

The answer is ‘no’. Only those solutions which satisfy certain general conditions are admissible for the description of any physical system. The conditions arise partly from the physical interpretation of ψ and partly from the nature of the wave equation itself. We now turn to consider these.

2.4 | NORMALIZATION AND PROBABILITY INTERPRETATION

We have already noted that the Schrödinger equation is *linear* and *homogeneous* in ψ and its derivatives, i.e. every term contains ψ or one of its derivatives in the first power only. Consequently if we multiply any solution of the equation by a constant, the resulting function is still a solution. We can take advantage of this arbitrariness in the definition of the wave function to *normalize* it in a convenient way. Suppose $\psi'(\mathbf{x}, t)$ is a solution of the Schrödinger equation (2.19). Let

$$\int |\psi'(\mathbf{x}, t)|^2 d^3x = N^2 \quad (2.26)$$

Since $|\psi'|^2$, which is the absolute value squared of a complex number, is by definition a positive real number, its integral is also a positive real number as indicated by the notation N^2 . The number N^2 is called the *norm* of the wave function ψ' . Let us now define

$$\psi(\mathbf{x}, t) = \frac{1}{N} \psi'(\mathbf{x}, t) \quad (2.27)$$

As explained above, ψ , which differs from ψ' only by a constant factor, will also be a solution of Eq. (2.19). Further,

$$\int |\psi(\mathbf{x}, t)|^2 d^3x = 1 \quad (2.28)$$

Any wave function ψ which has unit norm, i.e. which has the property (2.28), is said to be *normalized*. Evidently the step (2.27) through which the normalized wave function is defined makes sense only if N is finite. Thus *normalizable* wave functions are those with finite norm. Since the norm is defined as the integral of $|\psi|^2$ over *all* of space, its finiteness implies that $|\psi(\mathbf{x}, t)|^2$ vanishes at infinity, and hence

$$\psi(\mathbf{x}, t) \rightarrow 0 \quad \text{as} \quad r \rightarrow \infty \quad \text{where } r = |\mathbf{x}|. \quad (2.29)$$

This is a *boundary condition* which holds for all normalizable wave functions.

It should be noted that even after normalization, the wave function ψ remains undetermined to the extent of an *arbitrary phase factor* (of the form $e^{i\alpha}$, $\alpha = \text{real constant}$). In other words, ψ may be multiplied by $e^{i\alpha}$ without affecting Eq. (2.28).

Incidentally, if Eq. (2.28) is to be valid for all times t , the integral on the left hand side has to be time-independent. We shall verify in Sec. 2.6, with the aid of the Schrödinger equation, that this is indeed the case.

The motivation for normalizing wave functions in the above fashion comes from the probability interpretation² of ψ . We recall our conclusions in Chapter 1 that the position (or any other dynamical variable) of a particle cannot, in general, be precisely defined. One can only say that there is a certain probability that the particle is within any specified volume element. According to the discussion of Sec. 1.17, this probability has to be assumed to be proportional to the value of $|\psi|^2$ within the volume element. The normalization (2.28) enables us to sharpen this statement and say that $|\psi(\mathbf{x}, t)|^2 d^3x$ is equal to (rather than just proportional to) the probability that the particle is within the volume element d^3x around the point \mathbf{x} . The total probability that the particle is somewhere in space is then $\int |\psi|^2 d^3x$. Since the particle certainly has to be somewhere in space,³ this total probability must be unity. This is precisely what Eq. (2.28) says:

Example 2.2 To normalize the function $\psi' = e^{-|x|} \sin \alpha x$. Note that ψ' has the explicit forms, $\psi'_I = e^x \sin \alpha x$ for $x < 0$ and $\psi'_{II} = e^{-x} \sin \alpha x$ for $x > 0$.

Therefore

$$\int_{-\infty}^{\infty} |\psi'|^2 dx = \int_{-\infty}^0 |\psi'_I|^2 dx + \int_0^{\infty} |\psi'_{II}(x)|^2 dx = \frac{\alpha^2}{2(1+\alpha^2)},$$

on actual evaluation of the integrals. The normalized wave function is therefore

$$\psi(x) = \sqrt{\frac{2(1+\alpha^2)}{\alpha^2}} e^{-|x|} \sin \alpha x$$

Example 2.3 If a particle has the wave function $\psi(x)$ of the last example, what is the probability that its position is to the right of the point $x = 1$? Clearly, the answer is

$$\int_1^{\infty} |\psi|^2 dx = \frac{e^{-2}}{2\alpha^2} [1 + \alpha^2 - \cos 2\alpha + \alpha \sin 2\alpha]$$

2.5 NON-NORMALIZABLE WAVE FUNCTIONS AND BOX NORMALIZATION

We have already noted above that normalization will be possible only if the integral (2.26) is itself not infinite in the first place. Actually there exist wave functions of physical interest for which the integral is infinite. An outstanding example is the wave function (2.11) describing a particle of definite momentum. For this function $\int |\psi|^2 d^3x = |a|^2 \int d^3x = \infty$, since a is a constant and $|\exp[i(\mathbf{k} \cdot \mathbf{x} - \omega t)]| = 1$. The fact that $|\psi|^2$ has the same value $|a|^2$ everywhere implies that the probability of finding

² M. Born, *Z. Phys.*, **37**, 863, 1926.

It has been suggested that the need for a statistical interpretation arises from a lack of knowledge regarding the values of some hidden variables pertaining to the system (A. Einstein, B. Podolsky and N. Rosen, *Phys. Rev.*, **47**, 777, 1935). However, an experimental test of hidden variable theories based on an analysis by J. S. Bell (*Rev. Mod. Phys.*, **38**, 447, 1966) has given evidence against this suggestion (S. J. Freedman and J. F. Clauser, *Phys. Rev. Lett.*, **28**, 938, 1972).

³ More precisely stated, the assertion is that it is possible to say with certainty that any physical particle will be found in a finite region of space, provided the region is chosen sufficiently large. It is hard to conceive of a particle which cannot be localized even in this broad sense.

the particle in any given region of space is directly proportional to its volume. Consequently the chance of finding the particle in any *finite* region, however large, is vanishingly small compared to the chance of its being in the infinite volume of space outside of this region. This must be considered *unphysical* thus it should not be possible rigorously for a particle to have an unnormalizable wave function. Nevertheless the use of such wave functions in quantum mechanics is very widespread, on account of the considerable mathematical advantages resulting therefrom. A convenient way of interpreting such functions is to say that the infinite value of $\int |\psi|^2 d^3x$ represents an infinite number of *noninteracting particles* each of which has a wave function proportional to ψ . Then $|\psi|^2 d^3x$ is the number of particles in the volume d^3x at any instant.

An alternative method of handling non-normalizable wave functions is by regarding them as an idealization— some kind of limit— of physically realizable (normalizable) wave functions. One particularly useful way of visualizing this limit is the following. Imagine the particle to be confined within a large box, and define the norm to be the integral of $|\psi|^2$ taken over the interior of the box only, entirely disregarding the (infinite) region of space outside. This makes the norm finite; it can be made unity by multiplying the wave function by a suitable constant. Use this normalized wave function for calculations; after completion of the calculations, pass to the limit of infinite volume for the box. This procedure is called *box normalization*. It leads to the correct results because physical systems are essentially of finite extent, and therefore as long as the wave functions in a sufficiently large finite region of space are given correctly, it does not really matter what one assumes about the infinitely distant reaches of space.

