Unit I

Wave nature of particles, Schrödinger equation and its application

Waves and Particles, de Broglie Hypothesis, Matter waves, Davisson and Germer's Experiment, G.P. Thomson Experiment, Heisenberg's Uncertainty Principle, Schrödinger's Time Independent Wave Equation–Physical Significance of the Wave Function – Application of Schrödinger wave equation: Particle in One Dimensional Potential Box.

'**Quantum Mechanics** is the description of motion and interaction of particles at the small scale where the discrete nature of the physical work becomes important.'

Waves and Particles:

WAVES:

A wave is nothing but disturbance which is occurred in a medium and it is specified by its frequency, wavelength, phase, amplitude and intensity.

PARTICLES:

A particle or matter has mass and it is located at a some definite point and it is specified by its mass, velocity, momentum and energy.

de-Broglie hypothesis (1924) and Matter waves

According to de-Broglie hypothesis any moving particle is associated with a wave. The waves associated with particles are known as de-Broglie waves or matter waves.

- The entire universe consists of **matter and radiation(energy)** only.
- Nature is symmetrical in so many respects; therefore, the two physical entities viz. **matter and energy** must be **mutually symmetrical.**

He derived an expression for the wavelength of matter waves on the analogy of radiation.

- According to Planck's theory of radiation , the energy of photon is

$$E = h\nu$$

$$= h\frac{c}{\lambda} \text{...........}(1)$$

Where **'c'** is a velocity of light and **'λ'** is a wave length.

- According to Einstein mass-energy relation

$$E = mc^2 \text{......}(2)$$

From equation (1) & (2),

$$mc^2 = h\frac{c}{\lambda}$$

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

$$\boxed{\lambda = \frac{h}{m\text{v}} = \frac{h}{p}}$$

Where '**p**' is momentum of the quantum particle, **'λ'** is de-Broglie wavelength and '**m**' is relativistic mass.

The above relation is called de- Broglie's matter wave equation. This equation is applicable to all atomic particles.

de Broglie wavelength associated with Kinetic Energy:

- If '**E**' is kinetic energy of a particle

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

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

$$\therefore p = \sqrt{2mE}$$

- Hence the de Broglie's wavelength

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

de Broglie wavelength associated with electrons:

Let us consider the case of an electron of rest mass **m** and charge **'e'** being accelerated by a potential difference '**V**' volts.

If '**v**' is the velocity attained by the electron due to acceleration

$$\frac{1}{2}mv^2 = eV$$

$$v = \sqrt{\frac{2eV}{m}}$$

$$\text{but } \lambda = \frac{h}{p} = \frac{h}{mv}$$

$$\lambda = \frac{h}{mv} \Rightarrow \lambda = \frac{h}{m\sqrt{\frac{2eV}{m}}}$$

- The de Broglie's wavelength

$$\boxed{\lambda = \frac{h}{\sqrt{2meV}} \text{ or } \lambda = \frac{12.26}{\sqrt{V}} A^0}$$

Characteristics of Matter waves

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

- Lighter the particle, greater is the wavelength associated with it.
- Lesser the velocity of the particle, longer the wavelength associated with it.
- For **v= 0**, **λ=∞ and** if **v=** ∞, **λ=0**, this shows that matter waves are generated by the motion of particles.
- Whether the particle is charged or not, matter wave is associated with it. This reveals i.e., these waves are not electromagnetic waves but a **new kind of waves.**
- Matter waves faster than velocity of light, i.e., the wave velocity **ω=c^2/v** as particle velocity (**v**) cannot exceed the velocity of light(**c**).
- No single phenomena exhibit both particle nature and wave nature simultaneously.
- The wave nature of matter introduces an uncertainty in the location of the particle and the momentum of the particle exists when both are determined simultaneously.

