UNIT 6 SCHRÖDINGER EQUATION

Structure

6.1 INTRODUCTION

In Unit 4, you have seen that a microscopic particle is essentially represented by a matter wave with its wavelength given by the de Broglie relation. How do we describe the motion of such a particle or a system of such particles? Clearly, we cannot make use of Newton's laws of motion for this purpose. So a new theoretical description is needed for the motion of quantum mechanical particles. The new theory should be consistent with the wave nature of particles. It should also reduce to Newtonian mechanics for macroscopic particles. Recall that this condition is similar to the special theory of relativity which reduces to Newtonian mechanics at velocities much smaller than the velocity of light.

In this connection, we would like to recount a story. At the end of a seminar, in **1926,** on de Broglie waves, the physicist Peter Debye said to another physicist that if matter is a wave, there should be a wave equation to describe a matter wave. Debye promptly forgot about it but the other physicist, Erwin Schrodinger proceeded to discover the wave equation for matter waves. This equation is named after him as the Schrödinger equation.

In this unit you will study the one-dimensional Schrödinger equation, and learn about its solutions, We shall also discuss the physical meaning of these solutions. These solutions are acceptable only under certain conditions about which you will study towards the end of the unit. An appendix has been given at the end of the Unit to explain the basic complex algebra used in the text. In the next unit we shall introduce another way of describing quantum mechanical systems, given by Heisenberg and Dirac which makes use of operators and observables.

Objectives

After studying this unit you should be able to

● write the onedimensional time dependent Schrödinger equation and derive the time independent Schrödinger equation from it,

● give a statistical interpretation of the wave function,

● derive the continuity equation for the probability current density,

● normalise a given wave function,

● apply the boundary conditions to a given wave function.

6.2 ONE-DIMENSIONAL SCHRÖDINGER EQUATION

You have already learnt that wave nature is an inherent property of every particle. We now need a wave equation which suitably describes the time evolution of matter waves

representing the particle. In Unit 5, you have learnt that one way of **localising** a particle **is** by constructing a wave packet. However, by solving the **terminal** question 4 you have **also** seen that a wave packet spreads with time. This means that, a wave packet cannot represent a **particle.**

Hence, in quantum mechanics it is postulated that

> Every particle (or a system of particles) is represented by a **"wave function"**, which is a function of space coordinates and time. The wave function determines **all** that can be known about the system it represents.

Postulate 1: Description of the system

For one-dimensional motion of a particle, the wave function may be represented by $\psi(x, t)$. Now you may **ask:** What is the form of $\psi(x, t)$ in terms of x and t? To answer this question, consider a classical (macroscopic) particle moving under the influence of a force. Its dynamical behaviour is described by Newton's second law, which is a differential equation. Similarly, Maxwell's equations of classical electromagnetism are also differential equations. Since all objects exhibit particle as well as wave nature, it is natural to expect that the **quantum mechanical** wave function will also be a solution of a certain differential equation, **involving** derivatives of x and t.

The credit for discovering such a differential equation goes to Erwin **Schrödinger** (Fig. 6.1). How did he arrive at his equation? The answer is, he created it intuitively breaking all traditions of such wave equations. The **Schrödinger** equation is one of the most successful equations of quantum mechanics because it predicts results which can be verified experimentally. We will now give you some idea of how he visualised the particular form of his equation.

Let us first state certain preconditions for establishing this equation. Firstly, for a particle of mass m, energy E and momentum p, the equation should be consistent with

(i)   the de Broglie relation $\lambda = \dfrac{h}{P}$, and   (6.1)

(ii) Planck formula $v = \dfrac{E}{h}$ (6.2)

It should also satisfy the relation

(iii) $E = \dfrac{p^2}{2m} + V(x, t)$ (6.3)

for all x and t, where $V(x, t)$ is the potential energy of the particle,

(iv) Finally, the SchrGdinger equation must be linear in x and t. That is, if $\psi_1(x, t)$ and $\psi_2(x, t)$ are two **solutions** of the **Schrödinger** equation for a given potential energy $V(x, t)$ then any linear combination of ψ_1 and ψ_2, say, $C_1 \psi_1 + C_2 \psi_2$, with C_1 and C_2 as arbitrary constants, must also be the solution of the same SchrGdinger equation. This linearity is required so that two waves may be added to produce interference. If the linearity property is to be satisfied, the SchrGdinger (differential) equation must be of degree 1, **i.e.,** the wave functions and its derivatives appearing in it should be only of the first power.

We now put Eqs. (6.1) and (6.2) in (6.3) to obtain

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V(x, t) \qquad (6.4)$$

where $\omega = 2\pi v$ and $k = 2\pi/\lambda$. We now consider a simpler situation where the potential energy is constant, say equal to V_0. Under such a situation, if we take the particle to be a photon then it will have a fixed wavelength and frequency (as **given** by Eqs. (6.1) and (6.2)) and its wavefunction as given by the electromagnetic theory (see Unit 14, PHE-07 entitled Electric and Magnetic Phenomena), will be

$$\psi(x, t) = A\, e^{i(kx - \omega t)} \qquad (6.5)$$

Differentiating the **above** equation once with respect to time you can easily obtain

Fig. 6.1 : Erwin **Schrödinger,** 1887-1961, **Austrian** theoretical physicist. Another **of the** founders **of the** new quantum mechanics, he received the Nobel Prize in 1933.