It is to the case of de Broglie waves (2.11) describing particles of definite momentum ($p = \hbar k$) that the box normalization procedure is most frequently applied. Let us consider these functions at some instant of time, say $t = 0$. If the box is taken to be a cube with edges of length L parallel to the x , y , z axes, the wave functions

$$\psi_{\mathbf{k}}(\mathbf{x}) = L^{-3/2} \cdot e^{i\mathbf{k}\cdot\mathbf{x}} \quad (2.30)$$

are evidently normalized within the box, since

$$\int_{-\frac{1}{2}L}^{\frac{1}{2}L} \int_{-\frac{1}{2}L}^{\frac{1}{2}L} \int_{-\frac{1}{2}L}^{\frac{1}{2}L} |\psi_{\mathbf{k}}(\mathbf{x})|^2 dx dy dz = \int_{-\frac{1}{2}L}^{\frac{1}{2}L} \int_{-\frac{1}{2}L}^{\frac{1}{2}L} \int_{-\frac{1}{2}L}^{\frac{1}{2}L} \frac{dx dy dz}{L^3} = 1 \quad (2.31)$$

The boundary condition (2.29) is not applicable in this case. Instead, we have to prescribe conditions on the ‘walls’ of the box. For reasons which will become clear in the next section (Example 2.4, p. 45), we require that the functions (2.30) be *periodic* with respect to the size of the box. This means that if x (or y or z) is increased by L , the wave function should remain unchanged. Hence

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1 \quad (2.32a)$$

so that k_x, k_y, k_z must be integer multiples of $(2\pi/L)$:

$$\mathbf{k} = \frac{2\pi}{L} \mathbf{n}, (n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots) \quad (2.32b)$$

Thus the admissible momentum vectors get *quantized* for the ‘particle in a box’.

In a variety of problems one needs to know the *number* of periodic waves in a box, which have wave vectors within some specified range. This is easily computed from the fact that the tips of the wave vectors (2.32b) form a regular ‘lattice’ of points with spacing $(2\pi/L)$ along each of the directions in a ‘**k**-space’. There is one such point per volume $(2\pi/L)^3$ of **k**-space. So the number of vectors **k** whose tips lie within an infinitesimal volume element $d\tau_{\mathbf{k}}$ is given by $(L/2\pi)^3 \cdot d\tau_{\mathbf{k}}$. Usually one is interested in the number of waves for which the length of **k** is between k and $k + dk$ and the orientations are within a solid angle $d\Omega \equiv \sin \theta \, d\theta \, d\varphi$ around some direction with polar angles (θ, φ) . The corresponding volume element is $k^2 \, dk \, d\Omega$, and so the required number is $(L/2\pi)^3 \, k^2 \, dk \, d\Omega$. If all directions are considered, the total angle 4π replaces $d\Omega$, and the number is $(L/2\pi)^3 \, k^2 \, dk \cdot 4\pi$.

Incidentally it may be noted that in the case of electromagnetic waves the above numbers are to be doubled because for each k , two polarizations are possible. Since in this case $k = 2\pi \nu/c$, the number of light waves (periodic in a box) with frequencies between ν and $\nu + dv$ is $n(\nu)dv = (8\pi\nu^2 L^3/c^3) dv$.

2.6 | CONSERVATION OF PROBABILITY

We have seen in Sec. 2.4 that according to the probability interpretation of the normalized wave function, Eq. (2.28) says simply that the particle is sure to be found somewhere in space. This statement has to be true at all times as long as the particle is a stable one which cannot decay or disappear in some other way. Therefore, the total probability must be *conserved*, i.e. $|\psi|^2$ must be time-independent, and

$$\frac{\partial}{\partial t} \int |\psi|^2 \, d^3x \equiv \int \frac{\partial}{\partial t} |\psi|^2 \, d^3x = 0 \quad (2.33)$$

Let us verify that this requirement is actually satisfied. We note first that

$$\begin{aligned} \frac{\partial}{\partial t} |\psi|^2 &= \frac{\partial}{\partial t} (\psi^* \psi) = \psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t} \psi \\ &= (i\hbar)^{-1} [\psi^* (H\psi) - (H\psi)^* \psi] \end{aligned} \quad (2.34)$$

In the last step we have made use of the Schrödinger equation (2.19), namely $i\hbar \partial\psi/\partial t = H\psi$, together with its complex conjugate, $-i\hbar \partial\psi^*/\partial t = (H\psi)^*$. In the case of a single particle in a potential $V(\mathbf{x}, t)$ the explicit form of the quantum Hamiltonian operator is given by

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}, t) \quad (2.35)$$

Equation (2.34) then becomes

$$\begin{aligned} \frac{\partial}{\partial t} |\psi|^2 &= \frac{i\hbar}{2m} [\psi^* \nabla^2 \psi - (\nabla^2 \psi^*) \psi] \\ &= \frac{i\hbar}{2m} \nabla \cdot [\psi^* \Delta \psi - (\nabla \psi^*) \psi] \end{aligned}$$

or

$$\frac{\partial}{\partial t} P(\mathbf{x}, t) + \operatorname{div} \mathbf{S}(\mathbf{x}, t) = 0 \quad (2.36)$$

where

$$P(\mathbf{x}, t) = \psi^* \psi \quad (2.37a)$$

and

$$\mathbf{S}(\mathbf{x}, t) = -\frac{i\hbar}{2m} [\psi^* \nabla \psi - (\nabla \psi^*) \psi] \quad (2.37b)$$

On integrating Eq. (2.36) overall space we get

$$\begin{aligned} \frac{\partial}{\partial t} \int P d^3x &= - \int \operatorname{div} \mathbf{S} d^3x \\ &= - \int_{\sigma} \mathbf{S} \cdot \mathbf{n} d\sigma \end{aligned} \quad (2.38)$$

where we have used Gauss' theorem to reduce the volume integral of $\operatorname{div} \mathbf{S}$ to the integral of the normal component of \mathbf{S} over the surface σ bounding the volume. Since the volume integral in Eq. (2.38) is overall of space, the surface σ is at infinity, where ψ and $\nabla \psi$ vanish (for normalizable wave functions). Consequently \mathbf{S} also vanishes, and in fact it vanishes sufficiently fast as $|\mathbf{x}| \rightarrow \infty$, that the surface integral (2.38) itself vanishes. In the case of box-normalized functions, ψ and $\nabla \psi$ do not necessarily vanish on the surface σ of the box. But the boundary conditions specifying their values on σ are chosen in such a way that once again, the integral (2.38) is zero. (See Example 2.4 below.)

Thus we have verified that the condition (2.33) for conservation of total probability is indeed satisfied, and hence the normalization (2.28) is time-independent.

