Schrödinger's Wave equation.

Let us consider a particle is moving and a group of waves (de Broglie waves) ~~are~~ is associated with it. Let $\psi(r,t)$ represents the displacement of these waves at a position r ~~at~~ at any time t.

Then the classical wave equation can be written as

$$\nabla^2\psi = \frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2}, \longrightarrow (1)$$

where v is the velocity. ~~The~~ The solution of eq(1) is the function $\psi(r,t)$. Let us assume that the wave amplitude at r is ~~an~~ periodic in t.

$$\psi(r,t) = \psi(r)\, e^{-i\omega t} \quad ---- (2)$$

Substituting eq.(2) in eq.(1) we get

$$\nabla^2\psi = -\frac{\omega^2}{v^2}\psi \qquad \left(\because \frac{\omega}{v} = \frac{2\pi\nu}{\lambda\nu} = \frac{2\pi}{\lambda}\right)$$

$$= -\frac{4\pi^2}{\lambda^2}\psi$$

where ν and λ are the frequency and wavelength of the de Broglie waves.

Rearanging, we get

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0 \quad ...... (3)$$

Again we know that $\lambda = \frac{h}{p} = \frac{h}{mv}$

$$\Rightarrow \nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \quad ...... (4)$$

If E and V are the total energy and the potential energy of the particle respectively then.

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

$$mv = \sqrt{2m(E-V)}$$

Eq.(4) becomes,

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \ldots\ldots (5)$$

or

$$\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0} \quad \ldots\ldots (5)$$

Eq.(5) is known as Schrödinger time-independent wave equation. It is a 2nd order homogeneous linear equation. The function ψ is known as the wave function.

Schrödinger time-dependent equation:

Now, multiply eq.(5) by $e^{-i\omega t}$ on the right and rearrange the terms:

$$-\nabla^2\psi(r).e^{-i\omega t} + \frac{8\pi^2 m}{h^2}V\psi(r)e^{-i\omega t} = \frac{8\pi^2 m}{h^2}E\psi(r)\,e^{-i\omega t}$$

$$\ldots\ldots (6)$$

let us consider, the RHS term,

$$\frac{8\pi^2 m}{h^2}E\psi(r,t) = \frac{8\pi^2 m}{h^2}\left(\frac{E}{-i\omega}\right)\frac{\partial}{\partial t}[\psi(r,t)]$$

$$= \frac{8\pi^2 m}{h^2}\,\frac{ih}{2\pi}\,\frac{\partial\psi(r,t)}{\partial t} \quad \ldots\ldots (7)$$

where $E = h\nu = \frac{h}{2\pi}.\omega$

Now, Eq(6) can be written as

$$-\nabla^2\psi(r,t) + \frac{8\pi^2 m}{h^2} V\,\psi(r,t) = \frac{8\pi^2 m}{h^2}\,\frac{ih}{2\pi}\,\frac{\partial}{\partial t}\psi(r,t)$$

Dividing throughout by $\frac{8\pi^2 m}{h^2}$, we get

$$\boxed{\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)\psi(r,t) = i\hbar\frac{\partial}{\partial t}\psi(r,t)} \quad \ldots (8)$$

This equation is called the Schrödinger time-dependent wave equation.

The ~~LHS~~ operator on the LHS in eq.(8) $\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)$ is called as the Hamiltonian operator or simply Hamiltonian and is denoted by H. The operator on the RHS $i\hbar\frac{\partial}{\partial t}$ is called the energy operator. This can be seen as follows:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi(r,t) &= i\hbar\frac{\partial}{\partial t}\left[\psi(r)\,e^{-i\omega t}\right] \\ &= i\hbar(-i\omega)\left[\psi(r)\,e^{-i\omega t}\right] \\ &= \hbar\omega\,\psi(r,t) \\ &= E\,\psi(r,t) \longrightarrow (9) \end{aligned}$$

Thus Eq.(8) can be written as

$$H\psi = E\psi \quad \ldots\ldots (10)$$

Now $\psi^*_{(r,t)}\psi(r,t) = \psi^*(r)\,e^{i\omega t}\,\psi(r)\,e^{-i\omega t}$

$$= \psi^*(r)\,\psi(r) \quad \ldots (11)$$

Here, $\psi^*\psi$ is known as probability density.