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$$\omega = i \frac{1}{\psi(x, t)} \frac{\partial \psi(x, t)}{\partial t} \tag{6.6}$$

and

$$k^2 = -\frac{1}{\psi(x, t)} \frac{\partial^2 \psi(x, t)}{\partial x^2} \tag{6.7}$$

Putting Eqs. (6.6) and (6.7) in Eq. (6.4) we obtain a differential equation connecting the wave function $\psi(x, t)$ and its derivatives:

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V_0 \psi(x, t) \tag{6.8}$$

The above equation has been obtained for a special case of constant potential energy V_0. However, Schrödinger made a bold extrapolation and postulated that the form of the Eq. (6.8) does not change even for a particle of mass m moving in a potential which varies with x and t. Thus,

Postulate 2:
Time Evolution
of a System

The time-dependent **Schrödinger** equation for one-dimensional motion of a particle of mass m moving in a potential $V(x, t)$ is given by

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t) \psi(x, t) \tag{6.9}$$

While reading this discussion, did you wonder what would happen if we had a wave equation with a second order time derivative? We would then have ended up with the relativistic energy-momentum relationship. Actually, to begin with, this is what Schrödinger himself attempted. But very soon he realised that such an equation did not work for electrons — it did not give the correct spectrum for the hydrogen atom. Incidentally, the correct relativistic equation for electrons, discovered by Dirac, does retain the first-order time derivative.

You should note that Eq. (6.9) is consistent with (i) to (iv). The appearance of $\hbar$ in the Schrödinger equation is, of course, crucial. This is how Schrodinger imposed the' "quantum condition" on the wave equation of matter.

The **Schrödinger** equation is unlike any of the wave equations you have come across so far. Recall that wave equations usually connect a second-order time derivative of the function with its second order spatial derivative. But **Schrödinger's** equation contains only the first-derivative with respect to **time** but the second derivative with respect to space, Hence, time and space coordinates are not treated on an equal footing in this equation. Thus Eq. (6.9) cannot be .correct in the relativistic domain. Hence, it is a **non-**relativistic time dependent **Schrödinger** equation.

And, there is a price to pay for having only a first order time derivative in the wave equation. The solutions of the **Schrödinger** equation are not real physical waves; they we complex functions with both a real and an imaginary part. This gives rise to the problem of interpretation of the wave function. What exactly does the wavefunction $\psi(x, t)$ mean physically? We shall discuss the interpretation of ψ given by **Max** Born in the next section.

But before that you might like to verify the linearity property of $\psi(x, t)$. Try the following SAQ.

Spend
5 min

SAQ 1

If $\psi_1(x, t)$, and $\psi_2(x, t)$ we **two** solutions of the Schrodinger equation **(6.9)**, show that $a\psi_1$ and $a\psi_1 + b\psi_2$ **are** also solutions of Eq. **(6.9)**, where a and b are arbitrary constants.

6.3 STATISTICAL INTERPRETATION OF THE WAVE FUNCTION

The coefficient of the time derivative of ψ in Eq. (6.9) is imaginary. Therefore, it is evident that the wave function ψ, which is the solution of **(6.9)**, will, in general, be complex. Thus, in order to extract any physical information from $\psi(x, 't)$, we must establish a quantitative connection between $\psi(x, t)$ and the observables of the **particle.** In 1926, Max Born proposed the following connection:

> If, at any instant t, a measurement is made to locate the object represented by the wave function $\psi(x, t)$, then the probability $P(x, t)\, dx$ that the object will be found between the coordinates x and $x + dx$ is
>
> $$P(x, t)\, dx = \psi^*(x, t)\, \psi(x, t)\, dx = |\psi(x, t)|^2 dx, \qquad (6.10)$$
>
> where "*" on a function represents its complex conjugate.

You can see that $|\psi(x, t)|^2$ is the modulus square of the wave function. Here, $P(x, t) = \psi^*(x, t)\, \psi(x, t) = |\psi(x, t)|^2$ is also termed the **probability density.** To put it in words:

The probability of finding a quantum mechanical object in a small interval dx is given *by* the product of the modulus square of the wave function representing the object and the interval *itself.*

The probability of finding the particle within some finite length $L = (x_2 - x_1)$ is given by

$$P_L(t) = \int_{x_1}^{x_2} P(x, t)\, dx \qquad (6.11)$$

Thus, according to Max Born, the **Schrödinger** equation gives probability waves. The wave function just tells us probabilistically where the likelihood of finding the particle will be greater: there the wave will be strong, its amplitude will be larger. If the probability of finding a particle in a region is small, the wave will be weak and its amplitude will be small. It may seem from the above probabilistic interpretation that the phase of the wave function is not important, since it is the modulosquare $|\psi(x, t)|^2$ that we interpret as the probability. However, this is not so. We shall very briefly discuss this aspect.

To **visualise** this concept, **imagine** you are in a **metropolis** like Delhi and looking for traffic **jams** on Its **roads** from a **helicopter.** If tho vehicles were **described** by Schrödinger **waves, we** would say that the wave **was strong** at **the** location of traffic jam. **Elsewhere,** the wave would be weak.

The phase of the wave function

From the linearity property of **Schrödinger** equation and SAQ 1, you know that if ψ_1 and ψ_2 are solutions of the **Schrödinger** equation, the linear combination

$$\psi(x, t) = a_1\, \psi_1(x, t) + a_2\, \psi_2(x, t) \qquad (6.12)$$

is also a solution of the **Schrödinger** equation where a_1 and a_2 are arbitrary complex numbers. This is the **superposition principle.** Now, calculate $|\psi(x, t)|^2$ using Eq. (6.5) with a phase difference, say ϕ, between ψ_1 and ψ_2. You will see that it depends on the relative phase of ψ_1 and ψ_2. Such a superposition is called **coherent superposition** — it gives rise to the interference of matter waves. Thus, the phase of the wave function is important and cannot be ignored.