Example 2.4 Let us verify that the boundary conditions (2.32) on the wave functions of a particle in a box are necessary for probability conservation. Consider a particle in one dimension, having a wave function which is a simple superposition of two de Broglie waves:

$$\psi = a_1 \exp [i(k_1 x - \omega_1 t - \alpha_1)] + a_2 \exp [i(k_2 x - \omega_2 t - \alpha_2)]$$

where a_1, a_2 are the (real) amplitudes and α_1, α_2 the phases of the waves. The position probability density is $P = a_1^2 + a_2^2 + 2a_1a_2 \cos [(k_1 - k_2)x - (\omega_1 - \omega_2)t - (\alpha_1 - \alpha_2)]$. If the particle is confined to a 'box' (which, in one dimension, is simply the interval of x between $-\frac{1}{2}L$ and $+\frac{1}{2}L$), conservation of probability within the box requires that $\int_{-\frac{1}{2}L}^{\frac{1}{2}L} P dx$ should be time-independent.

If this is to be true with the above expression for P , it is evidently necessary that

$$\begin{aligned} &\int_{-L/2}^{L/2} \cos [(k_1 - k_2)x - (\omega_1 - \omega_2)t - (\alpha_1 - \alpha_2)] dx \\ &\equiv [2/(k_1 - k_2)] \sin [\frac{1}{2}L(k_1 - k_2)] \cos [(\omega_1 - \omega_2)t + (\alpha_1 - \alpha_2)] \end{aligned}$$

should be time-independent. The only way this can happen is by the vanishing of the sine factor, which means that $(k_1 - k_2)L = 2n\pi$ where n is any integer. Thus the admissible values for k are restricted to a set wherein the differences are integral multiples of $(2\pi/L)$. By taking $k = (2\pi n/L)$ we satisfy the above condition on the differences (and thus ensure conservation of probability), and further ensure that along with every admissible k , $-k$ also is admissible. Clearly there should be no discrimination between one direction of propagation and the opposite direction, since the ‘box’ itself has no asymmetry.

Equations (2.32) are a straightforward generalization of the above result to three dimensions, and can be obtained directly from probability conservation in a three-dimensional box.

It may be noted here that Eq. (2.36) has exactly the same form as the continuity equation, $\partial\rho/\partial t + \text{div } \mathbf{j} = 0$, of hydrodynamics. Instead of the matter density ρ and the matter current density \mathbf{j} , we have in Eq. (2.36) the *probability density P and the probability current density S*. Just as the continuity equation says that no sources or sinks of matter are present, Eq. (2.36) asserts that there is no creation or destruction of probability: any increase or decrease $(\partial P/\partial t)$ $d\tau dt$ in the probability for finding the particle in a given volume element $d\tau \equiv d^3x$ is compensated by a corresponding decrease or increase elsewhere through an inflow or outflow of probability ($\text{div } \mathbf{S}$) $d\tau dt$ across the boundaries of $d\tau$. ■

2.7 | EXPECTATION VALUES; EHRENFEST'S THEOREM⁴

The probability interpretation tells us what results to expect if a large number of observations are made of the positions of particles having a specified wave function ψ . We imagine we have an apparatus which can prepare particles with this particular wave function. Each observation causes the wave function inevitably to undergo some change. So before the next observation is made, the apparatus is to be used to restore the wave function to the original form.

Suppose we now make a large number of observations of the position of the particle. Though we take care to ensure that the particle has the same wave function ψ before each observation, we do not expect to get the same result each time. What is expected is that, of all the observations, a fraction equal to $|\psi|^2 d^3x$ will show the particle as being within the volume element d^3x . Therefore if we take the *mean* or *average* of all the observed values of the position vectors, the result is expected to be

$$\langle \mathbf{x} \rangle = \int \mathbf{x} |\psi|^2 d^3x = \int \psi^* \mathbf{x} \psi d^3x \quad (2.39)$$

i.e., the integral of possible results \mathbf{x} weighted by the function $|\psi(\mathbf{x})|^2$. Remember, $|\psi(\mathbf{x})|^2$ represents the frequency with which (i.e. the fraction of the total number of times) the various values \mathbf{x} occur. Equation (2.39) gives the expected mean position of the particle; it is usually referred to simply as the *mean position* or *expectation value* of the position variable \mathbf{x} .

⁴ P. Ehrenfest, *Z. Physik.*, **45**, 455, 1927.

Now, how does the mean position change with time? By direct differentiation of Eq. 2.39 we obtain

$$\begin{aligned}\frac{d\langle \mathbf{x} \rangle}{dt} &= \int \left(\frac{\partial \psi^*}{\partial t} \mathbf{x} \psi + \psi^* \mathbf{x} \frac{\partial \psi}{\partial t} \right) d^3x \\ &= \frac{1}{i\hbar} \int \left[-\left(-\frac{\hbar^2}{2m} \nabla^2 \psi^* + V \psi^* \right) \mathbf{x} \psi + \psi^* \mathbf{x} \left(-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi \right) \right] d^3x \\ &= \frac{i\hbar}{2m} \int [\psi^* \mathbf{x} \nabla^2 \psi - (\nabla^2 \psi^*) \mathbf{x} \psi] d^3x\end{aligned}$$

Here we have assumed that the particle is moving in a potential V , and used the Schrödinger equation (2.17) as well as its complex conjugate. By carrying out two integrations by parts on the second term in the above expression and using the fact that ψ (and its derivatives) vanish at infinity according to Eq. (2.29), we obtain

$$\begin{aligned}\frac{d\langle \mathbf{x} \rangle}{dt} &= \frac{i\hbar}{2m} \int [\psi^* \mathbf{x} \nabla^2 \psi - \psi^* \nabla^2 (\mathbf{x} \psi)] d^3x \\ &= -\frac{i\hbar}{m} \int \psi^* \nabla \psi d^3x\end{aligned}\quad (2.40)$$

Now we know that in classical mechanics, the velocity is related to momentum through $\mathbf{p} = m d\mathbf{x}/dt$. We have seen in the last chapter that for the motion of a quantum mechanical wave packet *as a whole* (which is what the rate of change of the *mean* position describes), the classical relations should apply at least approximately. Therefore Eq. (2.40) suggests that we define the *mean* momentum or *expectation value* of the momentum as

$$\langle \mathbf{p} \rangle = m \frac{d\langle \mathbf{x} \rangle}{dt} = \int \psi^* (-i\hbar \nabla) \psi d^3x \quad (2.41)$$

Observe that the integral has a very interesting form: it is the integral of the product of ψ^* and $\mathbf{p}_{op} \psi$ where \mathbf{p}_{op} is the operator $(-i\hbar \nabla)$ representing momentum in quantum mechanics. This suggests that the expectation value of *any* dynamical variable, say $A(\mathbf{x}, \mathbf{p})$ is to be identified as

$$\langle A \rangle = \int \psi^* A_{op} \psi d^3x \quad (2.42)$$

where A_{op} is the operator $A(\mathbf{x}, -i\hbar \nabla)$ which represents A in quantum mechanics. Note that A_{op} acts only on the wave function ψ standing to its right. More generally, when the wave function is *not* normalized as in Eq. (2.28),

$$\langle A \rangle = \frac{\int \psi^* A_{op} \psi d^3x}{\int \psi^* \psi d^3x} \quad (2.42a)$$

