lambda}$ then wavelength for de-Broglie wave is given by

$$\boxed{\lambda = \frac{h}{p}}$$

Special Cases

1) de-Broglie wavelength for material particle

If $E = \frac{1}{2}mv^2$ then $2E = mv^2$ (or) $2Em = m^2v^2 \Rightarrow \sqrt{2mE} = mv = p$

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

2) de-Broglie wavelength for particle in gaseous state

According to kinetic theory of gas $E = 3/2\,kT$

Also $E = p^2/2m$ $[\because \sqrt{2Em} = p]$

Then $\frac{p^2}{2m} = \frac{3}{2}kT \Rightarrow p^2 = \frac{\cancel{2}m \times 3}{\cancel{2}}kT \Rightarrow p = \sqrt{2kTm}$

$\therefore \boxed{\lambda = \frac{h}{\sqrt{2kTm}}}$

3) de-Broglie wave length for accelerated electron

If electron is accelerated with potential (V), then workdone on electron appears as gain in kinetic Energy $(E) = eV$

We know $E = p^2/2m$

Then $p^2/2m = eV \Rightarrow p = \sqrt{2meV}$

$\therefore \boxed{\lambda = \frac{h}{\sqrt{2meV}}}$

Wave function

In quantum mechanics, wave function is variable quantity that mathematically describes the wave characteristics of a particle. The value of wavefunction of a particle at a given point in space and time is related to particle being there at the time.

It is represented by (ψ) and it consist of real and imaginary part

(ie) $\psi = A + iB$

Physical significance of wavefunction

1) The wavefunction itself has no physical significance but the square of absolute magnitude $|\psi|^2$ has significance when evaluated at a particular point and at particular time

$|\psi|^2$ gives probability of finding particle there at a time

2) Probability of finding the particle in the length dx is

$$P.dx = \psi^*(x,t) \times \psi(x,t)\, dx$$

Total probability of finding particle along x-direction

$$\int P\, dx = \int \psi^*(x,t) \cdot \psi(x,t)\, dx$$

3) If the particle exists, it must be somewhere in x-direction then

$$\int P dx = \int \psi^*(x,t)\, \psi(x,t)\, dx = 1$$

If the above condition is satisfied then it is called normalised wave function.

Schrodinger wave equation - (1926)

If particle exhibits wave property - some sort of wave equation associated with the particle describing the behaviour of wave nature in addition to particle nature.

It is mathematical equation derived by connecting de-Broglie wavelength into classical mechanical equation for moving particle

This equation is applicable to both macro & microscopic particles

(i) Schrodinger Time independent wave equation

We know that total Energy of particle (E) = K.E + P.E

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

If momentum of particle is $p = mv$, we write $V = p/m$ then,

$$E = \frac{p^2}{2m} + V$$

If ψ is wavefunction associated to particle we write

$$E\psi = \left[\frac{p^2}{2m} + V\right]\psi \longrightarrow (1)$$

According to demoivers theorem, the solution for $\psi = e^{i(kx-\omega t)} \longrightarrow (2)$

Differentiate eq (2) w.r.to. x

$$\frac{\partial\psi}{\partial x} = ik\, e^{i(kx-\omega t)}$$

$$\frac{\partial\psi}{\partial x} = ik\psi \quad \text{(using eq-2)}$$

Again differentiate above eq. w.r.to. x

$$\frac{\partial^2\psi}{\partial x^2} = i^2k^2\psi$$

$$\frac{\partial^2 \psi}{\partial x^2} = (-1)\, k^2 \psi \qquad (\because i^2 = -1)$$

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2 \psi \rightarrow (3)$$

In the above equation 'k' is called propagation constant is given by $k = 2\pi/\lambda$ where λ is de-Broglie's wavelength $(\lambda) = h/p$

Then $k = \frac{2\pi p}{h}$, we know $h = \hbar 2\pi$ then $\boxed{k = \frac{p}{\hbar}} \rightarrow (4)$

sub (4) in (3) we get $\frac{\partial^2 \psi}{\partial x^2} = -\left(\frac{p^2}{\hbar^2}\right)\psi \rightarrow (5)$

If $p = mv$ then $p^2 = m^2 v^2$

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

$$2E = mv^2 + V$$

$\times$ by $m \Rightarrow$ $2mE = m^2 v^2 + mV$

$$2m(E-V) = m^2 v^2 \rightarrow (6)$$

sub (6) in eq (5) then

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

$$\boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E-V)}{\hbar^2}\psi = 0}$$