Note:

It can be proved that the matter waves travel faster than light. We know that

$$E = h\nu$$

$$E = mc^2$$

$$h\nu = mc^2 \rightarrow \nu = \frac{mc^2}{h}$$

The wave velocity (ω) is given by $\omega = \nu\lambda$

$$\omega = \left(\frac{mc^2}{h}\right)\left(\frac{h}{m\text{v}}\right)$$

$$where\ \nu = \frac{mc^2}{h}\ \&\ \lambda = \frac{h}{m\text{v}}$$

$$\boxed{\omega = \frac{c^2}{\text{v}}}$$

As the particle velocity **v** cannot exceed velocity of light **c**, **ω** is greater than velocity of light.

Experimental evidence for matter waves

After de-Broglie's work, Davisson and Germer in USA and G.P. Thomson in England independently demonstrated that streams of electrons are diffracted when they are scattered from crystals. The diffraction pattern's they observed were in complete accord with electron wavelength predicted by **λ=h/mv**

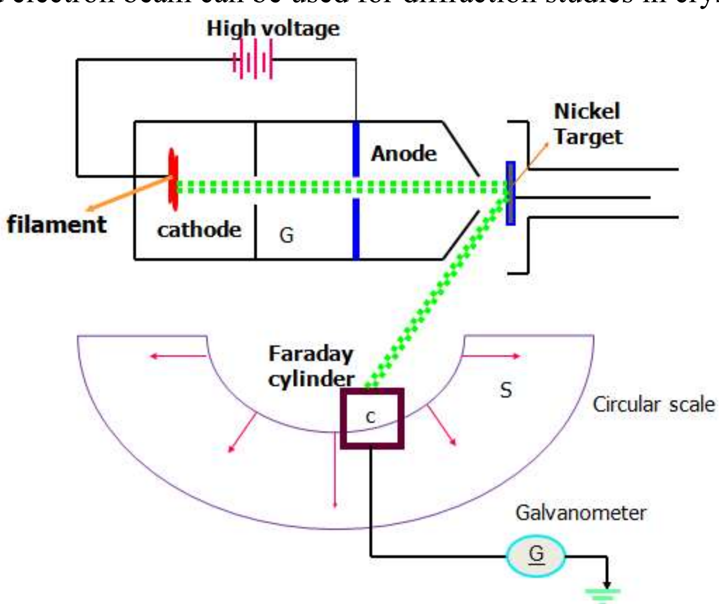
1. Davisson and Germer's Experiment 2. G.P. Thomson Experiment

DAVISSON & GERMER'S EXPERMENT

- Davison and Germer's first detected electron waves in 1927.
- They have also measured de Broglie wave lengths of slow electrons by using diffraction methods.

Principle:

Based on the concept of wave nature of matter **fast moving electrons behave like waves**. Hence accelerated electron beam can be used for diffraction studies in crystals.



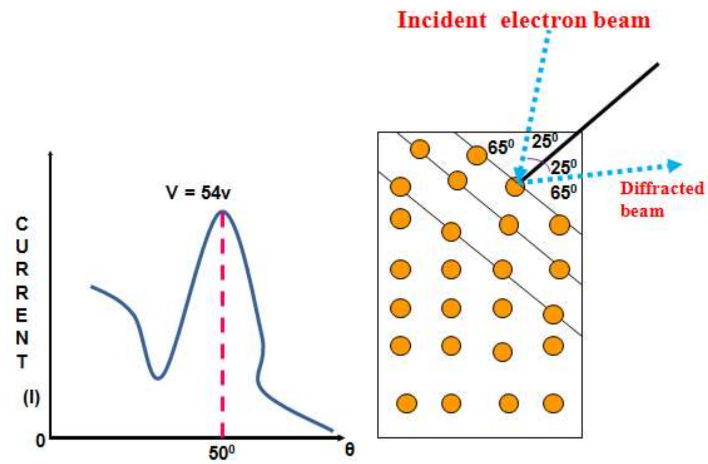
Experimental arrangement:

- The electron gun **G** produces a fine beam of electrons.
- It consists of a heated filament **F**, which emits electrons due to thermo ionic emission
- The accelerated electron beam of electrons is incident on a nickel plate, called target **T**.

