

## Quantum Mechanics (PartI) by SDG [2<sup>nd</sup> yr , PHYS2001]

### Recapitulation of quantum Physics:

#### 1) **The Wave-Particle duality**

In classical physics energy is transported either by waves or by particles. Classical physicists observed water waves carrying energy over the water surface or bullets transferring energy from gun to target. From such experiences they built a wave model for certain macroscopic phenomena and a particle model for other macroscopic phenomena, and they quite naturally extended these models into visually less accessible regions. Thus they explained sound propagation in terms of a wave model and pressures of gases in terms of a particle model (kinetic theory). Their successes conditioned them to expect that all entities are either particles or waves. Indeed, these successes extended into the early twentieth century with applications of Maxwell's wave theory to radiation and the discovery of elementary particles of matter, such as the neutron and positron. Hence, classical physicists were quite unprepared to find that to understand radiation they needed to invoke a particle model in some situations, as in the Compton effect, and a wave model in other situations, as in the diffraction of x rays. Perhaps more striking is the fact that this same wave-particle duality applies to matter as well as to radiation.

#### 2) **de Broglie hypothesis**

The hypothesis of de Broglie shows that dual wave-particle behavior of radiation applies equally well to matter. Just as a photon has a light wave associated with it that governs its motion, so a material particle (e.g., an electron) has an associated matter wave that governs its motion. Since the universe is composed entirely of matter and radiation, de Broglie's suggestion is essentially a statement about a grand symmetry of nature. Indeed, he proposed that the wave aspects of matter are related to its particle aspects in exactly the same quantitative way that is the case for radiation. According to de Broglie, for matter *and* for radiation alike the total energy  $E$  of an entity is related to the frequency  $\nu$  of the wave associated with its motion by the equation

$$E = h\nu$$

and the momentum  $p$  of the entity is related to the wavelength  $\lambda$  of the associated wave by the equation

$$p = h/\lambda$$

Here the particle concepts, energy  $E$  and momentum  $p$ , are connected through Planck's constant  $h$  to the wave concepts, frequency  $\nu$  and wavelength  $\lambda$ .  $p = h/\lambda$  is called the **de Broglie relation**. It predicts the **de Broglie wavelength  $\lambda$  of a matter wave** associated with the motion of a material particle having a momentum  $p$ .

#### 3) **The Uncertainty Principle**

The use of probability considerations is not foreign to classical physics. Classical statistical mechanics makes use of probability theory, for example. However, in classical physics the basic laws (such as Newton's laws) are deterministic, and statistical analysis is simply a practical device for treating very complicated systems. According to Heisenberg and Bohr, however, the probabilistic view is the fundamental one in quantum physics and determinism must be discarded. Let us see how this conclusion is reached. In classical mechanics the equations of motion of a system with given forces can be solved to give us the position and momentum of a

particle at all values of the time. All we need to know are the precise position and momentum of the particle at some value of the time  $t = 0$  (the initial conditions) and the future motion is determined exactly. This mechanics has been used with great success in the macroscopic world, for example in astronomy, to predict the subsequent motions of objects in terms of their initial motions. Note, however, that in the process of making observations the observer interacts with the system. An example from contemporary astronomy is the precise measurement of the position of the moon by bouncing radar from it. The motion of the moon is disturbed by the measurement, but due to the very large mass of the moon the disturbance can be ignored. On a somewhat smaller scale, as in a very well-designed macroscopic experiment on earth, such disturbances are also usually small, or at least controllable, and they can be taken into account accurately ahead of time by suitable calculations. Hence, it was naturally assumed by classical physicists that in the realm of microscopic systems the position and momentum of an object, such as a electron, could be determined precisely by observations in a similar way. Heisenberg and Bohr questioned this assumption.

We must ask ourselves how we actually measure position and momentum. Can we determine by actual experiment at the same instant both the position and momentum of matter or radiation? The answer given by quantum theory is: not more accurately than is allowed by the Heisenberg *uncertainty principle*. There are two parts to this principle. The first has to do with the simultaneous measurement of position and momentum. It states that experiment cannot simultaneously determine the exact value of a component of momentum,  $p_x$  say, of a particle and also the exact value of its corresponding coordinate,  $x$ . Instead, our precision of measurement is inherently limited by the measurement process itself such that

$\Delta p_x \Delta x \geq \hbar/2$  where the momentum  $p_x$  is known to within an uncertainty  $\Delta p_x$  and the position  $x$  at the same time to within an uncertainty  $\Delta x$ . Here,  $\hbar = h/2\pi$ .

The second part of the uncertainty principle has to do with the measurement of the energy  $E$  and the time  $t$  required for the measurements, as for example, the time interval  $\Delta t$  during which a photon of energy spread  $\Delta E$  is emitted from an atom. In this case  $\Delta E \Delta t \geq \hbar/2$  where  $\Delta E$  is the uncertainty in our knowledge of the energy  $E$  of a system and  $\Delta t$  the time interval characteristic of the rate of change in the system.

## Introduction

We know that the particles of microscopic systems move according to the laws of some form of wave motion, and not according to the Newtonian laws of motion obeyed by the particles of macroscopic systems. Thus a microscopic particle acts as if certain aspects of its behavior are governed by the behavior of an associated de Broglie wave, or wave function.

We want to develop a procedure that can be used to treat the behavior of the particles of any microscopic system. *Schrödinger's theory of quantum mechanics* provides us with such a procedure. The theory specifies the laws of wave motion that the particles of any microscopic system obey. This is done by specifying, for each system, the equation that controls the behavior of the wave function, and also by specifying the connection between the behavior of the wave function and the behavior of the particle. The theory is an extension of the de Broglie postulate. Furthermore, there is a close relation between it and Newton's theory of the motion of particles in macroscopic systems. Schrödinger's theory is a generalization that includes Newton's theory as a special case (in the macroscopic limit), much as Einstein's theory of relativity is a generalization that includes Newton's theory as a special case (in the low velocity limit).