The above equation is called schrodinger time independent wave equation

(ii) Schrodinger time dependent wave equation

According to eq (1) we write $E\psi = \left[\frac{p^2}{2m} + V\right]\psi$

From eq (5) we have $\frac{\partial^2\psi}{\partial x^2} = -\left(\frac{p^2}{\hbar^2}\right)\psi$

$\times$ by $\hbar^2 \Rightarrow \quad -\hbar^2\left(\frac{\partial^2\psi}{\partial x^2}\right) = p^2\psi \rightarrow (7)$

Sub eq (7) in eq (1) we get

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

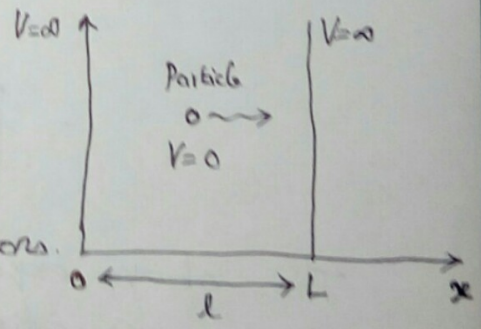
$$\boxed{E\psi = H\psi} \qquad \text{where } H = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right) + V\right]$$

Above equation is called schrodinger time dependent wave equation
Here E is Energy operator & H is Hamiltonian operator

Application of schrodinger wave equation:

(i) Wave function and Energy associated to particle (electrons) enclosed in 1-dimensional potential box

Consider particle of mass (m) moving along x-axis which is enclosed in 1-D potential box



At wall and outside of 1D potential box $V = \infty$, so particle does not penetrate & so confined within length (l) has elastic collisions.
Then Potential energy (V) = Constant, for simplicity V is taken zero inside

Therefore boundary conditions are

$V(x) = 0$ when $0 < x < L$

$V(x) = \infty$ when $0 \geq x \geq L$

As particle cannot exist outside so $\psi = 0$

Hence to find wavefunction of particle within 1D potential box, consider Schrodinger time independent wave equation

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

Inside $V = 0$ then $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E\psi = 0 \rightarrow (1)$

(or) $\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \rightarrow (2)$ $\left[\because k^2 = \frac{2mE}{\hbar^2}\right]$

Eq. (2) is second order differential equation, its solution must contain 2 - arbitrary constants

(ie) $\psi(x) = A \sin kx + B \cos kx \rightarrow (3)$

To find arbitrary constant, Applying boundary conditions

(ie) $V(x) = \infty$ when $x = 0$ & $x = L$

When $x = 0 \Rightarrow V(x) = \infty$ & $\psi(x) = 0$ then eq (3) becomes

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

$0 = 0 + B(1) \Rightarrow \boxed{B = 0} \rightarrow (4)$

When $x = L \Rightarrow V(x) = \infty$ & $\psi(x) = 0$ then eq (3) becomes

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

$0 = A \sin kL + (0) \cos kL$ (using eq - 4)

$0 = A \sin kL + 0$

Since $B = 0$ then $A \neq 0$ so $\sin kL = 0$

we know that $\sin n\pi = 0$ then

$$kL = n\pi$$

$$k = \frac{n\pi}{L} \rightarrow (5)$$

Sub (4) & (5) in eq (3) we get $\psi(x) = A\sin\left(\frac{n\pi}{L}\right)x + 0$

$$\therefore \boxed{\psi(x) = A\sin\left(\frac{n\pi}{L}\right)x} \rightarrow (6)$$

Above equation is wavefunction associated to particle enclosed in 1D potential box

Energy associated to particle in 1D potential box

We know $k^2 = \frac{2mE}{\hbar^2}$ (From eq -2)

$$k^2 = \frac{2mE}{(h^2/4\pi^2)} \quad (\because \hbar = h/2\pi)$$

$$k^2 = \frac{8\pi^2 mE}{h^2} \rightarrow (7)$$

Also squaring eq (5) we get $k^2 = \frac{n^2\pi^2}{L^2}$ — (8)

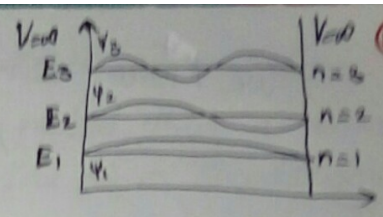
If (7 = 8) then $\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{L^2}$

$$\boxed{E = \frac{n^2h^2}{8mL^2}} \rightarrow (9)$$

Above relation is energy associated to particle enclosed in 1D potential box

To find energy level of particles, from eq (9)

when $n = 1 \Rightarrow E_1 = \frac{h^2}{8mL^2}$



when $n = 2 \Rightarrow E_2 = \frac{4h^2}{8mL^2} = 4E_1$

when $n = 3 \Rightarrow E_3 = \frac{9h^2}{8mL^2} = 9E_1$

In general n^{th} value (or) Energy level we write $\boxed{E_n = n^2 E_1} \rightarrow (10)$

Eq (10) refers energy level of particle in 1-D potential box.

Normalisation of wave function

It is process by which the probability (P) of finding the particle (electron) inside the box can be done

We know total probability (P) is equal to 1 means then there is a particle inside the box

For one dimensional potential box of length (L), Probability is

$$P = \int_0^L |\psi^2| dx = 1$$

$$P = \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1 \quad \text{(using eq - 6)}$$

$$= A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

$$= A^2 \int_0^L \frac{[1 - \cos 2n\pi L]/L}{2} dx = 1$$

(Integrating w.r.to.x) $\Rightarrow A^2 \left[\frac{x}{2} - \frac{1}{2} \frac{\sin 2n\pi x/L}{(2n\pi/L)}\right]_0^L = 1$

$$= A^2 \left[\frac{L}{2} - \frac{1}{2} \frac{\sin 2n\pi L/L}{(2n\pi/L)}\right] = 1$$

We know $\sin n\pi = 0$ then $\sin 2n\pi = 0$ then

$$\frac{A^2 L}{2} = 1 \Rightarrow A^2 = \frac{2}{L} \text{ (or) } A = \sqrt{\frac{2}{L}} \rightarrow (11)$$

Sub eq (11) in eq (6) we get

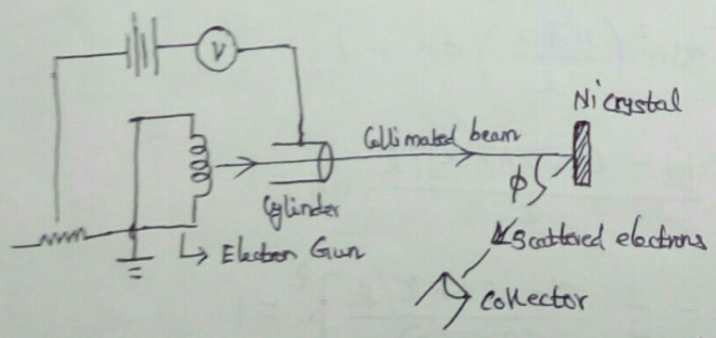
$$\boxed{\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}\right)x} \rightarrow (12)$$

Above eq (12) is called normalized wavefunction for particle enclosed in 1D - potential box.

Verification of matter waves - Davisson and Germer's diffraction Experiment

Davisson and Germer in 1927 conducted an experiment to explain wave nature of electrons through electron diffraction like light diffraction. This confirmed the earlier hypothesis by Louis de-Broglie in 1924 states particle like electrons have wave like property.

Experimental setup



Electron Beam were emitted at desired velocity, by heating electron gun at low power supply. The electrons were made to pass through cylinder thus forming finally collimated beam. The collimated beam

was made to fall on nickle target surface. The scattered electron beam was analysed through the detector. It was noted that certain scattered electrons was high at voltage of 54V and at a scattering angle of 50°

Using Bragg's law condition $2d\sin\theta = n\lambda$ the wavelength was found to be 0.167 nm with $d = 2.15$ Å

If de-Broglie wavelength is considered $(\lambda) = \frac{h}{p}$ where $p = mv$

If a electron is accelerated with 50V, then K.E is given by

$$\frac{1}{2}mv^2 = eV$$
$$mv^2 = 2eV$$
$$m^2v^2 = 2meV$$
$$mv = \sqrt{2meV}$$

Then de-Broglie wavelength $(\lambda) = \frac{h}{\sqrt{2meV}}$

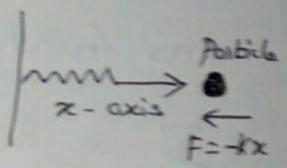
On applying $V = 50V$ & $h = 1.223 \times 10^{-23}$ Js the wavelength for diffracted electron was found to be 0.165 nm which is in close agreement with wavelength of diffracted electron calculated using Bragg's law by Davisson and Germer.

This shows beam of electrons behaves like X-ray, suffers diffraction at reflecting surface and thus has wave like characteristics.

Concept of classical harmonic oscillator

A particle in state of equilibrium such that when it is displaced slightly from its equilibrium position, a restoring force proportional to displacement from equilibrium position acts on it, then it is called harmonic oscillator

Force on 1D harmonic oscillator capable of oscillating along x-axis can be expressed as



$$F = -kx \rightarrow (1)$$

The potential energy $V(x)$ of harmonic oscillator is related with (F) as

$$-\frac{dV}{dx} = F \rightarrow (2)$$

Therefore V is given by $V(x) = -\int_0^x F\,dx + V_0$ (using eq-2)

$$= -\int_0^x (-kx)\,dx + V_0$$

$$V(x) = \frac{1}{2}kx^2 + V_0$$

where V_0 is constant of integration, If we assume $V=0$ when $x=0$ then $V_0 = 0$ then $V(x)$ for harmonic oscillator is given by

$$V(x) = \frac{1}{2}kx^2 \rightarrow (3)$$

If 'm' is mass and 'ω' is angular frequency then $k = m\omega^2$ then

$$\boxed{V(x) = \frac{1}{2}m\omega^2x^2} \rightarrow (4)$$

Above eq (4) is P.E of one dimensional harmonic oscillator

Quantum harmonic Oscillator - Ground state wavefunction & Energy Quantization

To find wave function & Energy of 1-D harmonic oscillator. Consider Schrodinger time independent wave equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0 \rightarrow (1)$$

Above equation is considered for particle oscillation along x-axis

From classical mechanics we write $V = \frac{1}{2}m\omega^2x^2$ then eq (1)

$$\frac{\partial^2\psi}{\partial x^2} + \left[\frac{2m}{\hbar^2}E - \frac{\cancel{2}m}{\hbar^2} \times \frac{1}{\cancel{2}}m\omega^2x^2\right]\psi = 0$$

$$\boxed{\frac{\partial^2\psi}{\partial x^2} + \left[\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2}x^2\right]\psi = 0} \rightarrow (2)$$

Above eq (2) is schrodinger wave eq for 1D harmonic oscillator

To find solution, eq (2) must be written in simplified form.

For this introduce dimensionless independent variable 'y' for particle oscillating in x-axis such that

$$y \propto x = y = ax \quad \text{where } a = \frac{y}{x} \rightarrow (3)$$

If ψ is function of particle oscillating x-axis then

$$\frac{\partial\psi}{\partial x} = \frac{\partial\psi}{\partial y}\cdot\frac{\partial y}{\partial x} = \frac{\partial\psi}{\partial y}\cdot a \quad (\text{using eq-3})$$

Differentiating again w.r.to x

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial^2\psi}{\partial y^2}a\left(\frac{\partial y}{\partial x}\right) = \frac{\partial^2\psi}{\partial y^2}a^2 \rightarrow (4)$$

Sub. eq (3) and (4) in eq (2)

$$\frac{\partial^2\psi}{\partial y^2}a^2 + \left[\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2}\left(\frac{y^2}{a^2}\right)\right]\psi = 0$$

$\div$ by a^2 $\Rightarrow$ $$\frac{\partial^2\psi}{\partial y^2} + \left[\frac{2mE}{\hbar^2 a^2} - \frac{m^2\omega^2}{\hbar^2 a^4}y^2\right]\psi = 0 \rightarrow (5)$$

Let us select [a] such that coefficient of y^2 in eq (5) becomes unity

$$\frac{m^2\omega^2}{\hbar^2 a^4} = 1 \Rightarrow a^4 = \frac{m^2\omega^2}{\hbar^2} \text{ then } a^2 = \frac{m\omega}{\hbar}$$

$$a = \sqrt{\frac{m\omega}{\hbar}}$$

Then eq (5) becomes

$$\frac{\partial^2\psi}{\partial y^2} + \left[\frac{2mE}{\hbar^2(m\omega/\hbar)} - \frac{m^2\omega^2}{\hbar^2(m^2\omega^2/\hbar^2)}y^2\right]\psi = 0$$

$$\frac{\partial^2\psi}{\partial y^2} + \left[\frac{2E}{\hbar\omega} - y^2\right]\psi = 0$$

(or) $$\boxed{\frac{\partial^2\psi}{\partial y^2} + [\lambda - y^2]\psi = 0} \rightarrow (6) \text{ where } \lambda = \left[\frac{2E}{\hbar\omega}\right]$$

Above eq (6) is reduced form of wave equation for 1D harmonic oscillator. In eq (6) compared to y^2, λ is small and can be neglected then

$$\frac{\partial^2\psi}{\partial y^2} - y^2\psi = 0 \rightarrow (7)$$

The solution for wave function from eq (7) for 1D harmonic oscillator is given as

$$\boxed{\psi_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}(2^n n!)^{-1/2} e^{-y^2/2} H_n(y)} \rightarrow (8)$$

where $H_n(y)$ is Hermite polynomial in either odd (or) even power of y.
eq (8) is called wavefunction for 1D harmonic oscillator

Energy associated to 1D harmonic oscillator

From eq (6) we know $\lambda = \frac{2E}{\hbar\omega}$

The wave equation for oscillator is satisfied only for discrete value of total energy is given by

$$\frac{2E}{\hbar\omega} = 2n+1$$

$$E = \frac{1}{2}(2n+1)\hbar\omega$$

$$E = \left[n+\frac{1}{2}\right]\hbar\omega$$

If $\hbar = h/2\pi$ and $\omega = 2\pi\nu$ then $\boxed{E = \left[n+\frac{1}{2}\right]h\nu} \rightarrow (9)$

Eq. (9) refers Energy of 1D harmonic oscillator

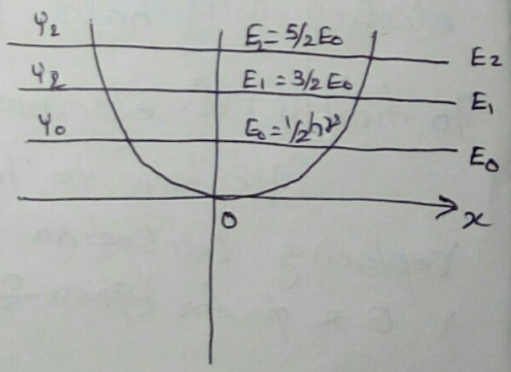
Energy level of 1D - harmonic oscillator

From eq (9) $E = \left(n+\frac{1}{2}\right)h\nu$

when $n = 0 \Rightarrow E_0 = \frac{1}{2}h\nu$

$n = 1 \Rightarrow E_1 = \frac{3}{2}h\nu = 3E_0$

$n = 3 \Rightarrow E_2 = \frac{5}{2}h\nu = 5E_0$



In general $\boxed{E_n = (2n+1)E_0}$

Hydrogen atom problem - (Finding wave function for electrons)

Hydrogen atom has proton (+ve) around which electrons revolve. Proton is assumed to be rest and electron is rotating at distance (r) from fixed hydrogen atom under the influence of attractive Coulomb field of the system.

The Potential Energy function due to Coulomb field $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \rightarrow (1)$

For a rectangular system with x, y, z coordinates, we write Schrodinger equation as

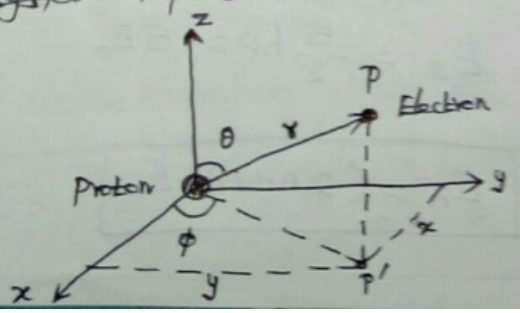
$$\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0 \rightarrow (2)$$

where $\nabla^2 = \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$

In our case, atom is spherical, For given potential energy V(r) electron will have permitted energy (E) for wave function (ψ)

To find (ψ) for electrons in Hydrogen atom

We have to modify equation (2) using spherical polar coordinates replacing Cartesian coordinates. Let the spherical coordinates are r, θ & φ for given system represented as follows



In the diagram r - radius vector from origin o to p

θ - Angle between radius vector & +z axis (polar Angle)

ϕ - Angle between projection (op') of radius vector on XY plane and +x axis (Azimutal angle)

Thus the spherical coordinates are related to rectangular coordinates as follows

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

$y = r\sin\theta \sin\phi$

$z = r\cos\theta$

Substituting above terms, eq (2) is modified interms of polar coordinates as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right) + \frac{2m}{\hbar^2}(E-V)\psi = 0 \longrightarrow (3)$$

Sub (1) in eq (3)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right) + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi = 0 \longrightarrow (4)$$

Above equation is called modified schrodinger equation to find wavefunction of electron in hydrogen atom. where

$\psi(r,\theta,\phi) = \psi_1(r), \psi_2(\theta), \psi_3(\phi)$

(ie) The product of wavefunction $\psi(r,\theta,\phi)$ depends on $\psi_1(r)$, $\psi_2(\theta)$ and $\psi_3(\phi)$. Thus to find $\psi(r,\theta,\phi)$ of electron we have to find $\psi_1(r)$, $\psi_2(\theta)$ and $\psi_3(\phi)$. by seperating variables using simple mathomatical rule called separation of variables.