The definition of expectation values through the Eq. (2.42) is one of the basic postulates of quantum mechanics. The qualitative arguments of Sec. 1.16 regarding the approximately classical motion of small wave packets (in slowly varying fields) can be made precise on the basis of this definition. Indeed, by differentiating $\langle \mathbf{p} \rangle$,

Eq. (2.41), and proceeding exactly as we did for determining $d\langle \mathbf{x} \rangle/dt$, we can easily show that

$$\frac{d\langle \mathbf{p} \rangle}{dt} = -\langle \nabla V(\mathbf{x}, t) \rangle \quad (2.43)$$

Since $\langle \mathbf{p} \rangle = m d\langle \mathbf{x} \rangle/dt$, this equation seems very similar to Newton's equation of motion. In fact it would have been identical to Newton's equation (except for the appearance of $\langle \mathbf{x} \rangle$ instead of the plain \mathbf{x} of classical mechanics) if the right hand side of Eq. (2.40) had been

$$-[\nabla V(\mathbf{x}, t)]_{\mathbf{x} = \langle \mathbf{x} \rangle} \quad (2.44)$$

The difference between this expression (∇V at $\langle \mathbf{x} \rangle$) and the average of ∇V which appears in Eq. (2.43) is small when the size of the wave packet is small, and in this limit the overall motion of the quantum wave packet is well approximated by classical mechanics. This important result, and more particularly Eq. (2.43), is known as Ehrenfest's Theorem.

Example 2.5 Let us calculate $\langle x \rangle$ and $\langle p^2 \rangle$ for the wave function considered in Example 2.2 (p. 42), namely

$$\psi = [2(1 + \alpha^{-2})]^{1/2} e^x \sin \alpha x, x < 0, \text{ and } \psi = [2(1 + \alpha^{-2})]^{1/2} e^{-x} \sin \alpha x, x > 0$$

Then

$$\begin{aligned} \langle x \rangle &= \int \psi^* x \psi dx \\ &= 2(1 + \alpha^{-2}) \left[\int_{-\infty}^0 x e^{2x} \sin^2 \alpha x dx + \int_0^\infty x e^{-2x} \sin^2 \alpha x dx \right] = 0, \end{aligned}$$

since the two integrals cancel each other. This can be seen by changing the variable of integration in the first integral from x to $x' = -x$. Since $p_{op}^2 = -\hbar^2 d^2/dx^2$, we have $\langle p^2 \rangle = -\hbar^2 \int \psi^* (d^2\psi/dx^2) dx$. On substituting the above wave function, evaluating the integrals from $-\infty$ to 0 and 0 to ∞ and adding up, we get

$$\langle p^2 \rangle = \hbar^2 (1 + \alpha^2). \quad \blacksquare$$

Example 2.6 As an example in three dimensions, let us evaluate $\langle r \rangle$ when the wave function (in spherical polar coordinates) is $\psi = (1/\pi a^3)^{1/2} e^{-r/a}$ where a is a constant. In this case it is simplest to express the integral in terms of the polar coordinates:

$$\begin{aligned} \int \psi^* r \psi d\tau &= \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi (\psi^* r \psi) \\ &= \left(\frac{1}{\pi a^3} \right) 4\pi \int_0^\infty r^3 e^{-2r/a} dr = \frac{3a}{2} \end{aligned}$$

Note that since the integral was independent of θ and φ , the integrations over these angles could be trivially evaluated, leading to the factor 4π . \blacksquare

2.8 | ADMISSIBILITY CONDITIONS ON THE WAVE FUNCTION

So far we have not raised any questions as to what kinds of mathematical functions can serve as wave functions for a particle in quantum mechanics. Actually, the probability interpretation of the wave function makes it necessary that ψ should satisfy

certain general conditions. The conditions are intended to ensure that $|\psi|^2 d\tau$ does have the properties of a probability magnitude. We require that ψ should be (a) finite and (b) single-valued⁵ everywhere.

Finiteness is needed in order that $|\psi|^2 d\tau$, for an infinitesimal volume element $d\tau$, should lie between 0 and 1, as any probability should. This argument does not rule out square integrable singularities (where ψ becomes infinite without making $\int |\psi|^2 d\tau$ infinite); but condition (c), stated below, does. Single-valuedness is the requirement that at any given physical point the wave function should have a unique value, in order that the probability density $|\psi|^2$ may be uniquely defined. This condition makes its appearance in non-trivial form whenever there exist several alternative values for the coordinates of a given physical point. This is the case, for example, when spherical polar coordinates (r, θ, φ) are employed: as is well known, changing φ by any integer multiple of 2π does not affect the point which is referred to. In this context, single-valuedness of the wave function means that we must have $\psi(r, \theta, \varphi) = \psi(r, \theta, \varphi + 2n\pi)$ for every integer n .

There is a further property which is required of the wave function, namely (c) that: ψ and its first partial derivatives $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ and $\frac{\partial\psi}{\partial z}$ should be continuous functions of \mathbf{x} , for all \mathbf{x} .

This requirement arises from an implicit assumption regarding the nature of the potential function V , namely that V is a continuous function of \mathbf{x} except perhaps for a certain number of finite discontinuities. When V is of this kind, the condition (c) is necessary for consistency of the Schrödinger equation. To see this, let us consider the simplest case of a particle in one dimension, when the Schrödinger equation becomes

$$i\hbar \frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2\psi}{\partial x^2} + V\psi \quad (2.45)$$

If ψ is a continuous function of x at all times in accordance with (c), then $\partial\psi/\partial t$ is also evidently a continuous function of x . Therefore, the right hand side of Eq. (2.45) must be continuous, and any departure from continuity in one of the two terms must be cancelled by an opposite behaviour in the other term. For example if V (and hence $V\psi$) has a finite discontinuity at some point a , $\partial^2\psi/\partial x^2$ also must have a finite discontinuity at a , i.e. $(\partial\psi/\partial x)$ must be continuous at a but its slope (which is $\partial^2\psi/\partial x^2$) to the right of a must be unequal to that on the left of a . (See Fig. 2.1.) Conversely, if $(\partial\psi/\partial x)$ has this behaviour, V must necessarily have a finite discontinuity. If $(\partial\psi/\partial x)$ behaves any worse, e.g., if it has a finite discontinuity of its own [violating the condition (c)], then the curve for $\partial\psi/\partial x$ becomes ‘vertical’ at that point, and its slope, $\partial^2\psi/\partial x^2$ at that point is infinite. This would force V to have an infinite discontinuity. Such potentials are artificial, e.g., a potential function in the shape of a square well with infinitely high walls.

⁵ For single-valuedness of $|\psi|^2$ it is actually not essential that ψ be single-valued. Nevertheless it has been traditional to require the latter, and we have followed the tradition as a matter of expediency. See the discussion at the end of Sec. 4.10.