Actually, a better comparison can be made between the Schrödinger theory and Maxwell's theory of electromagnetism. The reason for this is that electromagnetic waves behave in a manner which is very analogous to the behavior of the wave functions of the Schrödinger theory. We shall use this analogy, when appropriate, to show how quantum mechanical results are related to results that are familiar from the study of electromagnetism, or of other forms of classical wave motion.

### Plausibility argument leading to Schrödinger's Equation

We begin our plausibility argument by listing four reasonable assumptions concerning the properties of the desired quantum mechanical wave equation:

1. It must be consistent with the de Broglie-Einstein postulates,  
That is  $\lambda = h/p$  and  $v = E/h$ .

2. It must be consistent with the non-relativistic equation

$$E = p^2/2m + V$$

relating the total energy  $E$  of a particle of mass  $m$  to its kinetic energy  $p^2/2m$  and its potential energy  $V$ .

3. It must be *linear* in  $\psi(x,t)$ . That is, if  $\psi_1(x,t)$  and  $\psi_2(x,t)$  are two different solutions to the equation for a given potential energy  $V$  (we shall see that partial differential equations have many solutions), then any arbitrary linear combination of these solutions,  
 $\psi(x,t) = c_1\psi_1(x,t) + c_2\psi_2(x,t)$ , is also a solution.

This combination is said to be linear since it involves the first power of  $\psi_1(x,t)$  and  $\psi_2(x,t)$ ; it is said to be arbitrary since the constants  $c_1$  and  $c_2$  can have any (arbitrary) values. This *linearity* requirement ensures that we shall be able to *add together wave functions* to produce the constructive and destructive interferences that are so characteristic of waves. Interference phenomena are commonplace for electromagnetic waves; all the diffraction patterns of physical optics are understood in terms of the addition of electromagnetic waves. But the Davisson Gerner experiment (proof of matter wave), and others, show that diffraction patterns are also found in the motion of electrons, and other particles. Therefore, their wave functions also exhibit interferences, and so they should be capable of being added.

4. The potential energy  $V$  is generally a function of  $x$ , and possibly even  $t$ . However, there is an important special case where,

$$V(x,t) = V_0.$$

**This is just the case of the free particle since the force acting on the particle is given by**

$$F = -dV(x,t)/dx, \text{ which yields } F = 0 \text{ if } V_0 \text{ is a constant.}$$

In this case Newton's law of motion tells us that the linear momentum  $p$  of the particle will be constant, and we also know that its total energy  $E$  will be constant. We have here the situation of a free particle with constant values of  $\lambda = h/p$  and  $v = E/h$ . , **Therefore,  $p = \hbar k$  and  $E = \hbar \omega$ .**

We therefore assume that, in this case, the desired differential equation will have sinusoidal traveling wave solutions of constant wavelength and frequency, similar to the sinusoidal wave function.

Using the de Broglie-Einstein relations of assumption 1 to write the energy equation of assumption 2 in terms of  $\lambda$  and  $\nu$  for a free particle, we obtain  $\frac{\hbar^2 k^2}{2m} + V_0 = \hbar \omega \dots (1)$ , where  $\hbar = h/2\pi$  is the reduced Planck's constant,  $\omega = 2\pi\nu$  is the angular frequency and  $k=2\pi/\lambda$  is the wave number.

In order to satisfy the linearity assumption 3, it is necessary that every term in the differential equation be linear in  $\psi(x,t)$ , i.e., be proportional to the first power of  $\psi(x,t)$ . Note that any derivative of  $\psi(x,t)$  has this property.

In order that the differential equation itself be linear in  $\psi(x,t)$ , it cannot contain any term which is independent of  $\psi(x,t)$ , i.e., which is proportional to  $[\psi(x,t)]^0$ , or which is proportional to  $[\psi(x,t)]^2$  or any higher power.

We choose a special case (free particle,  $V(x,t) = V_0$ ) where the wave function,

$$\psi(x,t) = \exp^{i(kx - \omega t)} \dots \dots \dots (2).$$

Differentiating  $\psi(x,t)$  once with respect to  $t$ , we get,

$$\frac{\partial \psi(x,t)}{\partial t} = -i \omega \exp^{i(kx - \omega t)} = -i \omega \psi(x,t) \dots (3a)$$

Or,

$$i \hbar \frac{\partial \psi(x,t)}{\partial t} = -(i\hbar)i\omega \psi(x,t) = \hbar \omega \psi(x,t) \dots (3b)$$

On the other hand differentiating  $\psi(x,t)$  twice with respect to  $x$ , we get,

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = -k^2 \exp^{i(kx - \omega t)} = -k^2 \psi(x,t) \dots (4a)$$

Or,

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} = \left( \frac{-\hbar^2}{2m} \right) (-k^2) \psi(x,t) = \frac{\hbar^2 k^2}{2m} \psi(x,t) \dots (4b)$$

Now, multiplying equation (1) by  $\psi(x,t)$ , we will get,

$$\frac{\hbar^2 k^2}{2m} \psi(x,t) + V_0 \psi(x,t) = \hbar \omega \psi(x,t) \dots (5),$$

Therefore inserting equation (5) and (6) in equation (7) we obtain,

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V_0 \psi(x,t) = i\hbar \frac{\partial \psi(x,t)}{\partial t} \dots \dots \dots (6a)$$

Generalized form of equation (6a) will be,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x,t)\psi(x,t) = i\hbar \frac{\partial \psi(x,t)}{\partial t} \dots \dots \dots (6b)$$

**At this point it seems plausible to argue that the quantum mechanical wave equation might be expected to have the same form as (6b) in the general case where the potential energy  $V(x,t)$  does actually vary as a function of  $x$  and/or  $t$  (i.e., where the force is not zero); but we cannot prove this to be true. We can, however, *postulate* it to be true.** We do this, and therefore take (6b) as the quantum mechanical wave equation whose solutions  $\psi(x,t)$  give us the wave function which is to be associated with the motion of a particle of mass  $m$  under the influence of forces which are described by the potential energy function  $V(x,t)$ . The validity of the postulate must be judged by comparing its implications with experiment, and we shall make such comparisons later. Equation (6) was first obtained in 1926 by Erwin Schrödinger, and it is therefore called the **time dependent *Schrödinger equation***.