- The target crystal can be rotated about an axis perpendicular to the direction of incident electron beam.
- The electrons, acting as the waves, are diffracted in different directions.
- The distribution of electrons is measured by using a detector called faraday cylinder **C** and which is moving along a graduated circular scale **S** between **29^0** to **90^0**.
- A sensitive galvanometer connected to the detector.

Results:

- When an electron beam accelerated by **54** volts was directed to strike the nickel crystal, a sharp maximum in the electron distribution occurred at scattered angle of **50^0** with the incident beam.
- For that scattered beam of electrons the diffracted angle becomes **65^0.**
- For a nickel crystal the inter planer separation is **d = 0.091nm.**



- According to Bragg's law

$$2d\sin\theta = n\lambda$$

$$2\times 0.091nm\times \sin 65^0 = 1\times\lambda$$

$$\lambda = 0.165nm$$

- For a **54** volts , the de Broglie's wave length associated with the electron is given by

$$\lambda = \frac{12.26}{\sqrt{V}}A^0$$

$$\lambda = \frac{12.26}{\sqrt{54}}A^0$$

$$\lambda = 0.166nm$$

- This is in excellent agreement with the experimental value.
- The Davison – Germer's experiment provides a direct verification of de Broglie hypothesis of the wave nature of moving particle.

G.P THOMSON'S EXPERIMENT

G.P Thomson's experiment proved that the diffraction pattern observed was due to electrons but not due to electromagnetic radiation produced by the fast moving charged particles.

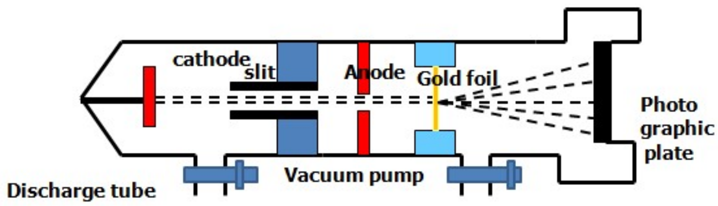
Experimental Arrangement:

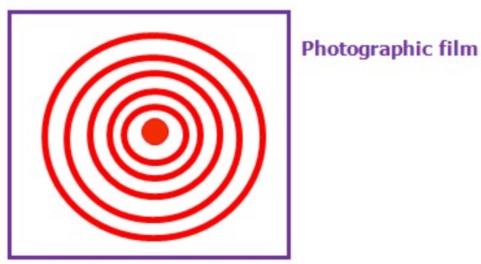
- G.P Thomson experimental arrangement consists of

(a) Filament or cathode **C**

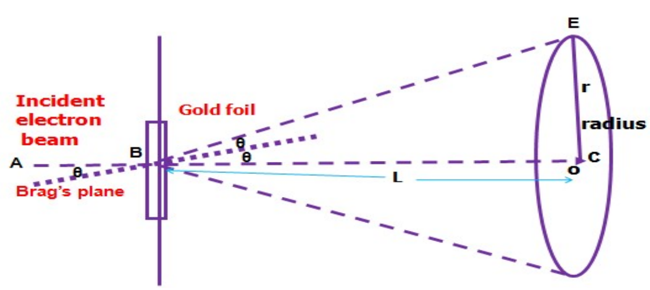
(b) Gold foil or gold plate
(c) Photographic plate
(d) Anode **A**.

- The whole apparatus is kept highly evacuated discharge tube.
- When we apply potential to cathode, the electrons are emitted and those are further accelerated by anode.
- When these electrons incident on a gold foil, those are diffracted, and resulting diffraction pattern getting on photographic film.
- After developing the photographic plate a symmetrical pattern consisting of concentric rings about a central spot is obtained.





Diffraction pattern.