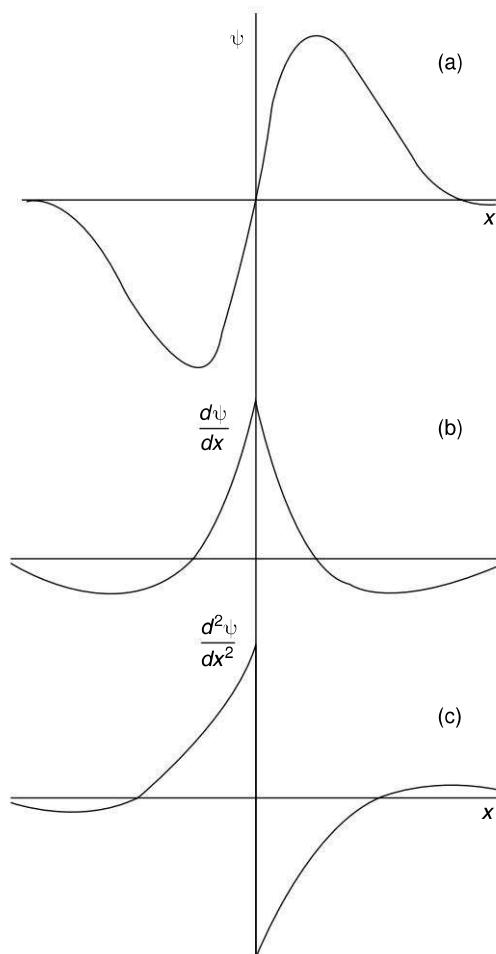


Fig. 2.1 **Illustration of continuity properties** (a) **The wave function** $\psi = e^{-|x|} \sin x$, **continuous everywhere**; (b) $d\psi/dx$: **It has a 'cusp' at $x = 0$, but is still continuous**; and (c) $d^2\psi/dx^2$: **It has a finite discontinuity at $x = 0$.**

However, we do have a very real and important case of a potential having a singularity, namely, the Coulomb potential due to a point particle carrying an electric charge, e.g., the nucleus of the hydrogen atom. This potential is proportional to $1/r$ when the particle is located at the origin; so it is singular, i.e., it goes to infinity, when $r \rightarrow 0$. In this case, one has to permit the gradient of the wave function of the particle moving in the potential (e.g., the electron in the hydrogen atom) to be discontinuous at the position of the charge, while the wave function itself remains continuous. This will become evident from the fact that the wave function for the $1s$ state of the hydrogen atom, which is proportional to $e^{-r/a}$ (see Table 4.1 of Chapter 4),

has a cusp at $r = 0$. The wave function increases with a finite slope as one approaches the origin from any side, and it starts decreasing with a finite slope as soon as one gets past the origin.

Any function which meets the requirements (a), (b), and (c) (or the relaxed version of (c) which permits discontinuities in the gradient of ψ) is *admissible* as a wave function. The requirements themselves are so natural as to be almost self-evident. But their consequences are of profound importance, as we shall see below. The matter of physical interpretation of the wave function will be taken up in Chapter 3 after we have illustrated a few of the typical properties of quantum systems with the aid of simple examples.

C. STATIONARY STATES AND ENERGY SPECTRA

We have already noted that the state of a quantum mechanical system is specified by giving its wave function ψ . We are now in a position to see that in the case of time-independent systems (such as a particle moving in a *static* or time-independent potential V) there exist a special category of solutions of the wave equation, which describe *stationary* states. In these states, the position probability density $|\psi|^2$ at every point \mathbf{x} in space remains independent of time; so also do the expectation values of all dynamical variables. Further when a particle is described by such a wave function its energy has a perfectly definite value. The energy spectrum (i.e. the set of energy values associated with the various stationary states) is, in general, at least partly discrete. We will now see (in the context of a simple example) how all these results follow in a very natural way from the Schrödinger equation and the admissibility conditions on wave functions. The existence of stationary states with discrete energies, which was *postulated* by Bohr in order to account for the nature of atomic spectra, thus finds a rational explanation on the basis of quantum mechanics.

2.9

STATIONARY STATES; THE TIME-INDEPENDENT SCHÖDINGER EQUATION

Let us consider a particle moving in a *time-independent* potential $V(\mathbf{x})$. It is easy to verify that the Schrödinger equation in this case has solutions of the form

$$\psi(\mathbf{x}, t) = u(\mathbf{x})f(t) \quad (2.46)$$

Substituting this assumed form in Eq. 2.17, and dividing throughout by $u(\mathbf{x})f(t)$, we obtain

$$\frac{1}{f} i\hbar \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{\nabla^2 u}{u} + V(\mathbf{x}) \quad (2.47)$$

The right hand side of this equation is independent of t , and the left hand side is independent of \mathbf{x} . Their equality implies, therefore, that *both* sides must be independent of \mathbf{x} and t , and hence must be equal to a constant, say E .

Thus Eq. (2.47) separates into two equations:

$$i\hbar \frac{df(t)}{dt} = Ef(t) \quad (2.48)$$

and

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}) \right] u(\mathbf{x}) = Eu(\mathbf{x}) \quad (2.49)$$

The former is readily solved, and shows that $f(t)$ is proportional to $\exp[-iEt/\hbar]$. The solution of Eq. (2.49) depends on the value assumed for E , and so we write it as $u_E(\mathbf{x})$. Thus Eq. (2.46) reduces to

$$\psi(\mathbf{x}, t) = u_E(\mathbf{x}) e^{-iEt/\hbar} \quad (2.50)$$

The value of E has to be real. For if it had an imaginary part ε , the wave function ψ would vanish for all \mathbf{x} as $t \rightarrow \infty$ or $-\infty$ according as the sign of ε is $-$ or $+$, and this is of course not admissible. It follows then that

$$|\psi(\mathbf{x}, t)|^2 = |u_E(\mathbf{x})|^2 \quad (2.51)$$

i.e. the probability density is independent of t . Similarly expectation values, as defined by Eq. (2.42), are also evidently time-independent. In other words, ψ of Eq. (2.50) describes a *stationary state* in which none of the particle characteristics changes with time.

Let us return now to Eq. (2.49) and the interpretation of E . This equation (called the *time-independent Schrödinger equation*) states that the action of the Hamiltonian operator of the particle (the quantity in square brackets) on the wave function $u_E(\mathbf{x})$ is simply to reproduce the same wave function multiplied by the *constant* E . This property is reminiscent of characteristic equations or eigenvalue equations in matrix theory, where a (column) vector u is called an eigenvector belonging to the eigenvalue λ of a matrix M if it satisfies the equation $Mu = \lambda u$ (with λ = a constant number). By analogy, we say that since $u_E(\mathbf{x})$ satisfies Eq. (2.49), it is an *eigen-function* belonging to the *eigenvalue* E of the (differential) operator $H = -(\hbar^2/2m) \nabla^2 + V$. Remember that this operator represents the energy of the particle as a function of the position and momentum. So $u_E(\mathbf{x})$ may be called an energy eigenfunction. Anticipating the general interpretation (Sec. 3.9) of eigenvalues and eigenfunctions, we now assert that *when the state of a particle is described by an energy eigenfunction, the energy of the particle has a definite value, given by the eigenvalue E*. The reader is invited to verify for himself that this interpretation is consistent with what he already knows about the free-particle case, by substituting the wave function (2.11) into Eqs (2.48) and (2.49) with $V = 0$.