For conservative systems, Potential energy will be only a function of  $x$  and equation (6b) will then reduces to

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) = i\hbar \frac{\partial \psi(x,t)}{\partial t} \dots \dots \dots (7)$$

### **Born's interpretation of wave functions**

A wave function actually contains all the information which the uncertainty principle allows us to know about the associated particle. The basic connection between the properties of the wave function  $\psi(x,t)$  and the behavior of the associated particle is expressed in terms of the *probability density*  $P(x,t)$ . This quantity specifies the probability, per unit length of the  $x$  axis, of finding the particle near the coordinate  $x$  at time  $t$ . According to a *postulate*, first stated in 1926 by Max Born, the relation between the probability density and the wave function is  $P(x,t) = \psi^*(x,t)\psi(x,t)$  where the symbol  $\psi^*(x,t)$  **represents the complex conjugate of  $\psi(x,t)$** .

For emphasis, and clarification, we shall restate Born's postulate as follows: ***If, at the instant  $t$ , a measurement is made to locate the particle associated with the wave function  $\psi(x,t)$ , then the probability  $P(x,t) dx$  that the particle will be found at a coordinate between  $x$  and  $x + dx$  is equal to  $\psi^*(x,t)\psi(x,t) dx$ .***

Justification of the postulate can be found in the following considerations. Since the motion of a particle is connected with the propagation of an associated wave function (the de Broglie condition), these two entities must be associated in space.

That is, the particle must be at some location where the waves have appreciable amplitude. Therefore  $P(x,t)$  must have an appreciable value where  $\psi(x,t)$  has an appreciable value.

**Since the measurable quantity probability density  $P(x,t)$  is real and non-negative, whereas the wave function  $\psi(x,t)$  is complex, it is obviously not possible to equate  $P(x,t)$  to  $\psi(x,t)$ . However, since  $\psi^*(x,t)\psi(x,t)$  is always real and non-negative, Born was not inconsistent in equating it to  $P(x,t)$ .**

[It was with the analogy of intensity of electro-magnetic field or radiation which is given as  $E^2$ , where  $E$  is the electric field, probability density is taken as  $|\psi(x, t)|^2 = \psi^*(x, t)\psi(x, t)$ ].

### Normalization of wave function

The total probability of finding the particle *somewhere* on the entire range of the  $x$  axis is necessarily equal to one if the particle exists. This total probability can be obtained mathematically by integrating the probability density function  $P$  over all  $x$ . Doing this, and setting the result equal to one, we have,

$$\text{Total probability} = \int_{-\infty}^{\infty} |\psi_N(x, t)|^2 dx = 1 \dots (8),$$

Since Schrödinger equation is linear, any wave function can be written as  $\psi_N(x, t) = A\psi(x, t)$ , where  $\psi_N(x, t)$  is the normalized wave function and  $A$  is called the normalization constant.

Thus, the normalization constant  $A$  can be evaluated by the following equation

$$\int_{-\infty}^{\infty} |A\psi(x, t)|^2 dx = 1 \dots (9)$$

### **Problem (Important)**

**Find the normalization constant  $C$  of the following wave function,**

$$\psi(x) = \begin{cases} C \sqrt{\frac{15}{a}} (a^2 - x^2) & \text{for } -a \leq x \leq a \\ = 0, & \text{otherwise.} \end{cases}$$

**Solution:**

$$\text{Normalization demands, } \int_{-\infty}^{\infty} \left| C \sqrt{\frac{15}{4a}} (a^2 - x^2) \right|^2 dx = 1$$

$$\text{Or, } \int_{-a}^a |C|^2 \frac{15}{a} (a^2 - x^2)^2 dx = 1$$

$$\text{Or, } \int_{-a}^a |C|^2 \frac{15}{a} (-2a^2 x^2 + x^4) dx = 1$$

$$\text{Or, } |C|^2 \frac{15}{a} \left( a^4 x - 2a^2 \frac{x^3}{3} + \frac{x^5}{5} \right) \Big|_{-a}^a = 1$$

$$\text{Or, } |C|^2 \frac{15}{a} 2 \left( a^5 - 2 \frac{a^5}{3} + \frac{a^5}{5} \right) = 1$$

$$\text{Or, } |C|^2 \frac{15}{a} \frac{16a^5}{15} = 1$$

$$\text{Or, } C = 1/4a^2$$

### Probability Current Density

In quantum mechanics, the **probability current** is a mathematical quantity describing the flow of probability (i.e. probability per unit time per unit area). **Since the total probability is constant at every instant of time, any decrease of probability in a given length (for 1-D) (dx) must be associated with the corresponding increase of probability in some other element.** Intuitively, if one pictures the probability density as an inhomogeneous fluid, then the probability current is the rate of flow of this fluid. This is analogous to mass currents in hydrodynamics and electric currents in electromagnetism. It is a real vector, like electric current density. The notion of a probability current is useful in some of the formalism in quantum mechanics.