You should also notice a crucial difference between the use of probability in classical physics and in quantum physics. In classical physics, probabilities add as you have studied in Unit 5 of the physics elective PHE-04 (Mathematical Methods in Physics-I), But in quantum physics, the probability amplitudes add, as in Eq. (6.12) and then we calculate the probabilities from Eq. (6.10) giving rise to interference.

Let us come back to the probabilistic interpretation. Since the object must always be somewhere in space, the **total probability of finding it in the whole space is unity.** We obtain this by integrating the probability over all space:

$$\int_{-\infty}^{\infty} \psi^*(x, t)\, \psi(x, t)\, dx = 1, \text{ at each instant of time t} \qquad (6.13)$$

The interpretation of the wave function given by Eqs. (6.10) to (6.13) requires that ψ should be **finite** and **single-valued** everywhere, otherwise the probability of finding an object in a **region** of space will not be finite and unique. Further, Eq. (6.13) requires that we restrict the wave functions used in quantum mechanics to the class of **square integrable functions for** which

$$|\psi(x, t)|^2\, dx < \infty$$

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i.e., $\psi(x, t)$ must approach 0 as $x \to \infty$ at least as fast as $x^{-1/2-\epsilon}$, with $\epsilon > 0$ and arbitrarily small. In addition, certain continuity conditions need to be imposed on ψ. We will discuss these in Sec. 6.4.1 in detail. Meanwhile, let us further explore the meaning of ψ.

6.3.1 Probability Current Density and the Continuity Equation

Since Eq. (6.13) is true for every t, *the total probability is conserved.* But this can be accomplished only when *the probability, is conserved at each point, and at all times.* Let us examine this aspect in some detail.

Let us consider the concrete example of a fluid moving in the positive x-direction between two points $x = x_1$ and $x = x_2$ with a velocity v which changes with x. Let $\rho(x)$ denote the mass per unit length of the fluid around the point x. The quantity $S_x = v(x)\,\rho(x)$ is then the mass of the fluid crossing a given point x per unit time. What is the net mass accumulated per unit time in between the two points $x = x_1$ and $x = x_2$? Clearly, it is equal to $S_{x=x_1} - S_{x=x_2}$. And if the fluid is to be conserved in this region then this should be equal to the rate of change of mass in this region. Thus

$$\frac{\partial}{\partial t} \int_{x_1}^{x_2} \rho(x)\,dx = S_{x=x_1} - S_{x=x_2} \tag{6.14}$$

We can extend this analogy to the probabilistic interpretation. We say that *if the total probability is to be conserved, the conservation equation should look like* Eq. (6.14) *where ρ should be replaced by the probability density $P(x, t)$ and S_x by a function which we term the probability flux or the probability current density $S(x, t)$.* Thus, we must have

$$\frac{\partial}{\partial t} \int_{x_1}^{x_2} P(x, t)\,dx = S(x_1, t) - S(x_2, t) \tag{6.15}$$

Let us now obtain the definition of the probability flux $S(x, t)$ so that the probability conservation equation (6.15) is obeyed. For this we shall use the Schrödinger equation:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \tag{6.16a}$$

Here and in future we will omit the arguments of ψ and V as long as it does not create any confusion. The complex conjugate of Eq. (6.16a) is

$$-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + V\psi^* \tag{6.16b}$$

where we have assumed that V is real so that $V^* = V$. You can now multiply Eq. (6.16a) from the left by ψ^* and Eq. (6.16b) by ψ and then subtract (6.16b) from (6.16a) and obtain

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

Now carry out a simple algebraic manipulation of the above equation to show that

$$\frac{\partial(\psi^*\psi)}{\partial t} = -\frac{\hbar}{2mi} \frac{\partial}{\partial x} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) \tag{6.17}$$

We now integrate Eq. (6.17) with respect to x from x_1 to x_2 and get

$$\frac{\partial}{\partial t} \int_{x_1}^{x_2} \psi^* \psi\,dx = -\frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) \Bigg|_{x_1}^{x_2} \tag{6.18}$$

A comparison of Eqs. (6.15) and (6.18) shows that the **probability** density $P(x, t)$ and the *probability* **flux** or **probability** *current* density $S(x, t)$ should be defined as

$$P(x, t) = \psi^*(x, t)\,\psi(x, t)$$

and

$$S(x, t) = \frac{\hbar}{2mi}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right) \qquad (6.19)$$

We may rewrite Eq. (6.18) in terms of P and S as

$$\frac{\partial P(x, t)}{\partial t} + \frac{\partial S(x, t)}{\partial x} = 0 \qquad (6.20)$$

Doesn't this equation look familiar to you? It has the form of a continuity equation analogous to the continuity equation between the charge density and current density in electrodynamics. This is one reason why $P(x, t)$ is referred to as the probability density and $S(x, t)$ is called the probability current density. In this equation, the first term

$\frac{\partial P}{\partial t}$ denotes the rate of change of probability density in a certain fixed length. The second term denotes the net outward flux coming out of the same length. Eq, (6.20) then says that the time rate of change of probability density (which is a negative quantity because as t increases $\partial P/\partial t$ decreases) is numerically equal to the net *outward* flux (an outward flux is always assumed to be positive quantity). This means that within the above length, the particles are neither created nor destroyed (i.e., there are neither sources, nor sinks).