The following question still remains: If we assign an *arbitrary* real value to E in Eq. (2.49), does there exist a corresponding eigenfunction $u_E(\mathbf{x})$? The answer is in the negative. This is because the solution of Eq. (2.49) does not satisfy the admissibility conditions of Sec. 2.8, unless E is restricted to certain specific values.

Only these special values are to be considered as eigenvalues. The set of all such admissible values of E form what is called the eigenvalue spectrum of energy, or simply the *energy spectrum*. Following the terminology of old quantum theory, we shall frequently refer to the energy eigenvalues as *energy levels* of the system. We shall now determine the energy spectrum and energy eigenfunctions of a very simple system, in order to illustrate how the admissibility conditions on wave functions lead to restrictions on possible energy values.

2.10 | A PARTICLE IN A SQUARE WELL POTENTIAL

The example we consider is that of a particle whose potential energy function has the shape of a ‘well’ with vertical sides. It is depicted in Fig. 2.2 and is defined by

$$\begin{aligned} V(x) &= 0 && \text{for } x < -a && \text{(Region I)} \\ V(x) &= -V_0 && \text{for } -a < x < a && \text{(Region II)} \quad (2.52) \\ V(x) &= 0 && \text{for } x > a && \text{(Region III)} \end{aligned}$$

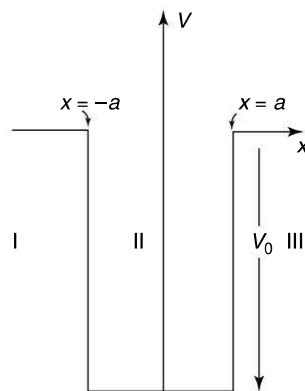


Fig. 2.2 The square well potential.

If we were considering this problem in classical mechanics, we would have to keep in mind that the kinetic energy $(E - V)$ can never be negative. Since $V = 0$ for $|x| > a$, $(E - V)$ can be positive in this region only if $E > 0$. Therefore any particle with $E < 0$ cannot enter regions I and III, and will have to stay within the potential ‘well’, between $x = a$ and $x = -a$. We say in this case that the particle is *bound* by the potential. On the other hand if the particle has energy $E > 0$, it can go anywhere; it merely experiences momentary forces on crossing the points $x = -a$ and $x = +a$.

Let us now consider the quantum mechanical picture of this system. We confine our attention, for the present, to stationary states, which are described by solutions of Eq. (2.49). In the present case this equation, reduced to one dimension, takes distinct forms in the different regions:

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dx^2} = Eu, \quad |x| > a \quad (2.53a)$$

and

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dx^2} = -V_0 u = Eu, \quad |x| < a \quad (2.53b)$$

The set of Eqs (2.53) can be trivially solved. The nature of the solutions depends on whether $E < 0$ or $E > 0$. The former condition corresponds to bound states, as we shall see, and we take up this case first.

2.11 | BOUND STATES IN A SQUARE WELL: ($E < 0$)

(a) *Admissible Solutions of Wave Equation:* For $E < 0$, we write

$$\frac{2mE}{\hbar^2} = -\alpha^2 \text{ and } \frac{2m(E + V_0)}{\hbar^2} = \beta^2; \quad \alpha, \beta > 0 \quad (2.54)$$

Eqs (2.53) can then be conveniently rewritten in terms of the positive constants α^2 and β^2 as

$$\frac{d^2u}{dx^2} - \alpha^2 u = 0, \quad |x| > a \quad (2.55a)$$

$$\frac{d^2u}{dx^2} + \beta^2 u = 0, \quad |x| < a \quad (2.55b)$$

The general solution of the second of these equations is obviously

$$u^{II}(x) = A \cos \beta x + B \sin \beta x \quad (2.56)$$

where A and B are any constants. The superscript II on $u(x)$ here indicates that it is the solution valid in Region II, i.e. ($|x| < a$). The equation which holds in Region I, ($-\infty < x < a$), is (2.55a). Its general solution is a linear combination of its two independent solutions, $e^{\alpha x}$ and $e^{-\alpha x}$. However the latter does not remain finite everywhere in Region I. In fact, as $x \rightarrow -\infty$, it becomes infinitely large. Therefore the only admissible solution in Region I must be of the form

$$u^I(x) = C e^{\alpha x} \quad (2.57)$$

Region III, ($a < x < \infty$), is also governed by Eq. (2.55a) with the independent solutions $e^{\alpha x}$ and $e^{-\alpha x}$. But now it is $e^{-\alpha x}$ which remains well behaved everywhere and $e^{\alpha x}$ which is not admissible (since it diverges as $x \rightarrow +\infty$). Therefore, we have

$$u^{III}(x) = D e^{-\alpha x} \quad (2.58)$$

where D , like A , B , and C , is an undetermined constant.

Thus the solution $u(x)$ has three different forms u^I , u^{II} , u^{III} in the three regions. We must now make sure that $u(x)$ and its first derivative (du/dx) are continuous everywhere,⁶ as demanded by the condition (c) of Sec. 2.8. In particular, at the point $x = -a$ where Regions I and II meet, we should have

⁶In view of the relation (2.50) between $\psi(x, t)$ and $u(x)$, it is obvious that all the admissibility conditions on ψ must be equally satisfied by $u(x)$.

$$u^I = u^{II} \text{ and } \frac{du^I}{dx} = \frac{du^{II}}{dx}, (x = -a) \quad (2.59)$$

or explicitly,

$$C e^{-\alpha a} = A \cos \beta a - B \sin \beta a, \quad C \alpha e^{-\alpha a} = A \beta \sin \beta a + B \beta \cos \beta a \quad (2.60)$$

Similarly, at $x = a$, where Regions II and III meet, we must have

$$u^{II} = u^{III} \text{ and } \frac{du^{II}}{dx} = \frac{du^{III}}{dx}, (x = a) \quad (2.61)$$

These lead to

$$D e^{-\alpha a} = A \cos \beta a + B \sin \beta a, \quad -D \alpha e^{-\alpha a} = -A \beta \sin \beta a + B \beta \cos \beta a \quad (2.62)$$

From Eqs (2.60) and (2.62) we readily find that

$$2A \cos \beta a = (C + D) e^{-\alpha a} \quad (2.63a)$$

$$2A\beta \sin \beta a = (C + D) \alpha e^{-\alpha a} \quad (2.63b)$$

$$2B \sin \beta a = -(C - D) e^{-\alpha a} \quad (2.64a)$$

$$2B\beta \cos \beta a = (C - D) \alpha e^{-\alpha a} \quad (2.64b)$$

Eqs (2.63) show that if $(C + D) \neq 0$, then $A \neq 0$, and further,

$$\alpha = \beta \tan \beta a \quad (2.65a)$$

This relation implies that

$$C = D \quad \text{and} \quad B = 0 \quad (2.65b)$$

and hence

$$D = A e^{\alpha a} \cos \beta a \quad (2.65c)$$

To verify this, we substitute for the factor α in Eq. (2.64b) the value determined above; then, multiplying the equation by $\sin \beta a$ and using Eq. (2.64a), we obtain $-(C - D) \cos^2 \beta a = (C - D) \sin^2 \beta a$. Since $\sin^2 \beta a$ cannot be equal to the negative quantity $-\cos^2 \beta a$, we must have $C = D$. Thus we obtain Eq. (2.65b), and on feeding this back into Eq. (2.63), Eq. (2.65c) follows.