According to Bragg's law **$n\lambda=2d\sin\theta$**

From the figure, $\tan 2\theta = r / L$

If θ is very small,

$2\theta = r / L$

$\theta=r/2L$ ………. (1)

Now Bragg's law can be written as

$n\lambda=2d(\theta)=2dr/2L$ (from eqn.(1))

$$\boxed{\therefore \lambda = \frac{rd}{nL}}$$

From the equation, the wavelength of electrons was calculated which matched well with those calculated values for de-Broglie equation. It is proved the ultimate confirmation for existence of matter waves or wave nature of electrons.

Differnce between the Matter waves and Electromagnetic wave(e.m):	
• Matter wave is associated with moving particle • Wavelength depends on the mass of the particle and its velocity • $\lambda = h/mv$ • Can travel with a velocity greater than the velocity of light • Matter wave is not electromagnetic wave	• Oscillating charged particle gives rise to e.m wave • Wavelength depends on the energy of photon • $\lambda = hc/E$ • Travels with velocity of light **c= 3X10^{8} m/s** • Electric field and magnetic field oscillate perpendicular to each other

Problems:

1) Calculate the wavelength associated with an electron raise to a potential 1600V(Ans: 0.306A^{0})
2) Calculate the wavelength associated with an electron with energy 200eV(Ans: 0.0275 nm)
3) Calculate the velocity and kinetic energy of an electron of wavelength 1.66X10^{-10}m.
4) Electrons are accelerated by 344 volts and are reflected from a crystal. The first reflection maximum occurs when the glancing angle is 60^{0}. determine the spacing of the crystal. (Ans: 0.3816A^{0})
5) If the kinetic energy of the neutron is 0.025eV. Calculate its de Broglie wavelength(mass of neutron =1.674X10^{-27}kg).(Ans:0.181nm)
6) An electron is moving under a potential field of 15kV. Calculate the wavelength of the electron wave.(Ans:0.1A^{0})
7) Calculate the wavelength of matter wave associated with a neutron whose kinetic energy is 1.5times the rest mass of electron. (Ans:9.76X10^{-6}m).
8) Calculate the de Broglie wavelength associated with proton moving with a velocity of 1/10th velocity of light. (Ans: 1.323X10^{-14}m)

Heisenberg uncertainty principle

This principle states that the product of uncertainties in determining both position and momentum of particle is approximately equal to **h / 4π**.

$$\boxed{\Delta x \Delta p \geq \frac{h}{4\pi}}$$

Where **Δx** is the uncertainty in determine the position and **Δp** is the uncertainty in determining momentum.

Its Mathematical form for the pairs of variables.

1. Angular momentum & angle $\quad \Delta j \Delta \theta \geq \frac{h}{4\pi}$
2. Time & energy $\quad \Delta t \Delta E \geq \frac{h}{4\pi}$

Consequences of uncertainty principle:

- Explanation for absence of electrons in the nucleus.
- Existence of protons and neutrons inside nucleus.
- Uncertainty in the frequency of light emitted by an atom.
- Energy of an electron in an atom.

Schrödinger time independent wave equation:

According to de-Broglie's hypothesis, the particle in motion is always associated with a wave. To describe the motion of a particle in terms of its associated wave, Schrödinger derived a wave equation, which is termed as Schrödinger's wave equation.

The classical differential equation of a wave motion is given

$$\frac{\partial^2\psi}{\partial t^2} = v^2\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right) = v^2\nabla^2\psi \quad ----(1)$$

The solution of equation (1) is given by

$$\boldsymbol{\psi(x)=A\ \sin(\omega t-kx)} \quad \text{-------}(2)$$

Where **A** is amplitude

k is wave number (= **2π/λ**)

