So far, we gathered the following ideas...

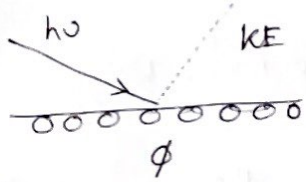
(1) Concept of 'Quanta' $E = nh\nu$ quantized energy levels

(2) Concept of particles and waves

- electron as a wave / a particle.

Particle theory

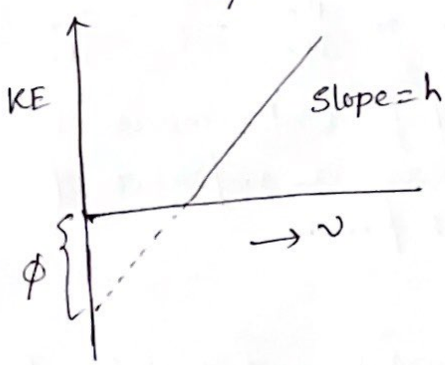
Electromagnetic radiation or light is composed of many photons - particles. Explaining photoelectric effect the analogy was that a photon hits on an electron on the metal surface kicks it out of the surface.



$h\nu = \phi + KE$

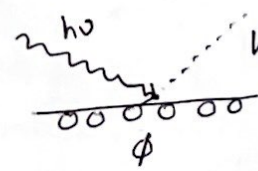
work function

h = Planck's constant $= 6.023 \times 10^{-34}$ J-s



Modified statement by Einstein

A photon resembles a particle but behave like a wave.



Q: Can ~~every~~ any particle behave like a wave?

- Yes?

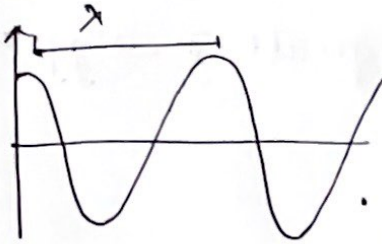
Louis de Broglie (1924) $\boxed{\dfrac{h}{p} = \lambda}$

$p = mv$ momentum

λ = wavelength

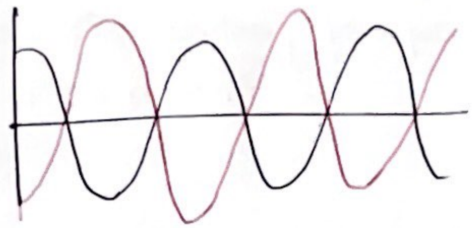
[Electron is a particle - JJ Thomson, Nobel prize 1906
Electron is a wave - GP Thomson, Nobel prize 1937]

Waves

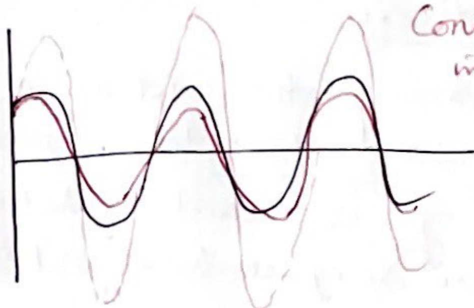


$\nu = c/\lambda$

Destructive Interference

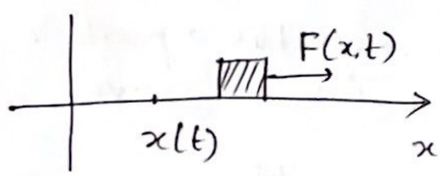


Constructive interference.

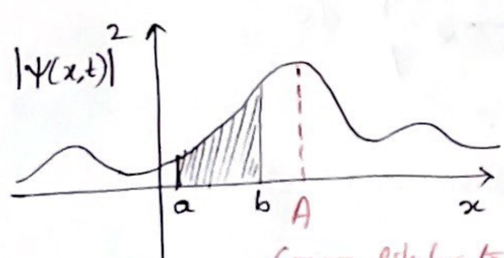


- Can we describe the motion of an electron using matthematics of waves?

$$F = m\frac{d^2x}{dt^2} \; ; \; F = -\frac{dV}{dx}$$



A classical particles moves along the x-axis under the influence of a specified force.



(more likely to find the particle in the vicinity)

$$\int_a^b |\Psi(x,t)|^2 dx$$ = probability of finding the particle between a and b at time 't'.

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right)\Psi = E\Psi$$

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

What is $\Psi(x,t)$? How do we calculate it? What is the use of $\Psi(x,t)$?

To obtain $\psi(x,t)$, we need to solve the Schrödinger's equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad \text{--- (1)}$$

Where $V(x)$ is a specified potential.