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 0 = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} |\psi(x, t)|^2 dx$$

$$\frac{\partial}{\partial t} |\psi(x, t)|^2 = \frac{\partial}{\partial t} (\psi^*(x, t) \psi(x, t)) = \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial t} + \frac{\partial \psi^*(x, t)}{\partial t} \psi(x, t) \dots \dots (A)$$

From equation (7) we can write,  $\frac{\partial \psi(x, t)}{\partial t} = \frac{1}{i\hbar} \left[ \frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x) \psi(x, t) \right]$

$$\text{and } \frac{\partial \psi^*(x, t)}{\partial t} = \frac{1}{-i\hbar} \left[ \frac{-\hbar^2}{2m} \frac{\partial^2 \psi^*(x, t)}{\partial x^2} + V(x) \psi^*(x, t) \right] \dots \dots \dots (B)$$

Equation (B) is obtained by taking the complex conjugate of equation (7), and taking  $V(x)$  as real, which gives,

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi^*(x, t)}{\partial x^2} + V(x) \psi^*(x, t) = -i\hbar \frac{\partial \psi^*(x, t)}{\partial t}$$

Substituting equation (B) in equation (A), we can write,

$$\begin{aligned} \psi^*(x, t) \left[ \frac{1}{i\hbar} \left[ \frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x) \psi(x, t) \right] \right] + \left[ \frac{1}{-i\hbar} \left[ \frac{-\hbar^2}{2m} \frac{\partial^2 \psi^*(x, t)}{\partial x^2} + V(x) \psi^*(x, t) \right] \right] \psi(x, t) = \\ \left[ \frac{-\hbar}{2mi} \frac{\psi^*(x, t) \partial^2 \psi(x, t)}{\partial x^2} + \frac{1}{i\hbar} V(x) \psi^*(x, t) \psi(x, t) \right] + \left[ \frac{\hbar}{2mi} \frac{\partial^2 \psi^*(x, t)}{\partial x^2} \psi(x, t) - \frac{1}{i\hbar} V(x) \psi^*(x, t) \psi(x, t) \right] = \\ \frac{-\hbar}{2mi} \frac{\psi^*(x, t) \partial^2 \psi(x, t)}{\partial x^2} + \frac{\hbar}{2mi} \frac{\partial^2 \psi^*(x, t)}{\partial x^2} \psi(x, t) = \frac{-\hbar}{2mi} \left[ \frac{\psi^*(x, t) \partial^2 \psi(x, t)}{\partial x^2} - \frac{\partial^2 \psi^*(x, t)}{\partial x^2} \psi(x, t) \right] \\ = \frac{-\hbar}{2mi} \frac{\partial}{\partial x} \left[ \left( \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} \right) - \left( \frac{\partial \psi^*(x, t)}{\partial x} \psi(x, t) \right) \right] \end{aligned}$$

$$\text{Or, } \frac{\partial}{\partial t} (\psi^*(x, t) \psi(x, t)) = \frac{i\hbar}{2m} \left[ \frac{\partial}{\partial x} \left\{ \left( \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} \right) - \left( \frac{\partial \psi^*(x, t)}{\partial x} \psi(x, t) \right) \right\} \right]$$

We know from continuity equation (1-D) that,  $\frac{\partial \rho}{\partial t} + \frac{\partial J_x}{\partial x} = 0$ ,

where,  $\rho$  is the charge density and  $J_x$  is the  $x$  – component of current density  $\mathbf{J}$

Therefore, we define the Probability current density as ,

$$J_x = \frac{-i\hbar}{2m} \left\{ \left( \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} \right) - \left( \frac{\partial \psi^*(x, t)}{\partial x} \psi(x, t) \right) \right\}$$

### Problem (Important)

Show that probability current density for a free particle is equal to the product of its probability density and its speed.

**Solution :** For a free particle,  $\psi(x, t) = Ae^{i(kx - \omega t)} = Ae^{i/\hbar(p_x x - Et)}$  since  $p = \hbar k$  and  $E = \hbar \omega$ .

$$\frac{\partial \psi(x, t)}{\partial x} = \frac{ip_x}{\hbar} Ae^{i/\hbar(p_x x - Et)} = \frac{ip_x}{\hbar} \psi(x, t)$$

and

$$\frac{\partial \psi^*(x, t)}{\partial x} = -\frac{ip_x}{\hbar} Ae^{-i/\hbar(p_x x - Et)} = -\frac{ip_x}{\hbar} \psi^*(x, t)$$

Therefore,

$$J_x = \frac{-i\hbar}{2m} \left\{ \left( \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x} \right) - \left( \frac{\partial \psi^*(x, t)}{\partial x} \psi(x, t) \right) \right\}$$

Or,

$$J_x = \frac{-i\hbar}{2m} \left\{ \left( \psi^*(x, t) \frac{ip_x}{\hbar} \psi(x, t) \right) - \left( -\frac{ip_x}{\hbar} \psi^*(x, t) \psi(x, t) \right) \right\}$$

Or,

$$J_x = \frac{-i\hbar}{2m} \left\{ \frac{ip_x}{\hbar} [\psi^*(x, t) \psi(x, t) + \psi^*(x, t) \psi(x, t)] \right\} = \frac{p_x}{m} \psi^*(x, t) \psi(x, t) \\ = v_x \psi^*(x, t) \psi(x, t)$$

Where,  $v_x$  is the speed and  $\psi^*(x, t) \psi(x, t)$  is the probability density.

### The Time-Independent Schrödinger Equation

The usefulness of wave functions can be seen by solving Schrödinger's equation (6),

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t) \psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t}$$

using the potential energy function  $V(x, t)$  that properly describes the forces acting on the particle of interest. The standard technique for solving partial differential equations consists of searching for solutions in the form of products of functions, each of which contains only a single one of the independent variables that are involved in the equation. The technique, called the **separation of variables**, is used because it immediately reduces the partial differential equation to a set of ordinary differential equations. As we shall see, this is a significant simplification. Here we are dealing with a partial differential equation involving a single space variable  $x$  plus the time variable  $t$ . Thus the technique consists in searching for solutions in which the wave function  $\psi(x, t)$  can be written as the product

$$\psi(x, t) = \phi(x)f(t) \dots \dots (10)$$

where the first term on the right side is a function of  $x$  alone and the second term is a function of  $t$  alone. We shall assume the existence of solutions of this form, substitute these solutions into the Schrödinger equation that they are supposed to satisfy, and see what happens.



However, our assumption is valid, **provided that the potential energy does not depend explicitly on the time  $t$**  so that the function can be written as  $V(x)$ . Since in quantum mechanics, as in classical mechanics, almost all systems have potential energies of this form, the condition is not a very serious restriction.