Eq. (6.20) is, therefore, the conservation law expressing the fact that a change in the particle density in a region of space is compensated for by a net change *of flux* from that region. You can now also see why we need to impose continuity conditions on ψ:

both ψ and its derivative $\frac{\partial \psi}{\partial x}$ must be finite and continuous for all values of x provided $V(x)$ is finite. That these restrictions on the solutions are necessary may be judged from the following considerations.

The probability density $P(x)$ and the probability flux $S(x, t)$ represent physical quantities and, therefore, have to be well defined. If $\psi(x)$ or its first derivative $\psi'(x)$ were not finite for some values of x then $P(x)$ and/or $S(x, t)$ would not be well defined for all values of x. Further, both $\psi(x)$ and $\psi'(x)$ must be continuous. Otherwise $S(x, t)$ would be singular at some points and these points would act as sources or sinks of probability current. In other words, creation or destruction of matter would take place. This, as you know, is impossible in non-relativistic physics.

Before proceeding further, we would like to point out that Eq, (6.20) is obtained under the condition that V is real. By writing $\psi = \psi_R + i\psi_I$ it is easy to see that both P and S are real and

$$S(x, t) = \frac{\hbar}{m}\,\text{Im}\left(\psi^* \frac{\partial \psi}{\partial x}\right) = \text{Re}\left(\psi^* \frac{\hbar}{im} \frac{\partial \psi}{\partial x}\right) \qquad (6.21)$$

where $\text{Im}(Z)$ denotes the magnitude of the imaginary part of Z and Re (Z) its real part. You may like to do an exercise to fix the ideas involved.

SAQ 2

Spend 15 min

(a) Show that for complex potential energy, the continuity equation (6.20) modifies to

$$\frac{\partial P(x, t)}{\partial t} + \frac{\partial S(x, t)}{\partial x} = \frac{2V_I}{\hbar}\,P(x, t)$$

where V_I is the imaginary part of the potential energy.

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(b) The wave function of an object of mass m is given by

$$\psi(x, t) = e^{-(\alpha + i\beta)x} e^{-i\omega t}$$

Obtain the values of $P(x, t)$ and $S(x, t)$.

The probabilistic interpretation of ψ also leads us to the concept of normalising a wave function.

6.3.2 Normalisation of **Wave Functions**

Recall Eq. (6.13) which tells us that since the particle must be somewhere in space, the probability integrated over all x (i.e., all space in one-dimension) must equal 1. A wave function satisfying Eq. (6.13) is said to be **normalised.**

Now in quantum mechanics we deal with two types of wave functions. For one of them the value of the integral $\int_{-\infty}^{\infty} \psi^{*\prime}(x, t) \psi'(x, t)\, dx$ is finite, say equal to N, where ψ' is the solution of the Schrödinger equation. Such *functions are* said to be normalisable and N is known as the **norm** of the wave **function.** It also means that ψ' is a square integrable function which vanishes as $|x| \to \infty$.

You also know that Schrodinger equation is linear. And you have shown in SAQ 1 that if ψ' is a solution of Eq. (6.9) then ψ' multiplied by a constant (independent of t and x) is also a solution. Hence we can always choose the constant to be $N^{-1/2}$ and take $\psi = N^{-1/2} \psi'$. Then for ψ, Eq. (6.13) is satisfied and the wave function ψ is said to be a **normalised** wave function. Note that N is independent of time (otherwise ψ will not be a solution of Eq. (6.9)). Hence, a wavefunction which is *normalised* at any instant of time stays normalised at all other times.

However, there exists a category of wave functions for which the value of the integral in Eq. (6.13) is infinite. Such functions do not represent a physical system in the strictest sense. But, we shall see later that such functions are extensively used in quantum mechanics to describe free particles. In fact, we have already used $e^{i(kx -\omega t)}$ to represent a free particle. It is a wave function whose norm is infinite or, in other words, it is unnormalisable. Wave functions of this form do not go to zero as $x \to \pm \infty$. We shall discuss the normalisation of such functions in detail in Block 3.

Let us now further analyse the Schrodinger Equation.

6.4 TIME INDEPENDENT SCHRÖDINGER EQUATION

The Schrodinger equation (6.9) represents the time development of the wave functions $\psi(x, t)$. We have seen that the position probability density of the particle is related to $\psi(x, t)$. We can also transform $\psi(x, t)$ in such a way that we obtain momentum probability distributions of the particle. (Such transforms are called Fourier transforms). Thus, given the position and momentum distributions of the particle at one time, the same can be obtained at any later time with the help of the Schrödinger equation. Isn't this situation analogous to the one in classical mechanics? In classical mechanics, if the position and momentum of a particle are known at some initial time then we can use Newton's equation of motion to find the position and momentum of the particle at any later time. However, there is a difference between classical and quantum mechanics. What is it? Recall the uncertainty principle which tells us that in quantum mechanics both the position and the momentum of the particle cannot be known precisely at the same instant of time. We can know only their distributions.