Thus the wave function represented in eq.(2) has a unique property that the probability density $\psi^*\psi$ is independent of time. The ~~wavefu~~ wavefunction $\psi(r,t)$ is said to represent a stationary state of the physical system.

Solution of the Time-dependent Schrödinger/ Schroedinger equation :

The Schrödinger time-dependent wave equation is

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\,\psi(x,t) = -\frac{h}{2\pi i}\frac{\partial\psi(x,t)}{\partial t} \quad \cdots (1)$$

Let us express $\psi(x,t)$ as the product of two functions, one involving the time alone and the other position coordinate alone:

$$\psi(x,t) = \psi(x)\,\phi(t) \quad \cdots\cdots (2)$$

Eq.(1) can be ~~exp~~ written as,

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2}\cdot\phi(t) + V(x)\,\psi(x)\,\phi(t) = \cancel{-\frac{h}{2\pi i}\frac{d\phi(t)}{dt}}$$

$$= -\frac{h}{2\pi i}\frac{d\phi(t)}{dt}\cdot\psi(x)$$

or, $$\frac{1}{\psi(x)}\left[-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x)\right] = -\frac{h}{2\pi i}\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} \quad \cdots\cdots (3)$$

In eq.(3), the LHS is a function of x whereas the RHS is a function of t alone.

This is only possible when they are separately equal to a constant. Let us call it E.

Thus we can write,

$$\frac{1}{\psi(x)}\left\{-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2}+V(x)\,\psi(x)\right\}=E \quad \cdots\cdots (4)$$

$$-\frac{h}{2\pi i}\,\frac{1}{\phi(t)}\,\frac{d\phi(t)}{dt}=E \quad \cdots\cdots (5)$$

Eq.(4) can be written as

$$\frac{d^2\psi(x)}{dx^2}+\frac{8\pi^2 m}{h^2}(E-V)\,\psi(x)=0 \quad \cdots\cdots (6)$$

which is the Schroedinger time-independent wave equation whose solution is $\psi(x)$.

Now Eq.(5) can be written as

$$\frac{d\phi(t)}{dt}=-\frac{2\pi i}{h}E\,\phi(t)$$

or, $$\frac{d\phi(t)}{\phi(t)}=-\frac{2\pi i}{h}E\,dt$$

Integrating $$\log\phi(t)=-\frac{2\pi i}{h}Et$$

$$\Rightarrow \phi(t)=\exp\left[-\frac{2\pi i Et}{h}\right] \quad \cdots\cdots (7)$$

From eq.(2) we can write

$$\Psi(x,t)=\psi(x)\,\phi(t)$$

$$=\psi(x)\exp\left[-\frac{2\pi i Et}{h}\right] \quad \cdots\cdots (8)$$

Hence, the general solution ~~is~~ can be written as,

$$\Psi(x,t) = \sum_n a_n \Psi_n(x,t)$$

$$= \sum_n a_n \psi_n(x) \exp\left[\frac{-2\pi i E_n t}{h}\right] \quad \cdots (9)$$

Stationary state:

If in a particular state, the probability density $(\psi\psi^*)$ is independent of time, the state is known as stationary state.

Physical significance of ψ:

According to Max Born, $|\psi|^2$ represents the probability of finding the particle at any given moment. $\psi\psi^* = |\psi|^2$

More exactly, the probability of the particle being present in a volume $dx\,dy\,dz$ is $|\psi|^2 dx\,dy\,dz$. For the total probability of finding the particle somewhere is unity i.e. particle is certainly to be found somewhere in space:

$$\iiint |\psi|^2 dx\,dy\,dz = 1$$

The wavefunction ψ which satisfies the above condition is said to be normalized wavefunction.

Properties of ψ

(i) ψ must be finite for all values of x, y, z.

(ii) ψ must be single-valued i.e. for each set of values of x, y, z, ψ must have one value only.

(iii) ψ must be continuous in all regions except where potential energy is infinite.