Substituting the assumed form of the solution,  $\psi(x,t) = \phi(x)f(t)$ , into the Schrödinger equation, and also restricting ourselves to time-independent potential energies that can be written as  $V(x)$ , we obtain from equation (7)

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\phi(x)f(t) = i\hbar \frac{\partial \phi(x)f(t)}{\partial t} \dots \dots (11)$$

$$\text{Now, } \frac{\partial^2 \phi(x)f(t)}{\partial x^2} = f(t) \frac{d^2 \phi(x)}{dx^2} \text{ and } \frac{\partial \phi(x)f(t)}{\partial t} = \phi(x) \frac{df(t)}{dt} \dots \dots (12)$$

In equation (12), partial derivatives  $\frac{\partial^2}{\partial x^2}$  and  $\frac{\partial}{\partial t}$  are replaced by the corresponding total derivatives  $\frac{d^2}{dx^2}$  and  $\frac{d}{dt}$  respectively as  $\phi$  is only a function of  $x$  whereas,  $f$  is only function of  $t$ .

Therefore, from equation (11) and (12), we have ,

$$\frac{-\hbar^2}{2m} f(t) \frac{d^2 \phi(x)}{dx^2} + V(x)\phi(x)f(t) = i\hbar \phi(x) \frac{df(t)}{dt}$$

Dividing both side by  $\phi(x)f(t)$  we get,

$$\frac{-\hbar^2}{2m} \frac{1}{\phi(x)} \frac{d^2 \phi(x)}{dx^2} + V(x) = i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} \dots (13)$$

Note that the right side of equation (13) does not depend on  $x$ , while the left side does not depend on  $t$ . Consequently, their common value cannot depend on either  $x$  or  $t$ . In other words, the common value must be a constant, which we shall call  $G$ . The result of this consideration is that equation (12) leads to two separate equations. One equation is obtained by setting the left side equal to the common value

$$\frac{-\hbar^2}{2m} \frac{1}{\phi(x)} \frac{d^2 \phi(x)}{dx^2} + V(x) = G \dots (14)$$

and the other equation is obtained by setting the right side equal to the common value

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = G \dots (15)$$

The constant  $G$  is called the **separation constant**, for the same reason that this technique for solving partial differential equations is called the separation of variables. In retrospect, we see that the effect of employing the technique has been to convert the single partial differential equation, involving two independent variables  $x$  and  $t$ , into a pair of ordinary differential equations, one involving  $x$  alone and the other involving  $t$  alone. These equations are coupled in the sense that they both contain the same separation constant  $G$ , but this type of coupling does not lead to any difficulty in obtaining solutions to the equations.

Solution of equation (15) can obtained as follows,

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = G$$

Or,

$$\frac{1}{f(t)} \frac{df(t)}{dt} = \frac{-i}{\hbar} G$$

Or,

$$\frac{df(t)}{f(t)} = \frac{-i}{\hbar} G dt$$

Upon integration,

$$\int \frac{df(t)}{f(t)} = \frac{-iG}{\hbar} \int dt$$

Or,

$$\ln f(t) = \frac{-iG}{\hbar} t + \ln C, \text{ where } \ln C \text{ is the integration constant}$$

Or,

$$f(t) = C e^{\frac{-iGt}{\hbar}} \dots \dots (16)$$

Now  $f(t)$  can be written as,  $f(t) = \cos (Gt/\hbar) - i \sin (Gt/\hbar) = \cos (2\pi Gt/h) - i \sin (2\pi Gt/h)$

Representing  $f(t)$  as an oscillatory function with frequency  $\nu = G/h$ .

According to the de Broglie-Einstein postulates  $\nu = E/h$ , where  $E$  is the total energy of the particle associated with the wave function corresponding to  $f(t)$ . Comparing these expressions, we see that the separation constant must be equal to the total energy of the particle.

That is  $G = E$ , so that

$$f(t) = C e^{\frac{-iEt}{\hbar}} \dots \dots (17)$$

Using this value of  $G$  in the space equation, (13), that we obtained from the separation of variables, we have

$$\frac{-\hbar^2}{2m} \frac{1}{\varphi(x)} \frac{d^2 \varphi(x)}{dx^2} + V(x) = E \dots (18)$$

Using this equation(10 and 17), the product form of the wave function becomes

$$\psi(x,t) = \varphi(x) C e^{\frac{-iEt}{\hbar}} \dots \dots (19) \text{ where } E \text{ is the total energy of the particle.}$$

Equation (18) is called the **time-independent Schrödinger equation**, because the time variable  $t$  does not enter the equation. Its time-independent solutions  $\varphi(x)$  determine, through (18), the space dependence of the solutions  $\psi(x,t)$  to the Schrödinger equation. For the one-dimensional cases that the time-independent Schrödinger equation can involve only one independent variable  $x$ , and it must, therefore, be an ordinary differential equation. However, if there are more space dimensions, the time-independent Schrödinger equation will involve more independent variables and will therefore be a partial differential equation. (It can usually be reduced to a set of ordinary differential equations, in such cases, by applying the technique of separation of variables.) In all cases the time-independent Schrödinger equation does not contain the imaginary number  $i$ , and its solutions  $\varphi(x)$  are therefore not necessarily complex functions. The functions  $\varphi(x)$  are called **eigenfunctions**. [will be disused in details later on]

### Required properties of eigen functions $\phi(x)$ / wave functions $\psi(x,t)$

To be an acceptable solution, an eigenfunction  $\phi(x)$  and its derivative  $d\phi(x)/dx$  are required to have the following properties:

- i)  $\phi(x)$  must be *finite*.
- ii)  $d\phi(x)/dx$  must be *finite*.
- iii)  $\phi(x)$  must be *single valued*.
- iv)  $d\phi(x)/dx$  must be *single valued*.
- v)  $\phi(x)$  must be *continuous*.
- vi)  $d\phi(x)/dx$  must be *continuous*.
- vii)  $\phi(x)$  as well as  $\psi(x,t)$  tends to zero, as  $x$  tends to  $\pm\infty$  to ensure total probability as 1.