Equation (1) can be solved by the method of separation of variables.

$$\Psi(x,t) = \underbrace{\psi(x)}_{x\text{-dependent}}\ \underbrace{\phi(t)}_{\text{time-dependent}}$$

$$\frac{\partial \Psi}{\partial t} = \psi \frac{d\phi}{dt}, \qquad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2\psi}{dx^2}\phi$$

Putting these into eq^n (1)

$$i\hbar \psi \frac{d\phi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2}\phi + V\psi\phi$$

dividing by $\psi\phi$

or $$\underbrace{i\hbar \frac{1}{\phi}\frac{d\phi}{dt}}_{\text{function of } t} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V}_{\text{function of } x} \quad \text{--- (2)}$$

The only way this equality holds is if both sides are in fact constant. Let us assume, for the time being, that this constant is E. Then we can write,

$$i\hbar \frac{1}{\phi}\frac{d\phi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V = E \quad \text{--- (3)}$$

Now, we can separately write

$$i\hbar \frac{1}{\phi}\frac{d\phi}{dt} = E$$

or $$\boxed{\frac{d\phi}{dt} = -\frac{iE}{\hbar}\phi} \quad \text{--- (4)}$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{\psi}\right)\frac{d^2\psi}{dx^2} + V = E$$

or $$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi} \quad \text{--- (5)}$$

Time-independent Schrödinger's equation.

Equation (4) has a simple solution,

$$\phi(t) = e^{-iEt/\hbar}$$

So, the total wavefunction can be written as

$$\Psi(x,t) = \psi(x)\, e^{-iEt/\hbar}$$

⇒ Now, we can calculate the probability density

$$|\Psi(x,t)|^2 = \psi^* \psi = \psi(x)\, e^{-iEt/\hbar} \cdot \psi(x)\, e^{+iEt/\hbar}$$
$$= |\psi(x)|^2$$

Although, the wavefunction $\Psi(x,t)$ depends on time the probability density $|\Psi(x,t)|^2 = |\psi(x)|^2$ is independent of time — '<u>stationary state</u>'

⇒ Equation (5) can be written as

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

or $\hat{H}\psi = E\psi$ where $\hat{H}$ is called the <u>Hamiltonian operator</u>

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$p = -i\hbar\left(\frac{\partial}{\partial x}\right)$

Note that the classical Hamiltonian is written as

$$H(x,p) = \frac{p^2}{2m} + V(x)$$

The expectation value of the total energy

$$\langle H \rangle = \int \psi^* \hat{H} \psi \, dx$$
$$= E \int \psi^* \psi \, dx$$
$$= E \int |\psi|^2 dx$$
$$= E$$

$|\psi|^2 = 1$ <u>normalized</u>

What is normalization?

A mathematical feature of the Schrödinger's equation is that if ψ is ~~the~~ one solution, then so is $N\psi$. where N is a constant

$$\int_{-\infty}^{\infty} N\psi^* N\psi\, dx = 1$$

or $N = \dfrac{1}{\left(\int_{-\infty}^{\infty} \psi^*\psi\, dx\right)^{1/2}}$

Born's interpretation of the wave function is
"If the wave function of a particle has the value ψ at x, then the probability of finding the particle between x and $x+dx$ is proportional to $|\psi|^2 dx$"

Properties of a wave function

1. Single valued -
2. Finite
3. Continuous
4. must have a continuous first derivative.

Postulates:

Postulate 1: Any dynamical state of a system is as completely described as possible by a wave function, also called a state function.

Which is a function of all the spatial coordinates and time.

$$\Psi = \Psi(q_i, t) \quad \text{or} \quad \psi(r_i, t)$$

$|\psi|^2$ is the probability density.

There are certain restrictions on the wave functions, mostly imposed by Born's interpretation of the wave function.

1. At any point in space, the probability density must have one and only one value. Therefore, the wave function must be single valued.
2. The wave function must be continuous. Otherwise probability density, obtained by integration, can not be calculated (defined).

3. The wave-function should be ~~finite~~ (bound) within certain boundaries such that the probability density is finite.

4. Notice that the Schrödinger's equation is second order differential equation.

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

The second derivative of $\psi(x)$ must exist. This implies that the first derivative of $\psi(x)$ must be continuous over the region of integration.

⇒ Postulate 2:

~~Corre~~ There exist an operator corresponding to every measurable physical quantity such that the average value of that quantity can be obtained from the expectation value equation.

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

Where ψ is the wave function (state function), $\hat{A}$ is the operator corresponding to a physical property.