



Figure 5.1. (a) The box potential. (b) The first two levels and wave functions in the box.

these equations we will get continuous $\psi'(x)$ and $\psi(x)$. This is the typical situation. There are, however, some problems where, for mathematical simplicity, we consider potentials that change abruptly at some point. This means that ψ'' jumps abruptly there. However, ψ' will still be continuous, for the area under a function is continuous even if the function jumps a bit. What if the change in V is infinitely large? It means that ψ'' is also infinitely large. This in turn means that ψ' can change abruptly as we cross this point, for the area under ψ'' can be finite over an infinitesimal region that surrounds this point. But whether or not ψ' is continuous, ψ , which is the area under it, will be continuous.†

Let us turn our attention to some specific cases.

5.2. The Particle in a Box

We now consider our first problem with a potential, albeit a rather artificial one:

$$\begin{aligned} V(x) &= 0, & |x| < L/2 \\ &= \infty, & |x| \geq L/2 \end{aligned} \quad (5.2.1)$$

This potential (Fig. 5.1a) is called the box since there is an infinite potential barrier in the way of a particle that tries to leave the region $|x| < L/2$. The eigenvalue equation in the X basis (which is the only viable choice) is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \quad (5.2.2)$$

We begin by partitioning space into three regions I, II, and III (Fig. 5.1a). The solution ψ is called ψ_I , ψ_{II} , and ψ_{III} in regions I, II, and III, respectively.

Consider first region III, in which $V = \infty$. It is convenient to first consider the case where V is not infinite but equal to some V_0 which is greater than E . Now

† We are assuming that the jump in ψ' is finite. This will be true even in the artificial potentials we will encounter. But can you think of a potential for which this is not true? (Think delta.)

Eq. (5.2.2) becomes

$$\frac{d^2 \psi_{\text{III}}}{dx^2} - \frac{2m(V_0 - E)}{\hbar^2} \psi_{\text{III}} = 0 \quad (5.2.3)$$

which is solved by

$$\psi_{\text{III}} = A e^{-\kappa x} + B e^{\kappa x} \quad (5.2.4)$$

where $\kappa = [2m(V_0 - E)/\hbar^2]^{1/2}$.

Although A and B are arbitrary coefficients from a mathematical standpoint, we must set $B=0$ on physical grounds since $B e^{\kappa x}$ blows up exponentially as $x \rightarrow \infty$ and such functions are not members of our Hilbert space. If we now let $V \rightarrow \infty$, we see that

$$\psi_{\text{III}} \equiv 0$$

It can similarly be shown that $\psi_{\text{I}} \equiv 0$. In region II, since $V=0$, the solutions are exactly those of a free particle:

$$\psi_{\text{II}} = A \exp[i(2mE/\hbar^2)^{1/2}x] + B \exp[-i(2mE/\hbar^2)^{1/2}x] \quad (5.2.5)$$

$$= A e^{ikx} + B e^{-ikx}, \quad k = (2mE/\hbar^2)^{1/2} \quad (5.2.6)$$

It therefore appears that the energy eigenvalues are once again continuous as in the free-particle case. This is not so, for $\psi_{\text{II}}(x) = \psi$ only in region II and not in all of space. We must require that ψ_{II} goes continuously into its counterparts ψ_{I} and ψ_{III} as we cross over to regions I and III, respectively. In other words we require that

$$\psi_{\text{I}}(-L/2) = \psi_{\text{II}}(-L/2) = 0 \quad (5.2.7)$$

$$\psi_{\text{III}}(+L/2) = \psi_{\text{II}}(+L/2) = 0 \quad (5.2.8)$$

(We make no such continuity demands on ψ' at the walls of the box since V jumps to infinity there.) These constraints applied to Eq. (5.2.6) take the form

$$A e^{-ikL/2} + B e^{ikL/2} = 0 \quad (5.2.9a)$$

$$A e^{ikL/2} + B e^{-ikL/2} = 0 \quad (5.2.9b)$$

or in matrix form

$$\begin{bmatrix} e^{-ikL/2} & e^{ikL/2} \\ e^{ikL/2} & e^{-ikL/2} \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad (5.2.10)$$

Such an equation has nontrivial solutions only if the determinant vanishes:

$$(5.2.3) \quad e^{-ikL} - e^{ikL} = -2i \sin(kL) = 0 \quad (5.2.11)$$

that is, only if

$$(5.2.4) \quad k = \frac{n\pi}{L}, \quad n = 0, \pm 1, \pm 2, \dots \quad (5.2.12)$$

To find the corresponding eigenfunctions, we go to Eqs. (5.2.9a) and (5.2.9b). Since only one of them is independent, we study just Eq. (5.2.9a), which says

$$A e^{-in\pi/2} + B e^{in\pi/2} = 0 \quad (5.2.13)$$

Multiplying by $e^{in\pi/2}$, we get

$$A = -e^{in\pi} B \quad (5.2.14)$$

Since $e^{in\pi} = (-1)^n$, Eq. (5.2.6) generates two families of solutions (normalized to unity):

$$(5.2.5) \quad \psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right), \quad n \text{ even} \quad (5.2.15)$$

$$(5.2.6) \quad = \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi x}{L}\right), \quad n \text{ odd} \quad (5.2.16)$$