These requirements are imposed in order to ensure that the eigenfunction be a mathematically "well-behaved" function so that measurable quantities which can be evaluated from the eigenfunction will also be well-behaved.

**If  $\phi(x)$  or  $d\phi(x)/dx$  have to be finite, and single valued, then the same would be true for the wave function  $\psi(x,t) = e^{-iEt/\hbar} \phi(x)$  or  $\partial\psi(x,t)/\partial x = e^{-iEt/\hbar} d\phi(x)/dx$ .**

In order that  $d\phi(x)/dx$  be finite, it is necessary that  $\phi(x)$  be continuous. The reason is that any function always has an infinite first derivative wherever it has a discontinuity. The necessity for  $d\phi(x)/dx$  to be continuous can be demonstrated by considering the time-independent Schrödinger equation, which we write as,

$$-\frac{\hbar^2}{2m} \frac{1}{\phi(x)} \frac{d^2\phi(x)}{dx^2} + V(x) = E$$

For finite  $V(x)$ ,  $E$ , and  $\phi(x)$ , we see that  $d^2\phi(x)/dx^2$  must be finite. This in turn, demands that we require  $d\phi(x)/dx$  to be continuous because any function that has a discontinuity in the first derivative will have an infinite second derivative at the same point. Eigen function as well as the wave function must be single valued so that the probability density can be defined uniquely.

### **Problem (Important)**

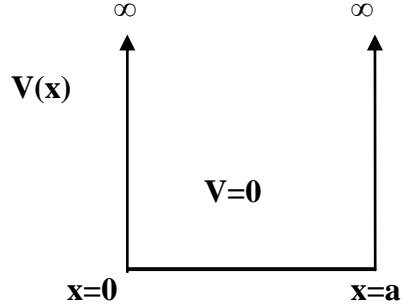
**Justify whether the following functions are acceptable wave function or not**

- 1)  $\psi(x) = e^{-\alpha x^2}$  ... .. **Yes, as  $x \rightarrow \pm\infty, \psi(x) \rightarrow 0$**
- 2)  $\psi(x) = e^{-\alpha x}$  ... .. **No, as  $x \rightarrow -\infty, \psi(x) \rightarrow \infty$**
- 3)  $\psi(x) = e^{\alpha x}$  ... .. **No, as  $x \rightarrow \infty, \psi(x) \rightarrow \infty$**
- 4)  $\psi(x) = \frac{1}{1-x}$  ... .. **No, at  $x = 1, \psi(x)$  diverges**
- 5)  $\psi(x) = \sin \frac{n\pi x}{a}$  for  $-a < x < a$ , **Yes, at  $x = \pm a, \psi(x) = 0$**

### THE INFINITE SQUARE WELL POTENTIAL (1-D case)

Now we shall discuss one of the simplest potentials having this property, the infinite *square well potential*. The potential can be written

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ \infty & \text{otherwise.} \end{cases}$$



It has the feature that it will bind a particle with any finite total energy  $E > 0$ . In *classical mechanics*, any of these energies are possible, but in *quantum mechanics* only *certain* discrete eigenvalues  $E_n$  are allowed.

We shall see that it is very easy to find simple and concise expressions for the eigenvalues and eigenfunctions of this potential because the time-independent Schrödinger equation happens to have simple solutions.

Since as per (19),  $V(x) = 0$  within  $0 < x < a$  and outside this region  $V(x) = \infty$

**Therefore, it's not possible for the particle to cross the boundary, thus  $\phi(x)$  must vanish at the boundary and outside.**

**Thus, the boundary conditions are  $\phi(0) = 0$  and  $\phi(a) = 0$  ....(20)**

In this case, time-independent Schrödinger equation becomes,

$$-\frac{\hbar^2}{2m} \frac{1}{\phi(x)} \frac{d^2 \phi(x)}{dx^2} = E \dots \dots (21)$$

$$\text{Or, } \frac{d^2 \phi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \phi(x), \text{ or, } \frac{d^2 \phi(x)}{dx^2} + \frac{2mE}{\hbar^2} \phi(x) = 0 \dots (22)$$

$$\text{Equation (22) can be written as, } \frac{d^2 \phi(x)}{dx^2} + k^2 \phi(x) = 0 \dots \dots (23), \text{ where, } k^2 = \frac{2mE}{\hbar^2}$$

Solution of equation (23) can be written as,  $\phi(x) = A \sin kx + B \cos kx$ .

Boundary conditions (equation 20) gives,  $\phi(0) = 0$ , therefore,  $B = 0$

and  $\phi(a) = 0$  or,  $\phi(a) = 0$ , or,  $A \sin ka = 0 = \sin n\pi$ ,

**Therefore,  $ka = n\pi$ , or  $k = n\pi/a$ , where  $n = 1, 2, 3 \dots$**

**Thus,  $\phi(x) = A \sin \frac{n\pi x}{a} \dots (22)$**

[Here  $n=0$  is not considered as it is the trivial solution and will represent that the particle does not exist, which is in contrary to our problem.  $n=0$  indicates  $k=0$ , thus  $E=0$ . Therefore particle with zero energy can't be present within the potential well. ]

As both the eigen function and the energy are dependent on n, so we will represent them as  $\varphi_n(x)$  and  $E_n$ .

We can evaluate the constant A by applying the normalization procedure to equation (22) ,

$$\int_{-\infty}^{\infty} |\varphi(x)|^2 dx = 1, \text{ or, } \int_0^a |A|^2 \sin^2 n\pi x/a dx = 1 \dots (23)$$

The limit integration taken as 0 to a, because outside that region  $\varphi(x)=0$

Evaluating (23) we get,  $A = \sqrt{2/a}$ , thus (22) becomes,  $\varphi_n(x) = \sqrt{2/a} \sin n\pi x/a \dots (24)$

And the corresponding energy values are obtained from the relation,  $k^2 = \frac{2mE}{\hbar^2}$  and  $k = n\pi/a$

As  $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \dots (25)$ , which shows the quantization of energy.