In many pmblems of classical mechanics such as Kepler's planetary orbits, Rutherford · scattering, we assume that the particle has definite energy and/or angular momentum. However, in quantum mechanics if we assume the energy of the particle to be known precisely, i.e., if AE = 0 then, according to the uncertainty relation ΔE At $\geq \hbar$, and At is infinite. This means that an infinite amount of time should be available to make energy measurements. In other words, the probability density $\psi^*(x, t) \psi(x, t)$ should not change

with time. Hence, for a system of constant energy the wave function $\psi(x, t)$ should take the form

$$\psi(x, t) = \psi(x) \exp \{ig(t)\} \tag{6.22}$$

where $g(t)$ is any function of t. For a system represented by such a wave function, the energy of the system does not change with time, i.e., its energy is conserved. Hence, if the particle is initially in a specified energy state represented by Eq. (6.22) then it stays in it indefinitely unless it is disturbed by some external agency. Such energy states are called *stationary* **states**.

Classically, the energy (which is also termed the I-Iamiltnnian) is a constant of motion if it does not contain time explicitly. Now, the *Hamiltortian is the sum of the kinetic energy and the potential energy.* Thus, for the total energy to be conserved, the potential in which the particle is moving should be independent of time. For such potentials, the Schrödinger equation (6.9) may be separated in x and t as follows. Substituting

$$\psi(x, t) = \psi(x) \, f(t) \tag{6.23}$$

in Eq. *(6.9)* and rearranging the terms, we get

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) = \frac{i\hbar}{f(t)} \frac{\partial f(t)}{\partial t} \tag{6.24}$$

The left side of this equation is constant for fixed x nt all t. Similarly, the right side is constant for Fixed t at all values of x. Hence, Eq. *(6.24)* will hold only when both the sides are equal to a constant C which is independent of x and t. Thus we obtain

$$i\hbar \frac{df}{dt} = C \, f(t) \tag{6.25}$$

and

$$-\frac{\hbar^2}{2m} \psi''(x) + V(x) \, \psi(x) = C \, \psi(x), \tag{6.26}$$

where.$\psi''(x) \equiv d^2 \psi(x)/dx^2$.

You can solve Eq. (6.25) to obtain

$$f(t) = A \exp \{-iCt/\hbar\} = A \exp \{-i\omega t\} \tag{6.27}$$

where A is the normalisation constant and $\omega = C/\hbar$. From Eqs. *(6.26)* and *(6.27)* it is clear that C should have dimensions of energy and be equal to the total energy E. Eq. *(6.27)* is, therefore, written as

$$\boxed{-\frac{\hbar^2}{2m} \psi''(x) + V(x) \, \psi(x) = E \, \psi(x)} \tag{6.28}$$

T i e independent Schrödinger **equation**

The above equation is known as **time** independent Schrödinger *equation.*

We can now write the general solution or the stationary state solution of the time-dependent Schrödinger equation for a particle of definite energy E as

$$\psi(x, t) = \psi(x) \exp (-iEt/\hbar), \tag{6.29}$$

where $\psi(x)$ satisfies Eq. *(6.28)*. The probability density and the probability flux in such cases are given by

$$P(x) = \psi^*(x) \, \psi(x) \tag{6.30}$$

and

$$S(x) = \frac{\hbar}{2mi} [\psi^*(x) \frac{d}{dx} \psi(x) - \psi(x) \frac{d}{dx} \psi^*(x)] \tag{6.31}$$

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It is evident that both $P(x)$ and $S(x)$ are independent of time. You should note that Eq. (6.28) contains no imaginary quantities and hence $\psi(x)$ is not necessarily complex although $\psi(x, t)$ is. The normalisation condition (6.13) for the stationary state function reduces to a form

$$\int_{-\infty}^{\infty} \psi^*(x)\, \psi(x)\, dx = 1 \tag{6.32}$$

You may now like to apply the concepts discussed so far.

SAQ 3

The wave function for a steady state is given by

$$\psi(x) = N \exp\left(-\frac{x^2}{2}\right)$$

Calculate the value of the normalisation constant N.

In this course we shall confine our study to those problems which require solutions of time independent Schrtidinger equation, i.e., we shall study stationary state problems. Let us now examine the conditions which the wave function $\psi(x)$ has to satisfy in order to be a physically acceptable solution.

6.4.1; / Boundary Conditions and Acceptable Solutions

Recall that the probabilistic interpretation imposes the following conditions on the wave function $\psi(x)$:

1) $\psi(x)$ should be finite and single-valued everywhere,

2) $\psi(x)$ should be square integrable and

3) both $\psi(x)$ and $\dfrac{\partial \psi}{\partial x}$ should be continuous everywhere.

We can rewrite the time independent Schrödinger equation (6.28) as

$$\frac{d^2\, \psi(x)}{dx^2} = \frac{2m}{\hbar^2}\, [V(x) - E]\, \psi(x) \tag{6.33}$$
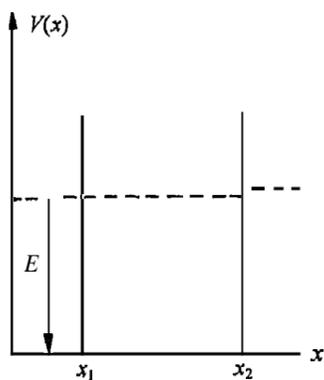
You know that $\psi(x)$ represents a probabilistic wave satisfying Eq. (6.13). Further, whether $\psi(x)$ is an acceptable solution of Eq. (6.33) or not is also determined by $V(x)$ as well as by the boundary conditions which depend upon the nature of the problem. Let us consider an example of a particle bound in a potential well shown in Fig. 6.2. Here $V(x) > E$ for x $< x_1$ and $x > x_2$.