Differentiating 'ψ' partially with respect to 'x' twice

$$\frac{\partial\psi}{\partial x} = -kA\cos(\omega t - kx)$$

$$\frac{\partial^2\psi}{\partial x^2} = -k^2A\sin(\omega t - kx)$$

$$= -k^2\psi \ (\because \text{ from eqn } (2))$$

$$\therefore \frac{\partial^2\psi}{\partial x^2} + k^2\psi = 0 \ ------(3)$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \ (\because k = \frac{2\pi}{\lambda})$$

$$\text{According to de-Broglie's } \lambda = \frac{h}{mv}$$

$$\therefore \frac{\partial^2\psi}{\partial x^2} + \frac{4\pi^2m^2v^2}{h^2}\psi = 0 \ ----- (4)$$

The total energy E of the particle is the sum of its kinetic energy and potential energy(V)

$$\text{i.e.,} \quad E = \frac{1}{2}mv^2 + V$$

$$\therefore m^2v^2 = 2m(E-V) -----(5)$$

Substituting the equation (5) into equation (4), we get

$$\boxed{\therefore \frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2m}{h^2}(E-V)\psi = 0 \ ----- (6)}$$

Now, extending above equation for a three dimensional wave

$$\therefore \frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2m}{h^2}(E-V)\psi = 0 -----(7)$$

(or)

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

$$(or)$$

$$\boxed{\therefore \nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0 \;\; (\because \frac{h}{2\pi} = \hbar)}$$

Where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is Laplacian Operator

This is the Schrödinger Time Independent wave equation.

Physical significance of the wave function

Max Born in 1926 gave a satisfactory interpretation of the wave function '**ψ**' associated with a moving particle.

- 'ψ' is the wave function and its measures the variation of the matter waves. Thus it connects the particles and its associated wave statistically.
- '**ψ**' is the complex amplitude of the matter wave.
- '**ψ**' must be finite, continuous, and single valued everywhere.
- $\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}$ & $\frac{\partial \psi}{\partial z}$ also, must be finite, continuous, and single valued.
- The wave function '**ψ**' is a complex function, it does not have a direct physical meaning, but when we multiply this with its complex conjugate **ψ***, the product **ψ* ψ** or **| ψ|²** has the physical meaning.
- The wave function **Ψ (r, t)** describes the position of a particle with respect to time.
- The probability of finding a particle in a particular volume is

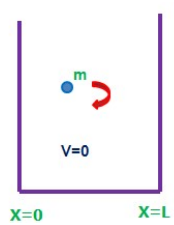
$$\boxed{\begin{gathered}\int_{-\infty}^{+\infty} \psi^* \psi \, d\tau = 1 \\ where\ d\tau = dx\ dy\ dz\end{gathered}}$$

i.e., 'ψ' must be normalizable.

Particle in a one dimensional potential box

Consider an electron of mass 'm' in an infinitely deep one-dimensional potential box with a width of a 'L' units in which potential is constant and zero.

$$V(x) = 0, 0 < x < L$$
$$V(x) = \infty, x \le 0 \ \& \ x \ge L$$



The motion of the electron in one dimensional box can be described by the Schrödinger's equation.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V]\psi = 0$$

Inside the box the potential V =0

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E]\psi = 0$$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \rightarrow where,, k^2 = \frac{2m}{\hbar^2}E$$

The solution to above equation can be written as

$$\psi(x) = A\sin kx + B\cos kx ----(1)$$

Where A,B and k are unknown constants and to calculate them, it is necessary to apply boundary conditions.

- When $X = 0$ then $\Psi = 0$ i.e. $|\Psi|^2 = 0$ ……. (a)
  $X = L$ then $\Psi = 0$ i.e. $|\Psi|^2 = 0$ …… (b)
- Applying boundary condition (a) to equation (1)

  A Sin k(0) + B Cos k(0) = 0 → B = 0
- Substitute B value in equation (1)

$$\boxed{\psi(x) = A\sin(kx)}$$

Applying second boundary condition for equation (1)

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

$$A\sin kL = 0$$

$$\sin kL = 0$$

$$kL = n\pi$$

$$\boxed{k = \frac{n\pi}{L}}$$

Substitute **B** & **k** value in equation (1)

$$\boxed{\psi(x) = A\sin\frac{(n\pi x)}{L}}$$

To calculate unknown constant **A**, consider normalization condition.