Of particular interest is the energy of the ground state energy. For the infinite square well it is,

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

This is called the **zero-point energy**. It is the lowest possible total energy the particle can have if it is bound by the infinite square well potential to the region  $0 < x < a$ . **The particle cannot have zero total energy**. The phenomenon is basically a result of the uncertainty principle.

### Problem (important)

**Find the value of x at which the probability density of finding the particle is maximum in a 1-D infinite potential well. [Consider ground state (n=1)]**

#### **Solution:**

Probability density for ground state can be written as (from equation 24, putting n=1) ,

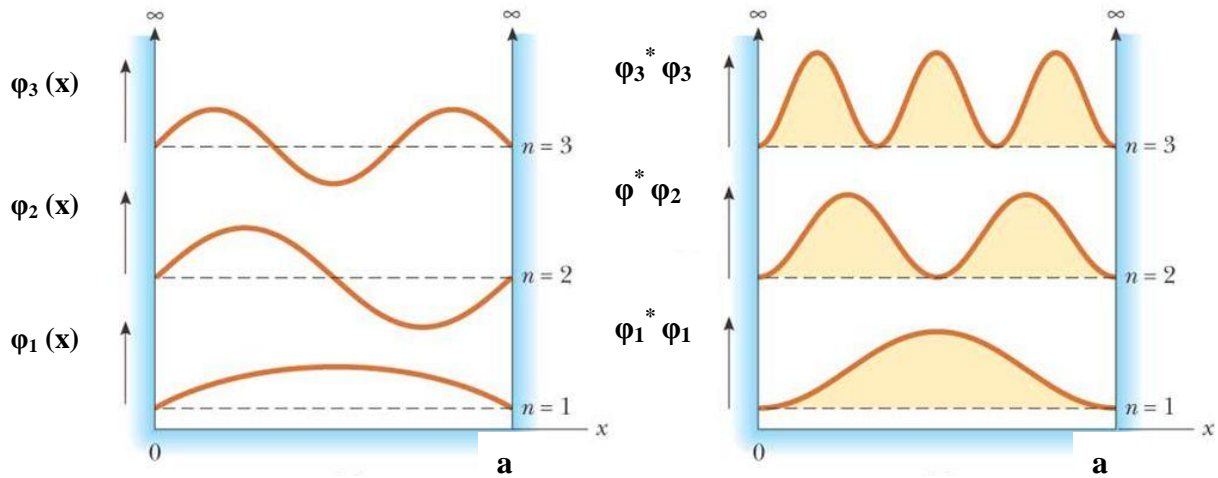
$$P_1(x) = \varphi_1^*(x)\varphi_1(x) = \frac{2}{a} \sin^2 \pi x/a,$$

Now we have to maximize it.

$$dP_1(x)/dx = 0 \text{ gives, } x = \frac{a}{2} \text{ and } d^2P_1(x)/dx^2 \text{ is negative at } x = a/2.$$

Therefore, the probability of finding the particle in a 1-D potential well is maximum at  $x=a/2$  for the ground state.

Different eigen functions ( $\varphi_n(x)$ ) and the corresponding probability density  $P_n(x)$  are plotted below as a function of  $x$ , within the limit  $0 < x < a$ .



### THE INFINITE SQUARE WELL POTENTIAL (3-D case)

Now we shall discuss one of the simplest potentials having this property, the infinite *square well potential*. The potential can be written as,

$$V(x, y, z) = \begin{cases} 0 & \text{for } 0 < x < a, \\ 0 & \text{for } 0 < y < b, \\ 0 & \text{for } 0 < z < c, \dots \dots \dots (26) \\ = \infty, & \text{otherwise.} \end{cases}$$

**It has the feature that it will bind a particle with any finite total energy  $E > 0$ . In classical mechanics, any of these energies are possible, but in quantum mechanics only certain discrete eigenvalues are allowed.**

We shall see that it is very easy to find simple and concise expressions for the eigenvalues and eigenfunctions of this potential because the time-independent Schrödinger equation happens to have simple solutions.

Since as per (26),  $V(x, y, z) = 0$  within  $0 < x < a, 0 < y < b$  and  $0 < z < c$ , and outside this region  $V(x, y, z) = \infty$

**Therefore, it's not possible for the particle to cross the boundary, thus  $\phi(x, y, z)$  must vanish at the boundary and outside.**

Thus, the boundary conditions are,

$$\phi(0, y, z) = 0 \text{ and } \phi(a, y, z) = 0 \dots (27)$$

$$\phi(x, 0, z) = 0 \text{ and } \phi(x, b, z) = 0 \dots (28)$$

$$\phi(x, y, 0) = 0 \text{ and } \phi(x, y, c) = 0 \dots (29)$$

In this case, time-independent Schrödinger equation becomes,

$$\frac{-\hbar^2}{2m} \left[ \frac{\partial^2 \phi(x, y, z)}{\partial x^2} + \frac{\partial^2 \phi(x, y, z)}{\partial y^2} + \frac{\partial^2 \phi(x, y, z)}{\partial z^2} \right] = E \phi(x, y, z) \dots \dots (30)$$

Let us consider,  $\phi(x, y, z) = X(x)Y(y)Z(z) \dots \dots (31)$ , which gives,

$$\frac{\partial^2 \phi(x, y, z)}{\partial x^2} = \frac{d^2 X(x)}{dx^2} Y(y)Z(z)$$

$$\frac{\partial^2 \phi(x, y, z)}{\partial y^2} = X(x) \frac{d^2 Y(y)}{dy^2} Z(z)$$

$$\text{And } \frac{\partial^2 \phi(x, y, z)}{\partial z^2} = X(x)Y(y) \frac{d^2 Z(z)}{dz^2}$$