Fig. 6.2 : Particle in a potential well

Classically, if the particle is initially between x_1 and x_2 then for all times to come it will be confined between the same space, i.e., the particle is bounded between x_1 and x_2. Then we say that the particle is in a bound state. Quantum mechanically we expect a large probability of finding the particle between the space $x_1 < x < x_2$. However, there also exists a decreasingly small probability of finding the particle outside this space, which is forbidden classically. This, in turn, demands for the (boundary) condition that the bound state wave functions must vanish at infinity, A very interesting result follows from the consideration of such a boundary condition which you shall study in the next block in detail. Here we just mention it: The (acceptable) solutions of the time independent Schrödinger equation exist only for certain discrete values of the total energy E. Thus the energy quantization is an inherent property of the *Schrödinger* equation for the bound states.

You have just learnt that the probabilistic interpretation puts another restriction on an acceptable (or well behaved) solution: the wave function and its first derivative must be finite *and* continuous. Eq. (6.28) shows that if $V(x)$, E and $\psi(x)$ are finite then $\psi''(x)$ is also finite. This, in turn, means that $\psi'(x)$ is continuous. However, if for certain values

of x, $V(x)$ becomes infinite then Eq. *(6.28)* yields an infinite value for $\psi''(x)$ at those points. Hence at those points $\psi'(x)$ may not be continuous.

We now end this section by summarising the properties and the boundary conditions that a wave function must satisfy to be acceptable:

Properties of the Wave Function

(1) $\psi(x)$ must be **single valued, finite** and **continuous** for all values of x.

(2) $\psi'(x)$ must be **finite** and **continuous** for all values of x, except at those points where $V \to \infty$. At these points $\psi'(x)$ has a finite discontinuity but ψ remains continuous.

(3) For bound states, the probability of finding the particle between x and $x + dx$, i.e., $|\psi|^2 dx$ must vanish as $|x| \to \infty$. Hence $|\psi(x)| \to 0$ as $|x| \to \infty$, i.e., $\psi(x)$ is a **square integrable** wave function.

Let us now summarise what you have studied in this unit.

6.5 SUMMARY

● In this unit we have concentrated on one-dimensional motion of particles. You have learnt **three postulates of quantum mechanics:**

1. Every system can be represented by a **wave function:**

2. The wave function satisfies a differential equation, called the **Schriidinger equation** given by

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

3. The **probability** $P(x, t)$ of finding a particle at (x, t) in the elementary element dx is given by

$$P(x, t)\, dx = \psi^*(x, t)\, \psi(x, t)\, dx$$

where $P(x, t)$ is the **probability density.**

● Schrödinger equation can be used to derive a **continuity equation** which connects the probability density with an associated probability current density $S(x, t)$ as follows:

$$\frac{\partial P(x, t)}{\partial t} + \frac{\partial S(x, t)}{\partial x} = 0$$

where

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

The continuity equation tells us that a particle moving under a real potential is neither destroyed nor is another particle created; the change in particle density in a region equals the net change of flux into or away from that region.

● The **total probability** of finding a particle in the whole space always remains unity:

$$\int_{-\infty}^{\infty} \psi^*(x)\, \psi(x)\, dx = 1$$

Wave functions which satisfy this condition are **said** to be **normalised.**

● For a conservative system we can write

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

where E is the total energy of the system and $\psi(x)$ is the solution of the time independent Schrodinger equation given by

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

● In order that $\psi(x)$ represent a physical system, the wave function $\psi(x)$ must be single valued, finite and continuous at all values of x. Its first derivative $d\psi(x)/dx$ must also be finite and continuous at all values of x, except at those points where $V(x) \to \infty$. At these points the first derivative has a finite discontinuity.

6.6 TERMINAL QUESTIONS

Spend 45 min

1. The wave function of an object of energy E and momentum p is given by

$$\psi(x,\ t) = A\ e^{i(px-Et)/\hbar}.$$

   (i) Does ψ represent a bound state?

   (ii) Is the wave function normalisable?

   (iii) Using the above calculate the probability current density $S(x,\ t)$ in terms of the velocity v of an object and a constant A, which is complex.

2. The unnormalised wave function of a system is given by $x \exp(-x^2/2)$. Obtain the value of its normalisation constant.

3. A certain function is given by

$$\psi(x) = N(1 + ix) \exp(-x) \text{ for } x > 1$$
$$= 0 \qquad\qquad \text{ for } x < 1$$

   Obtain the value of the normalisation constant N. Why can it not represent a physical system?

4. The potential energy of a simple harmonic oscillator of mass m and frequency v is equal to $2m(\pi v x)^2$. Write down its time independent Schrödinger equation and show that it can be rewritten as

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0$$

   where $\alpha = \frac{2m}{\hbar^2}E$, $\beta = 2\pi mv/\hbar$ and $\xi = \sqrt{\beta}\ x$, E being the total energy of the oscillator. For what values of α/β are the functions $\psi(\xi) = \exp(-\xi^2/2)$ and

$\psi(\xi) = \xi \exp(-\xi^2/2)$ solutions of the above equation?