Normalization condition $\int_0^L |\psi(x)|^2 dx = 1$

$$\int_o^L A^2\sin^2[\frac{n\pi x}{L}]dx = 1$$

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

$$\frac{A^2}{2}[x - \frac{L}{2\pi n}\sin\frac{2\pi nx}{L}]_0^L = 1$$

$$\frac{A^2}{2}L = 1$$

$$\boxed{A = \sqrt{2/L}}$$

The normalized wave function is

$$\psi_n = \sqrt{2/L}\sin\frac{n\pi}{L}x$$

$$k^2 = \frac{2mE}{\hbar^2} \rightarrow E = \frac{k^2\hbar^2}{2m}$$

$$E = \frac{\left(\frac{n\pi}{L}\right)^2\left(\frac{h}{2\pi}\right)^2}{2m}$$

$$where, k = \frac{n\pi}{L} \;\&\; \hbar = \frac{h}{2\pi}$$

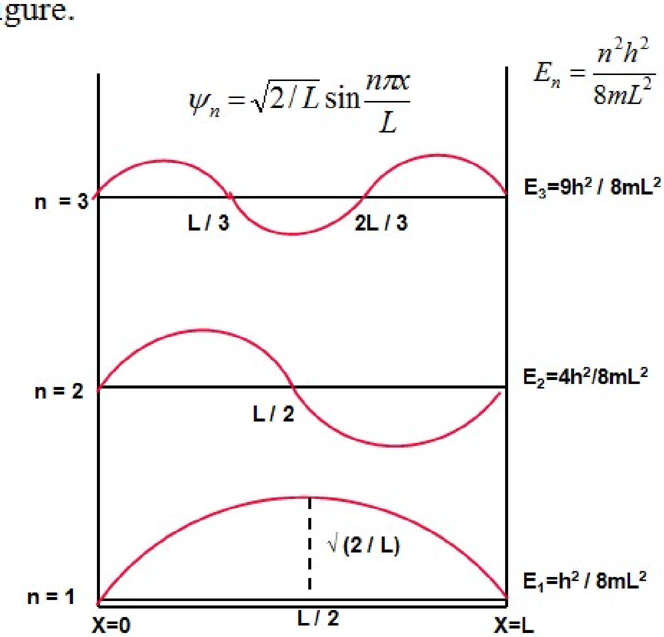
$$\boxed{E = \frac{n^2h^2}{8mL^2}}$$

The wave functions Ψ_n and the corresponding energies E_n which are called **Eigen functions** and **Eigen values**, of the quantum particle.

Normalized Wave function in **three** dimensions is given by

$$\boxed{\psi_n = \sqrt{(2/L)^3}\sin\frac{n_1\pi x}{L}\sin\frac{n_2\pi y}{L}\sin\frac{n_3\pi z}{L}}$$

The particle **Wave functions** & their energy **Eigen values** in a one dimensional square well potential are shown in figure.



Conclusions:

1. The three integers n_1, n_2 and n_3 called **Quantum numbers** are required to specify completely each energy state.
2. The energy 'E' depends on the sum of the squares of the quantum numbers n_1, n_2 and n_3 but not on their **individual values**.
3. Several combinations of the three quantum numbers may give different **wave functions**, but of the same **energy value**. Such states and energy levels are said to be **degenerate**.

Problems:

1). Find the lowest energy of an electron confined in a box of side 0.1nm each. (Ans: 112.9eV)

2). An electron is bound in one-dimensional box of size $4X10^{-10}$m. What will be its minimum energy? (Ans: $0.346X10^{-18}$ joule).

3). An electron is bound in one dimensional infinite well width $1X10^{-10}$m. Find the energy values in the ground state and first two excited states.

(Ans: E_1=$0.6031X10^{-17}$ joule, E_2= $2.412X10^{-17}$ joule and E_3=$5.428X10^{-17}$ joule)

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