Eqs (2.65) give one type of solution for our problem. Another type of solution exists for $C \neq D$ and $B \neq 0$, when we get from Eqs (2.64)

$$\alpha = -\beta \cot \beta a. \quad (2.66a)$$

Repetition of the kind of arguments used above will show that now

$$C = -D \text{ and } A = 0 \quad (2.66b)$$

and

$$D = B e^{\alpha a} \sin \beta a \quad (2.66c)$$

(b) *The Energy Eigenvalues—Discrete Spectrum:* We can now see that both the types of solutions exist only for certain discrete values of the energy parameter E . We observe first of all that by virtue of Eq. (2.54)

$$(\alpha^2 + \beta^2)a^2 = \frac{2mV_0a^2}{\hbar^2} = \frac{V_0}{\Delta} \quad (2.67)$$

where

$$\Delta = \frac{\hbar^2}{2ma^2} \quad (2.68)$$

The parameter Δ has an interesting interpretation. The half-width a of the potential well indicates the uncertainty in the position of a particle confined to the well, and associated with this, there is an uncertainty of the order of (\hbar/a) in the momentum. The corresponding energy $\Delta = (\hbar/a)^2/2m$ is a natural unit in terms of which the depth of the potential may be measured. Thus the non-dimensional parameter (V_0/Δ) of Eq. (2.67) is a measure of the *strength* of the potential.

Now, in the case of solutions of the first type, we have, besides Eq. (2.67), the further relation (2.65a) between α and β , which has two consequences. One is that since α and β have been defined to be positive, $(\alpha/\beta) = \tan \beta a$ must be positive and hence only values of βa lying in the intervals

$$2r \frac{\pi}{2} \leq \beta a \leq (2r+1) \frac{\pi}{2}, \quad (r = 0, 1, 2, \dots) \quad (2.69a)$$

are admissible. Secondly, the substitution of $\alpha = \beta \tan \beta a$ into Eq. (2.67) leads to the requirement

$$\frac{V_0}{\Delta} = \beta^2 a^2 \sec^2 \beta a, \quad \text{or} \quad \left(\frac{\Delta}{V_0} \right)^{1/2} \beta a = |\cos \beta a| \quad (2.69b)$$

The modulus sign arises because the left hand side of the equation is known to be positive.

Similarly, for the second type of solutions of the wave equation, given by (2.66), we find from Eqs (2.66a) and (2.67) that

$$(2r-1) \frac{\pi}{2} \leq \beta a \leq 2r \frac{\pi}{2}, \quad (r = 1, 2, \dots) \quad (2.70a)$$

and

$$\frac{V_0}{\Delta} = \beta^2 a^2 \operatorname{cosec}^2 \beta a, \quad \text{or} \quad \left(\frac{\Delta}{V_0} \right)^{1/2} \beta a = |\sin \beta a| \quad (2.70b)$$

Eqs (2.69) and (2.70) can be satisfied only by certain specific discrete values of β , which can be found graphically. These special values β_n are determined by the intersections of the straight line $(\Delta/V_0)^{1/2} \beta a$ with the curves for $|\cos \beta a|$ and $|\sin \beta a|$. The parts of $|\cos \beta a|$ and $|\sin \beta a|$ which lie within the respective allowed intervals—conditions (2.69a) and (2.70a)—are shown as solid lines and dashed lines respectively in Fig. 2.3. The parts to be ignored are indicated by dotted lines.

If the intersections occur at $\beta = \beta_n$ ($n = 0, 1, 2, \dots$) the corresponding allowed values of the energy are obtained from Eq. (2.54) as

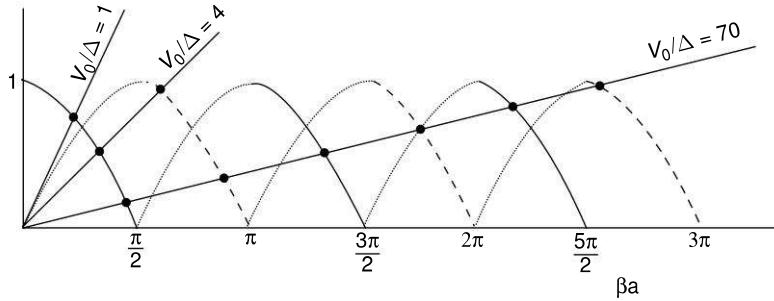


Fig. 2.3 | Graphical solution for allowed values of β .

$$E_n = \frac{\hbar^2}{2m} \beta_n^2 - V_0 = \left[(\beta_n a)^2 \frac{\Delta}{V_0} - 1 \right] V_0 \quad (2.71)$$

It may be noted that the value of the combination of parameters appearing in the square bracket may be read off directly from the figure. It is evident that the number of these energy levels is finite. Inspection of Fig. 2.3 shows that if $(\Delta/V_0)^{1/2} \beta a$ reaches the value unity for a value of βa in the interval $\frac{1}{2}\pi N \leq \beta a < \frac{1}{2}\pi(N+1)$, then there are $(N+1)$ intersections. In other words, the number of discrete energy levels is $(N+1)$ if $\frac{1}{2}\pi N(\Delta/V_0)^{1/2} \leq 1 < \frac{1}{2}\pi(N+1)(\Delta/V_0)^{1/2}$, that is, if

$$N \leq \frac{2}{\pi} \left(\frac{V_0}{\Delta} \right)^{1/2} < (N+1) \quad (2.72)$$

It is noteworthy that there exists at least one bound state, however weak the potential may be.

Note also from Eq. (2.71) that an energy level occurs at the brink of the potential well ($E_n = 0$) when $(\beta_n a)^2 = V_0/\Delta$; for this to happen either $\sin^2 \beta_n a$ or $\cos^2 \beta_n a$ must be equal to unity, as may be seen from Eqs (2.69b) and (2.70b).

(c) *The Energy Eigenfunctions; Parity:* We observe that the energy levels E_n with $n = 0, 2, 4, \dots$ correspond to solutions characterized by Eqs (2.65). In this case any solution $u_n(x)$ has the following explicit forms in the three regions:

$$\left. \begin{aligned} u_n^I(x) &= (A e^{\alpha_n x} \cos \beta_n a) e^{\alpha_n x} && (x < -a) \\ u_n^{II}(x) &= A \cos \beta_n x && (-a < x < -a) \\ u_n^{III}(x) &= (A e^{\alpha_n x} \cos \beta_n a) e^{-\alpha_n x} && (x > a) \end{aligned} \right\} \quad (n = 0, 2, \dots) \quad (2.73)$$

The nature of such functions is illustrated graphically in Fig. 2.4(a). It is evident that $u_n(x)$ is symmetric about the origin:

$$u_n(x) = u_n(-x) \quad (2.74)$$

In general, any wave function which has this symmetry property is said to be of *even parity*.