6.7 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. Substituting $\psi = a\psi_1 + b\psi_2$ in Eq. (6.9) we obtain.

$$i\hbar\left(a\frac{\partial\psi_1}{\partial t} + b\frac{\partial\psi_2}{\partial t}\right) = -\frac{\hbar^2}{2m}\left(a\frac{\partial^2\psi_1}{\partial x^2} + b\frac{\partial^2\psi_2}{\partial x^2}\right) + Va\psi_1 + Vb\psi_2$$

$$a \left(i\hbar \frac{\partial \psi_1}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi_1}{\partial x^2} - V\psi_1 \right) + b \left(i\hbar \frac{\partial \psi_2}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi_2}{\partial x^2} - V\psi_2 \right) = 0$$

Since ψ_1 and ψ_2 satisfy Eq. (6.9), the above equation is identically zero. Hence ψ satisfies Eq. (6.9). Similarly, you can show that $a\psi_1$ is also a solution of Eq. (6.9).

2. (a) Let us express the complex potential energy V as

$$V = V_R + iV_I$$

where V_R is its real part *and* V_I, its imaginary part. The Schrödinger equation (6.16a) and its complex conjugate are then, respectively, written as:

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

$$- i\hbar \frac{\partial \psi^*}{\partial t} = - \frac{\hbar^2}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + V_R\psi^* - iV_I \, \psi^*$$

Repealing the process of obtaining Eq. (6.20), we get

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

or

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

$$\frac{\partial P(x, \, t)}{\partial t} + \frac{\partial S(x, \, t)}{\partial x} = \frac{2 \, V_I}{\hbar} \, P(x, \, t)$$

(b) $P(x, \, t) = \psi^* \, \psi$

$$= e^{-(\alpha-i\beta)x} \, e^{i\omega t} \, e^{-(\alpha+i\beta)x} \, e^{-i\omega t}$$

$$= e^{-2\alpha x}$$

Using Eq. (6.21) we obtain

$$S(x, \, t) \; = \frac{\hbar}{m} \, \text{Im} \left[\psi^* \frac{\partial \psi}{\partial x} \right]$$

$$= \frac{\hbar}{m} \, \text{Im} \left[e^{-(\alpha-i\beta)x} \, e^{i\omega t} \, (-\alpha - i\beta) \, e^{-(\alpha + i\beta)x} \, e^{-i\omega t} \right]$$

$$= \frac{\hbar}{m} \, \text{Im} \left[e^{-2\alpha x} \, (-\alpha - i\beta) \right] = - \frac{\hbar\beta}{m} \, e^{-2\alpha x}.$$

3. The normalisation candition is

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

or

$$|N|^2 \int_{-\infty}^{\infty} e^{-x^2} \, dx = 1$$

or

$$2i\,|N|^2 \int_0^\infty e^{-x^2}\,dx = 1 \text{ since } e^{-x^2} \text{ is an even function.}$$

By making the substitution $x^2 = t$, the integral takes the form

$$|N|^2 \int_0^\infty t^{-1/2}\,e^{-t}\,dt. \text{ Thus we have}$$

$$|N|^2 \int_0^\infty t^{-1/2}\,e^{-t}\,dt = 1$$

or

$$|N|^2 \cdot \Gamma\left(\frac{1}{2}\right) = 1 \qquad \Gamma\left(\frac{1}{2}\right) = \int_0^\infty t^{-1/2}\,e^{-t}\,dt$$

$$= \sqrt{\pi}$$

or

$$|N|^2\,\sqrt{\pi} = 1$$

or

$$|N|^2 = \frac{1}{\sqrt{\pi}}$$

and

$$N = \left(\frac{1}{\pi}\right)^{1/4}$$

Terminal Questions

1. (i) NO, it does not as $\psi(x)$ does not go to zero as $|x| \to \infty$

  (ii) No, its norm is infinite.

  (iii) $S(x, t) = \dfrac{\hbar}{2mi}\left[A^* A e^{-i(px - Et)/\hbar}\left(\dfrac{ip}{\hbar}\right) e^{i(px - Et)/\hbar}\right.$

$$\left. -AA^*\,e^{i(px - Et)/\hbar}\left(-\dfrac{ip}{\hbar}\right)\,e^{-i(px - Et)/\hbar}\right]$$

$$= \dfrac{\hbar}{2mi}\,AA^*\left[\dfrac{2i\,p}{\hbar}\right]$$

$$= v\,AA^* \qquad (\because p = mv)$$

2. Applying the normalisation condition we get

$$|N|^2 \int_{-\infty}^\infty x^2\,e^{-x^2}\,dx = 1$$

or

$$2\,|N|^2 \int_0^\infty x^2\,e^{-x^2}\,dx = 1 \text{ since the **integrand** is **even**}$$

Substituting $x^2 = t$, we get

$$|N|^2 \int_0^\infty t^{1/2}\,e^{-t}\,dt = 1$$

or

$$|N|^2\,\frac{\sqrt{\pi}}{2} = 1, \text{ since } \int_0^\infty t^{1/2}e^{-t}\,dt = \frac{\sqrt{\pi}}{2}$$

Since $\Gamma(n + 1) = n\,\Gamma(n)$, $\Gamma\left(\dfrac{3}{2}\right) = \dfrac{1}{2}\,\Gamma\left(\dfrac{1}{2}\right) = \dfrac{\sqrt{\pi}}{2}$

$$\therefore \ |N|^2 = \frac{2}{\sqrt{\pi}} \text{ and } N = \left(\frac{4}{\pi}\right)^{1/4}.$$

3. The normalisation condition is

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

or

$$|N|^2 \int_{1}^{\infty} (1+ix)(1-ix) \exp(-2x) \, dx = 1$$

since

$$\psi(x) = 0 \text{ for } x < 1,$$

or

$$|N|^2 \int_{1}^{\infty} (1+x^2)e^{-2x} \, dx = 1$$

or

$$|N|^2 \int_{1}^{\infty} e^{-2x} \, dx + |N|^2 \int_{1}^{\infty} x^2 \, e^{-2x} \, dx = 1$$

or

$$|N|^2 \frac{e^{-2}}{2} + |N|^2 \int_{1}^{\infty} x^2 \, e^{-2x} \, dx = 1$$

Integrating the second term by parts, we get

$$|N|^2 \left(\frac{e^{-2}}{2} + \frac{5e^{-2}}{4}\right) = 1$$

or

$$|N| = 2e/\sqrt{7}$$

This wave function cannot represent a physical system because it is discontinuous at $x = 1$. Check this out by taking the limit $x \to 1$ from right ($+\infty$) and left ($-\infty$). Both the limits are unequal.