(iv) ψ is analytical i.e. it possesses continuous first order derivative.

(v) ψ vanishes at the boundaries.

Orthogonal, Normalised and Orthonormal Functions:

Let us consider two functions $\psi_1(x)$ and $\psi_2(x)$. If the product of $\psi_1(x)$ and the complex conjugate $\psi_2^*(x)$ vanishes when integrated ~~over~~ with respect to x over the interval $a \leq x \leq b$, if

$$\boxed{\int_a^b \psi_2^*(x)\, \psi_1(x)\, dx = 0} \quad \cdots\cdots (1)$$

then $\psi_1(x)$ and $\psi_2(x)$ are said to be mutually orthogonal or simply orthogonal in the interval (a, b).

~~If every two functions~~

Let us consider a set of functions $\varphi_1(x), \varphi_2(x) \ldots \varphi_n(x)$. If every two functions are mutually orthogonal in the interval (a,b) i.e. if

$$\boxed{\int_a^b \varphi_m^*(x)\, \varphi_n(x)\, dx = 0 \;, \quad \text{when } m \neq n \text{ and } n, m = 1, 2, 3 \ldots} \quad \ldots (2)$$

then the set of functions are said to be Orthogonal in the interval (a,b).

For example, the set

$$\left.\begin{matrix} 1, \cos x, \cos 2x, \cos 3x \ldots \ldots \\ \sin x, \sin 2x, \sin 3x \ldots \ldots \end{matrix}\right\}$$

is orthogonal in the interval $(-\pi, \pi)$ because the product of any member and the complex conjugate of any other member, when integrated between $-\pi$ to $+\pi$, comes out to be zero.

Let us consider two functions $\varphi_m(x)$ and $\varphi_n(x)$ in space. These two functions are said to be ~~not~~ normalised if

$$\boxed{\int_{-\infty}^{+\infty} \varphi_m^* \varphi_m \, d\tau = 1 \quad \text{and} \quad \int_{-\infty}^{+\infty} \varphi_n^* \varphi_n \, d\tau = 1} \quad \ldots (3)$$

These functions are said to be mutually orthogonal if

$$\boxed{\int_{-\infty}^{+\infty} \varphi_m^* \varphi_n \, d\tau = 0 \quad \text{or,} \quad \int_{-\infty}^{+\infty} \varphi_n^* \varphi_m \, d\tau = 0} \quad \ldots (4)$$

Questions

1. (a) Derive the time-independent Schrödinger wave equation for a particle.

   (b) Give the physical significance of the wavefunction.

2. (a) Obtain the time-dependent Schrödinger wave equation for a particle.

   (b) Find its ~~general~~ solution.

3. (a) What do you understand by (i) orthogonal (ii) normalised, (iii) orthonormal wavefunction?

   (b) ~~Explain~~ What do you mean by the expectation value of dynamical quantities in quantum mechanics?

4. Normalize the wavefunction $\psi(x) = A\exp(-ax^2)$, where A and a are constants, over the domain $-\infty \leq x \leq \infty$.

5. Using the time-independent Schrödinger equation, find the potential $V(x)$ and energy E for which the wavefunction

$$\psi(x) = \left(\frac{x}{x_0}\right)^n e^{-x/x_0},$$

where n, x_0 are constants, is an eigenfunction. Assume that $V(x) \rightarrow 0$ as $x \rightarrow \infty$.

References / suggested Books

1. David J. Griffiths, Introduction to Quantum Mechanics, Pearson Education, New Delhi (2007).

2. S.L. Gupta, V. Kumar, H.V. Sharma and R.C. Sharma, Quantum Mechanics, Jai Prakash Nath & Co., Meerut (1995-96).

3. S.P. Singh and M.K. Bagde, Quantum Mechanics, S. Chand & Company Ltd. (1994).

4. G. Aruldhas, Quantum Mechanics, PHI Learning Private Limited, New Delhi (2011).

5. R. Eisberg and R. Resnick, Quantum physics, John Wiley and Sons, Wiley India (P) Ltd., New Delhi (2010).

~~These references are applicable to all my Lectures~~.