Notice that the case $n=0$ is uninteresting since $\psi_0 \equiv 0$. Further, since $\psi_n = \psi_{-n}$ for n odd and $\psi_n = -\psi_{-n}$ for n even, and since eigenfunctions differing by an overall factor are not considered distinct, we may restrict ourselves to positive nonzero n . In summary, we have

$$(5.2.7) \quad \psi_n = \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi x}{L}\right), \quad n = 1, 3, 5, 7, \dots \quad (5.2.17a)$$

$$(5.2.8) \quad = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right), \quad n = 2, 4, 6, \dots \quad (5.2.17b)$$

and from Eqs. (5.2.6) and (5.2.12),

$$(5.2.9a) \quad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \quad (5.2.17c)$$

(5.2.9b) [It is tacitly understood in Eqs. (5.2.17a) and (5.2.17b) that $|x| < L/2$.]

(5.2.10)

bound. The uncertainty principle is often used in this fashion to provide a quick order-of-magnitude estimate for the ground-state energy.

If we denote by $|n\rangle$ the abstract ket corresponding to $\psi_n(x)$, we can write the propagator as

$$U(t) = \sum_{n=1}^{\infty} |n\rangle\langle n| \exp\left[-\frac{i}{\hbar}\left(\frac{\hbar^2\pi^2 n^2}{2mL^2}\right)t\right] \quad (5.2.21)$$

The matrix elements of $U(t)$ in the X basis are then

$$\begin{aligned} \langle x|U(t)|x'\rangle &= U(x, t; x') \\ &= \sum_{n=1}^{\infty} \psi_n(x)\psi_n^*(x') \exp\left[-\frac{i}{\hbar}\left(\frac{\hbar^2\pi^2 n^2}{2mL^2}\right)t\right] \end{aligned} \quad (5.2.22)$$

Unlike in the free-particle case, there exists no simple closed expression for this sum.

*Exercise 5.2.1.** A particle is in the ground state of a box of length L . Suddenly the box expands (symmetrically) to twice its size, leaving the wave function undisturbed. Show that the probability of finding the particle in the ground state of the new box is $(8/3\pi)^2$.

*Exercise 5.2.2.** (a) Show that for any normalized $|\psi\rangle$, $\langle\psi|H|\psi\rangle \geq E_0$, where E_0 is the lowest-energy eigenvalue. (Hint: Expand $|\psi\rangle$ in the eigenbasis of H .)

(b) Prove the following theorem: Every attractive potential in one dimension has at least one bound state. Hint: Since V is attractive, if we define $V(\infty)=0$, it follows that $V(x) = -|V(x)|$ for all x . To show that there exists a bound state with $E < 0$, consider

$$\psi_a(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

and calculate

$$E(\alpha) = \langle\psi_a|H|\psi_a\rangle, \quad H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - |V(x)|$$

Show that $E(\alpha)$ can be made negative by a suitable choice of α . The desired result follows from the application of the theorem proved above.

*Exercise 5.2.3.** Consider $V(x) = -aV_0\delta(x)$. Show that it admits a bound state of energy $E = -ma^2V_0^2/2\hbar^2$. Are there any other bound states? Hint: Solve Schrödinger's equation outside the potential for $E < 0$, and keep only the solution that has the right behavior at infinity and is continuous at $x=0$. Draw the wave function and see how there is a cusp, or a discontinuous change of slope at $x=0$. Calculate the change in slope and equate it to

$$\int_{-\varepsilon}^{+\varepsilon} \left(\frac{d^2\psi}{dx^2}\right) dx$$

(where ε is infinitesimal) determined from Schrödinger's equation.

Exercise 5.2.4. Consider a particle of mass m in the state $|n\rangle$ of a box of length L . Find the force $F = -\partial E/\partial L$ encountered when the walls are slowly pushed in, assuming the particle remains in the n th state of the box as its size changes. Consider a classical particle of energy E_n in this box. Find its velocity, the frequency of collision on a given wall, the momentum transfer per collision, and hence the average force. Compare it to $-\partial E/\partial L$ computed above.

*Exercise 5.2.5.** If the box extends from $x=0$ to L (instead of $-L/2$ to $L/2$) show that $\psi_n(x) = (2/L)^{1/2} \sin(n\pi x/L)$, $n=1, 2, \dots, \infty$ and $E_n = \hbar^2 \pi^2 n^2 / 2mL^2$.

Exercise 5.2.6. Square Well Potential.* Consider a particle in a square well potential:

$$V(x) = \begin{cases} 0, & |x| \leq a \\ V_0, & |x| \geq a \end{cases}$$

Since when $V_0 \rightarrow \infty$, we have a box, let us guess what the lowering of the walls does to the states. First of all, all the bound states (which alone we are interested in), will have $E \leq V_0$. Second, the wave functions of the low-lying levels will look like those of the particle in a box, with the obvious difference that ψ will not vanish at the walls but instead spill out with an exponential tail. The eigenfunctions will still be even, odd, even, etc.

(1) Show that the even solutions have energies that satisfy the transcendental equation

$$k \tan ka = \kappa \quad (5.2.23)$$

while the odd ones will have energies that satisfy

$$k \cot ka = -\kappa \quad (5.2.24)$$

where k and $i\kappa$ are the real and complex wave numbers inside and outside the well, respectively. