To unveil the secrets of nature and to explore the beauties of microworlds we need to hold the hands of theoretical tool.

In this regard, the faithful and promising one is Quantum Mechanics.

Upto the beginning of twentieth century, it was believed to the people that classical laws of Mechanics and energy are sufficient to describe all the things. But very soon it was discovered that they fail in Certain Cases, e.g.,

i) Black body radiation
ii) Photoelectric effect
iii) Compton effect
iv) Heat capacity of solid
v) Atomic and molecular spectra

The fields of failure paved the way towards the introduction of a new sophisticated theoretical instrument — QUANTUM MECHANICS

There are two paths to enter into the world of Quantum Mechanics:

Path I:

Black body radiation → Concept of Quanta applied by Bohr in atomic theory → Ultimately leads to the → Formulation of Heisenberg's Matrix Mechanics

Path II:

Photoelectric effect → de Broglie's wave particle duality → Schrödinger's wave Mechanics

Paul Dirac showed that two paths are equal. But for mathematical simplicity we will deal with mostly details of path - II.

Quantum Mechanics got its momentum from the Conceptual understanding of the term probability Coined by Max Born and with this probability the Mechanics started its glorious journey.

To start with, any mechanics introduces some assumptions and Quantum Mechanics is not of exception. So passing through the assumptions one will apply those assumptions in various cases like particle in box simple harmonic oscillation, rigid rotator and atoms and molecules - starting from simple H atom to large bio-molecules.

Here we will study the parts of the above introductory section in accordance with the WBSU syllabus - 2020.

de Broglie hypothesis || wave-particle duality

Introduction:

Let us first consider photoelectric effect put forth by Einstein. The noted points are:

i) It is instantaneous
ii) The kinetic energy of the photoelectron is independent of intensity of the light, rather, photoelectric current is dependent on the intensity of the radiation.

According to classical electromagnetic theory, intensity is related to energy. Thus, an alteration in the intensity of light should change in the kinetic energy of photoelectrons.
Again, according to this theory, a dim light is expected to show a time lag between the initial shining of light and photoejection. Also, photoelectric current should not depend on the intensity of radiation. But the experimental results fail to correlate the predictions made by the classical theory.

To resolve the problem Einstein proposed that the beam of light is a collection of discrete wave packets called photons.

Then Louis de Broglie took a wild decision that if light particle photon bears the wave behaviour, then material particle electron should be associated with matter wave and this lead to the formulation of wave-particle duality from wave- Photon relationship.

Illustration: According to de Broglie a moving material particle sometimes acts as a wave and sometimes as a particle or a wave is associated with a moving material particle controlling the particle in all respects.

we know energy of Photon

$E = h\nu$ —— ①

Again, according to Einstein's mass-energy relationship

$E = mc^2$ —— ②

Equating ① & ②

$mc^2 = h\nu$, ν = frequency of photon

$mc.c = h\nu$ c = velocity of light = velocity of photon

or, $p.c = h\nu$, p = momentum

$p = \frac{h\nu}{c}$ —— ③

From the wave- Photon relationship we have

(momentum of particle) $p' = \frac{h\nu'}{u}$, u is the velocity of matter wave

$= \frac{h}{\lambda}$ p' is mv, mass of particle & velocity of "

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

λ is the wave length of the matter wave or de Broglie wave or pilot wave.

Another form:

For moving particle

Total energy $E = K.E. = \frac{1}{2}mv^2$

or $m^2v^2 = 2mE$

or $p^2 = 2mE$

$p = \sqrt{2mE}$

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

For particle of charge q moving in the potential V

$$\boxed{\lambda = \frac{h}{\sqrt{2mqV}}}$$

For electron:

$$\lambda = \frac{h}{\sqrt{2m.e.V}} = \frac{12.26}{\sqrt{V}}\ \mathring{A}$$

Properties:

When particle is in rest,

i) for $v = 0 \rightarrow$ so $\lambda = \infty$, i.e, no existance of matter wave

ii) $v_{Mv} >> v_{light}$

iii) ~~Matter~~ Matter wave is not electromagnetic wave. It is a new one.

iv) If particle is charged or uncharged, then matter wave will arise, but electromagnetic wave will arise for charged particle.

v) velocity of matter wave is not constant but it changes, whereas velocity of electromagnetic wave remains constant.

Pictorial representation:

Rabbit & Duck in a single picture, but one at a time

Experimental proof:

i) Davission Germer Exp.
ii) G. P. Thomson Exp.

$\boxed{\text{problem}}$: Compare the λ of pilot waves of electron ~~of~~ velocity 6×10^6 m/s and a cricket ball of mass 45 g with velocity 20 m/s. Mass of electron: 9.11×10^{-31} kg

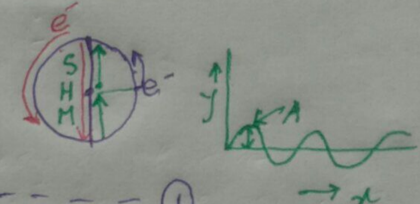
Schrödinger's wave equation: (time independent)

As matter wave is associated with the material particle like electron, so wave bears an equation and that is laid down by Schrödinger. In true sense the equation cannot be derived as it is the mathematical form of a physical process. But it can be done from the analogy of standing wave.

It includes several steps:

Step I: General equation of motion in 3D

- Arised from,
  - i) Equation of vibration of particle
  - ii) propagation of vibration



$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} = \frac{1}{u^2}\frac{\delta^2\psi}{\delta t^2} \quad ----- (1)$$

ψ, x, y, z, u, t usual meaning

ψ → 3D amplitude; x, y, z → Cartesian Co-ordinate; u → wave velocity; t → time period for oscillation

Step-II: variable separation by using wave property

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} = -\frac{4\pi^2}{\lambda^2}\psi$$

or $$\nabla^2\psi = -\frac{4\pi^2}{\lambda^2}\psi \quad ------- (2)$$

∇^2 = Laplacian operator

Step-III: Application of wave-particle duality

$$\nabla^2\psi = -\frac{4\pi^2 \cdot m^2 v^2}{h^2}\psi \quad , \quad \lambda = \frac{h}{mv}$$

$$\nabla^2\psi = -\frac{4\pi^2 m^2 v^2}{h^2}\psi \quad ----- (3)$$

Step-IV: Total energy, E, $= K.E. + P.E.$

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

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

eq^n (3) ⇒ $$\nabla^2\psi = -\frac{4\pi^2\, 2m(E-V)}{h^2}\psi$$

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

Schrödinger's wave equation

Other forms:

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

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

$\hbar = \frac{h}{2\pi}$, Ⓑ ⇒ $\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi}$ ---- Ⓒ

Operator form: $-\frac{\hbar^2}{2m}\nabla^2 \Rightarrow$ K.E. operator

$V \Rightarrow$ P.E. "

so, Ⓒ ⇒ $\left(\underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{K.E_{op}} + \underbrace{V}_{P.E_{op}}\right)\psi = E\psi$

$K.E_{op} + P.E_{op} = \hat{H}$ $\boxed{\hat{H}\psi = E\psi}$ ---- Ⓓ

Hamiltonian operator

Note:

In Hartree unit or atomic unit

$\hbar = m = e = 1$

so, $K.E_{op} = -\frac{1}{2}\nabla^2$

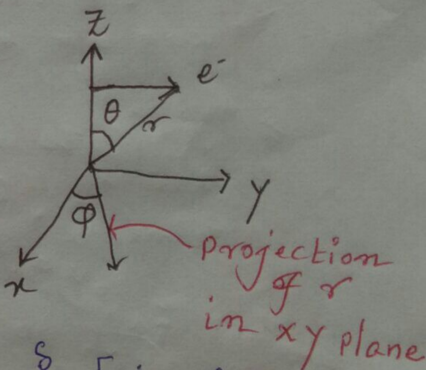
& $\hat{H} = -\frac{1}{2}\nabla^2 + V$

Schrödinger's equation in polar form

$z = r\cos\theta$

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

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



Using this Co-ordinate system ∇^2 turns as

$$\frac{1}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta}{\delta r}\right] + \frac{1}{r^2\sin\theta}\frac{\delta}{\delta\theta}\left[\sin\theta\frac{\delta}{\delta\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\delta^2}{\delta\phi^2}$$

Now, Schrödinger's eqn. becomes

$$\frac{1}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta\psi}{\delta r}\right] + \frac{1}{r^2\sin\theta}\frac{\delta}{\delta\theta}\left[\sin\theta\frac{\delta\psi}{\delta\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\delta^2\psi}{\delta\phi^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{---- Ⓔ}$$

Problem: Write down the Schrödinger's wave eqn. in polar form for He^+.

Quantum Mechanical origin of quantum numbers:

Using variable separation technick the eqn Ⓔ can be written in three separate eqn.s functions of only r, only θ and only φ, where $\psi(r,\theta,\phi)$ is written as $R(r)\,\Theta(\theta)\,\Phi(\phi)$ and they are:

i) $\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2 m r^2}{h^2}(E-V) = l(l+1)$ — Radial Equation

ii) $\frac{1}{\theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta = m^2$

iii) $\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$

Angular equations

Let us consider the solution of eqn. iii)

$$\Phi(\phi) = e^{im\phi}$$

For the continuity of the above function

$\Phi(\phi+2\pi) = \Phi(\phi)$, It is possible if m is integer

i.e, $m = 0, \pm1, \pm2, \cdots \pm l$

m is magnetic quantum no.

Thus, to make the solution of the ϕ dependent part of the Schrödinger's eqn. to be well behaved, magnetic quantum no. (m) arises

similarly,

To make the solution of the θ dependent part of the Schrödinger's eqn. to be well behaved, azimuthal quantum no. (l) arises, where associated Legendre function is used

Again, to make the solution of the r dependend part of the Schrödinger's eqn. to be well behaved, principal quantum no. (n) arises, where associated Laguerre function is used.

Finally, to make the solution of the spin dependent part of relativistic Schrödinger's eqn. to be well behaved, magnetic spin quantum no. (m_s) arises.

to be Contd.