Thus, equation (30) becomes,

$$\frac{d^2 X(x)}{dx^2} Y(y)Z(z) + X(x) \frac{d^2 Y(y)}{dy^2} Z(z) + X(x)Y(y) \frac{d^2 Z(z)}{dz^2} = \frac{-2mE}{\hbar^2} X(x)Y(y)Z(z)$$

Or, dividing both side by  $X(x)Y(y)Z(z)$ ,

$$\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2 Y(y)}{dy^2} + \frac{1}{Z(z)} \frac{d^2 Z(z)}{dz^2} = \frac{-2mE}{\hbar^2} \dots (31)$$

Therefore,

$$\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} = -\alpha_x^2 \dots (32)$$

$$\frac{1}{Y(y)} \frac{d^2 Y(y)}{dy^2} = -\alpha_y^2 \dots (33)$$

$$\frac{1}{Z(z)} \frac{d^2 Z(z)}{dz^2} = -\alpha_z^2 \dots (34)$$

$$\text{where, } \alpha_x^2 + \alpha_y^2 + \alpha_z^2 = \frac{2mE}{\hbar^2} \dots (35)$$

Solution of equation (32), (33) and (34) can be written as,

$$X(x) = A \sin \alpha_x x + B \cos \alpha_x x \dots (36)$$

$$Y(y) = C \sin \alpha_y y + D \cos \alpha_y y \dots (37)$$

$$Z(z) = E \sin \alpha_z z + F \cos \alpha_z z \dots (38)$$

Boundary conditions (equation 27) gives,  $X(0) = 0$ , therefore,  $B = 0$  and  $X(a) = 0$  or,  $A \sin \alpha_x a = 0 = \sin n_x \pi$ , Therefore,  $\alpha_x a = n_x \pi$ , or  $\alpha_x = n_x \pi / a$ , where  $n = 1, 2, 3 \dots$

$$\text{Thus, } X(x) = A \sin n_x \pi x / a \dots (39)$$

Similarly, equation (28) gives,  $Y(0) = 0$ , therefore,  $D = 0$  and  $Y(b) = 0$  gives,  $\alpha_y = n_y \pi / b$

$$\text{Thus, } Y(y) = C \sin n_y \pi y / b \dots (40)$$

And, equation (29) gives,  $Z(0) = 0$ , therefore,  $F = 0$  and  $Z(c) = 0$  gives,  $\alpha_z = n_z \pi / c$

$$\text{Thus, } Z(z) = E \sin n_z \pi z / c \dots (40)$$

Therefore, combining equation (31) with equation (38), (39) and (40) we obtain the energy eigen function as,

$$\varphi_{n_x n_y n_z}(x, y, z) = A \sin n_x \pi x / a C \sin n_y \pi y / b E \sin n_z \pi z / c \dots (41)$$

[Here,  $n_x = n_y = n_z = 0$  are not considered as they give the trivial solution and will represent that the particle does not exist, which is in contrary to our problem.  $n_x = n_y = n_z = 0$  indicates  $E = 0$ . Therefore particle with zero energy can't be present within the potential well.]

As both the eigen function and the energy eigen values are dependent on  $n_x$ ,  $n_y$ ,  $n_z$ , so we will represent them as  $\varphi_{n_x n_y n_z}(x, y, z)$  and  $E_{n_x n_y n_z}$  respectively.

We can evaluate the constant  $N = ACE$  by applying the normalization procedure to equation (41),



$$\int_{-\infty}^{\infty} |\varphi_{n_x n_y n_z}(x, y, z)|^2 dx dy dz = 1,$$

or,  $|N|^2 \int_{x=0}^a \sin^2 n_x \pi x / a dx \int_{y=0}^b \sin^2 n_y \pi y / b dy \int_{z=0}^c \sin^2 n_z \pi z / c dz = 1 \dots (42)$

Evaluating (42) we get,  $N = \sqrt{2/a} \sqrt{2/b} \sqrt{2/c}$ ,

thus the normalized eigen function (41) becomes,

$$\varphi_{n_x n_y n_z}(x, y, z) = \sqrt{8/abc} \sin n_x \pi x / a \sin n_y \pi y / b \sin n_z \pi z / c \dots (43)$$

And the corresponding energy values are obtained from the relation (35) as,

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2m} \left[ \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \dots (44), \text{ which shows the quantization of energy due to the bound states.}$$

### Degeneracy of energy states (Important)

Consider a 3-D potential well for which  $a=b=c = L$ (say), thus equ (43) and (44) becomes,

$$\varphi_{n_x n_y n_z}(x, y, z) = \sqrt{8/L^3} \sin n_x \pi x / L \sin n_y \pi y / L \sin n_z \pi z / L \dots (45)$$

$$\text{and } E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2mL^2} [n_x^2 + n_y^2 + n_z^2] \dots (46),$$

It is now clear from equation (46) that, the particle can have the same value of energy for more than one set of  $(n_x, n_y, n_z)$  and these various energy states corresponding to each set of  $(n_x, n_y, n_z)$  which result in the same energy eigen-value are termed as degenerate states.

Energy State	Value of $n_x$	Value of $n_y$	Value of $n_z$	Energy Eigen value, $E_{n_x n_y n_z}$	Degree of degeneracy
Ground state	1	1	1	$\frac{3\pi^2 \hbar^2}{2mL^2}$	1
1 <sup>st</sup> Excited state	2	1	1	$\frac{6\pi^2 \hbar^2}{2mL^2}$	3
	1	2	1		
	1	1	2		
2 <sup>nd</sup> Excited state	2	2	1	$\frac{9\pi^2 \hbar^2}{2mL^2}$	3
	1	2	2		
	2	1	2		
3 <sup>rd</sup> Excited state	3	1	1	$\frac{11\pi^2 \hbar^2}{2mL^2}$	3
	1	3	1		
	1	1	3		
4 <sup>th</sup> Excited state	2	2	2	$\frac{12\pi^2 \hbar^2}{2mL^2}$	1