To Seperate variables in eq (4), Let us divide by ψ_1, ψ_2 and ψ_3 and $\times$ by $r^2\sin^2\theta$ then

$$\frac{\sin^2\theta}{\psi_1}\frac{d}{dr}\left(r^2\frac{d\psi_1}{dr}\right)+\frac{\sin\theta}{\psi_2}\frac{d}{d\theta}\left(\sin\theta\frac{d\psi_2}{d\theta}\right)+\frac{1}{\psi_3}\left(\frac{d^2\psi_3}{d\phi^2}\right)+$$

$$\frac{2m\sin^2\theta}{\hbar^2}\left[E+\frac{e^2}{4\pi\varepsilon_0 r}\right]\psi=0 \longrightarrow (5)$$

on Seperating variable such that $\psi(r,\theta)=\psi(\phi)$ we write

$$\frac{\sin^2\theta}{\psi_1}\frac{d}{dr}\left(r^2\frac{d\psi_1}{dr}\right)+\frac{\sin\theta}{\psi_2}\frac{d}{d\theta}\left(\sin\theta\frac{d\psi_2}{d\theta}\right)+\frac{2m\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)\psi=-\frac{1}{\psi_3}\left(\frac{d^2\psi_3}{d\phi^2}\right)$$

$$\longrightarrow (6)$$

In eq (5) $\psi(r,\theta)=\psi(\phi)$, equality implies that each side must equal to a Constant. Consider that Constant as m_l^2 then if ψ_3 alone is considered

$$-\frac{1}{\psi_3}\frac{d^2\psi_3}{d\phi^2}=m_l^2 \quad (or) \quad \boxed{\frac{d^2\psi_3}{d\phi^2}+m_l^2\psi_3=0} \longrightarrow (7)$$

Eq (7) is called Azimutal equation gives solution for $\psi_3(\phi)$

Further substituting m_ℓ^2 in eq (5) we get

$$\frac{\sin^2\theta}{\psi_1}\frac{d}{dr}\left[r^2\frac{d\psi_1}{dr}\right]+\frac{\sin\theta}{\psi_2}\frac{d}{d\theta}\left[\sin\theta\frac{d\psi_2}{d\theta}\right]+\frac{2m}{\hbar^2}\left[E+\frac{e^2}{4\pi\varepsilon_0 r}\right]\psi = m_\ell^2$$

On rewritting above equation and ÷ by $\sin^2\theta$

$$\frac{1}{\psi_1}\frac{d}{dr}\left[r^2\frac{d\psi_1}{dr}\right]+\frac{2m}{\hbar^2}\left[E+\frac{e^2}{4\pi\varepsilon_0 r}\right]\psi = \frac{m_\ell^2}{\sin^2\theta}-\frac{1}{\psi_2\sin\theta}\frac{d}{d\theta}\left[\sin\theta\frac{d\psi_2}{d\theta}\right] \rightarrow (8)$$

In eq (8) $\psi(r)=\psi(\theta)$, equality implies that each side must be equal to constant. Consider that constant as $\ell(\ell+1)$ then

$$\boxed{\frac{1}{\psi_1}\frac{d}{dr}\left[r^2\frac{d\psi_1}{dr}\right]+\frac{2m}{\hbar^2}\left[E+\frac{e^2}{4\pi\varepsilon_0 r}\right]=\ell(\ell+1)} \rightarrow (9)$$

Eq (8) is called radial equation which gives solution for $\psi(r)$

Also

$$\boxed{\frac{m_\ell^2}{\sin^2\theta}-\frac{1}{\psi_2\sin\theta}\frac{d}{d\theta}\left[\sin\theta\frac{d\psi_2}{d\theta}\right]=\ell(\ell+1)} \rightarrow (10)$$

Eq (9) is called polar equation which gives solution for $\psi(\theta)$

Thus eq (4) has been seperated into three equation (7), (9) & (10) gives solution for $\psi(r,\theta,\phi)$ of electron in hydrogen atom