4. The time independent Schrödinger equation for a simple harmonic oscillator is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + 2m \, (\pi\nu x)^2 \, \psi = E\psi \tag{1}$$

where we have substituted $V(x) = 2m(\pi\nu x)^2$. Changing the variable to $\xi = \sqrt{\beta} \, x$, where

$$\beta = \frac{2\pi m\nu}{\hbar}, \text{ we get}$$

$$\frac{d\psi}{dx} = \frac{d\psi}{d\xi}\frac{d\xi}{dx} = \sqrt{\beta}\,\frac{d\psi}{d\xi}$$

$$\frac{d^2\psi}{dx^2} = \beta\,\frac{d^2\psi}{d\xi^2}$$

Thus, (1) becomes

$$-\frac{\hbar^2}{2m}\,\beta\,\frac{d^2\psi}{d\xi^2} + 2m\pi^2\nu^2\,\frac{\xi^2}{\beta}\,\psi = E\psi$$

or

$$-\frac{\hbar^2}{2m}\,\frac{2\pi m\nu}{\hbar}\,\frac{d^2\psi}{d\xi^2} + \frac{2m\pi^2\nu^2\hbar}{2\pi m\,\nu}\,\xi^2\,\psi = E\psi$$

or $\quad \dfrac{d^2\psi}{d\xi^2} - \dfrac{\pi \nu \hbar}{\pi \nu \hbar} - \xi 2\ \psi = -\dfrac{2m}{\hbar^2\beta}\ E\ \psi$

or $\quad \dfrac{d^2\psi}{d\xi^2} + \left(\dfrac{2mE}{\hbar^2\beta} - \xi^2\right)\psi = 0$

Defining $\alpha = \dfrac{2mE}{\hbar^2}$, we can write the equation as

$$\dfrac{d^2\psi}{d\xi^2} + \left(\dfrac{\alpha}{\beta} - \xi^2\right)\psi = 0 \qquad\qquad \text{(A)}$$

Substituting $\psi(\xi) = \exp\left(-\dfrac{\xi^2}{2}\right)$ in this equation, we get:

$$-\psi + \xi^2\ \psi + \dfrac{\alpha}{\beta}\ \psi - \xi^2\ \psi = 0 \qquad \left[\because \dfrac{d^2\psi}{d\xi^2} = -\psi + \xi^2\ \psi\ \right]$$

or $\quad \left(\dfrac{\alpha}{\beta} - 1\right)\psi = 0$

or $\quad \dfrac{\alpha}{\beta} = 1 \quad \text{since } \psi \neq 0$

Similarly, substituting $\psi(\xi) = \xi \exp\ (-\xi^2/2)$ in (A), we get:

$$-3\psi + \xi^2\ \psi + \left(\dfrac{\alpha}{\beta} - \xi^2\right)\psi = 0$$

or $\quad \left(\dfrac{\alpha}{\beta} - 3\right)\psi = 0$

or $\quad \dfrac{\alpha}{\beta} = 3 \ \text{since } \psi \neq 0.$

Appendix   Complex Numbers

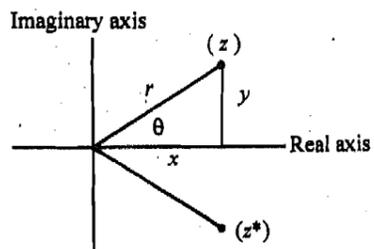|	
Imaginary number	$i = \sqrt{-1}$
Complex number	$z = x + iy$ (Cartesian form)
Real part	$x = \text{Re } z$
Imaginary part	$y = \text{Im } z$
Complex conjugate	$z^* = x - iy$
Modulus	$\lvert z \rvert$ where $\lvert z \rvert^2 = zz^* = x^2 + y^2 = r^2$
Phase	θ where $\tan \theta = \dfrac{y}{x}$

Complex plane

Power series	$x = r \cos \theta = r \left(1 - \dfrac{\theta^2}{2!} + \ldots \right)$
	$y = r \sin \theta = r \left(\theta - \dfrac{\theta^3}{3!} + \ldots \right)$
	$z = r (\cos \theta + i \sin \theta)$
	$= r \left[1 + i\theta + \dfrac{(i\theta)^2}{2!} + \dfrac{(i\theta)^3}{3!} + \ldots \right]$
Complex number	$z = re^{i\theta}$ (polar form)
Phase factors	$e^{i\theta} = \cos \theta + i \sin \theta$ and $e^{-i\theta} = \cos \theta - i \sin \theta$
Real part	$\text{Re } e^{i\theta} = \cos \theta = (e^{i\theta} + e^{-i\theta})/2$
Imaginary part	$\text{Im } e^{i\theta} = \sin \theta = (e^{i\theta} - e^{-i\theta})/2i$