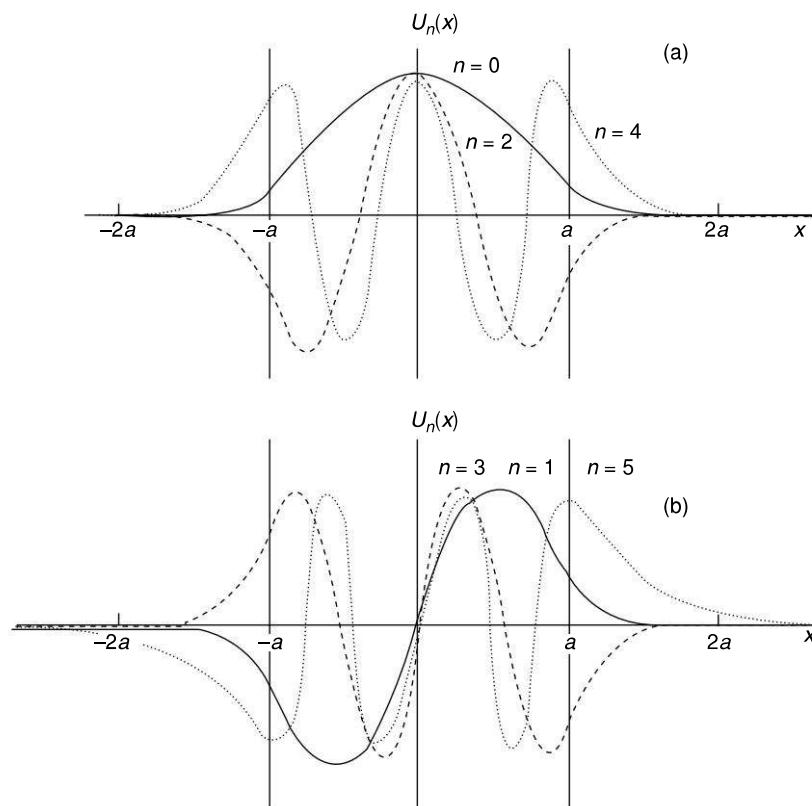


Fig. 2.4 | (a) Even parity eigenfunctions; and (b) Odd parity eigenfunctions.

The eigenfunctions corresponding to $n = 1, 3, \dots$ are characterized by Eqs (2.66). For these we have, explicitly,

$$\left. \begin{aligned} u_n^I(x) &= -\left(B e^{\alpha_n a} \sin \beta_n a \right) e^{\alpha_n x} && (x < -a) \\ u_n^{II}(x) &= B \sin \beta_n x && (-a < x < a) \\ u_n^{III}(x) &= \left(B e^{\alpha_n a} \sin \beta_n a \right) e^{-\alpha_n x} && (x > a) \end{aligned} \right\} \quad (n = 1, 3, \dots) \quad (2.75)$$

These functions are illustrated in Fig. 2.4(b). They are antisymmetric with respect to the origin, i.e.,

$$u_n(x) = -u_n(-x) \quad (2.76)$$

Any wave function which has this property of antisymmetry is said to be of *odd parity*.

Thus the eigenfunctions describing the stationary states of a particle in a square well potential, when considered in order of increasing energy, are alternately of

even and odd parity. The fact that the eigenfunctions have even or odd parity is a consequence of the symmetry of the potential V itself with respect to the origin. The proof of this statement, as well as the definition of parity in the case of more general systems (many particles, in three dimensions) will be given in Sec. 4.11.

(d) *Penetration into Classically Forbidden Regions:* The wave functions (2.74) and (2.75) provide an illustration of a feature of quantum mechanics which is of fundamental importance. We recall that as discussed at the beginning of this section, a classical particle of energy $E < 0$ can stay only in Region II and cannot at all enter Regions I and III. However, the quantum mechanical wave functions $u(x)$ have non-vanishing values in both these classically forbidden regions. Therefore, according to the probability interpretation, there exists a nonvanishing probability that the particle is somewhere within these regions. However as one goes from the boundary point ($x = -a$ or $x = +a$) deeper into the forbidden region, the probability density $|u(x)|^2$ decreases rapidly, (proportional to $e^{-2\alpha_n|x|}$) to zero. Therefore, the particle cannot escape to infinitely large distances; it stays bound to the potential well. Thus all the states which we have so far considered ($E < 0$) are *bound states*.

Example 2.7 The eigenfunctions (2.73) are normalized if we take $A = (a + \alpha_n^{-1})^{-1/2}$. Verify this. The probability of finding the particle in the classically forbidden regions is

$$\int_{-\infty}^{-a} (u^I)^2 dx + \int_a^{\infty} (u^{III})^2 dx = 2 \int_a^{\infty} (u^{III})^2 dx = \frac{\cos^2 \beta_n a}{1 + \alpha_n a} \quad \blacksquare$$

Example 2.8 Equation (2.71) gives the positions of the energy levels, as measured from the bottom of the potential well, as $E_n + V_0 = (\beta_n a)^2 \Delta$. For a very deep potential well ($V_0 \rightarrow \infty$) we see from Fig. 2.3 that $\beta a \rightarrow (n+1)\pi/2$. Hence the energy levels in this case are given by $E_n + V_0 = \frac{1}{4}\pi^2 \Delta(n+1)^2$.

Further, in this limit the wave function in the classically forbidden regions tends to zero, as can be seen from Eqs (2.73) and (2.75). \blacksquare

2.12 | THE SQUARE WELL: NON-LOCALIZED STATES ($E > 0$)

When $E > 0$, $(2mE/\hbar^2)$ is positive and, therefore, instead of Eq. (2.54) we write

$$\frac{2mE}{\hbar^2} = k^2 \quad \text{and} \quad \frac{2m(E + V_0)}{\hbar^2} = \beta^2, \quad (k, \beta > 0) \quad (2.77)$$

Clearly, the only change in the Schrödinger equations (2.55) is that $-\alpha^2$ is to be replaced by $+k^2$. The possible independent solutions in Regions I and III now become e^{ikx} and e^{-ikx} instead of $e^{\alpha x}$ and $e^{-\alpha x}$. But unlike the latter pair, of which one becomes infinite as $x \rightarrow +\infty$ or $x \rightarrow -\infty$, both e^{ikx} and e^{-ikx} remain finite. Therefore, both have to be retained in the general solution, and instead of Eqs (2.57) and (2.58) we now have

$$u^I(x) = C_+ e^{ikx} + C_- e^{-ikx} \quad (2.78a)$$

$$u^{III}(x) = D_+ e^{ikx} + D_- e^{-ikx} \quad (2.78b)$$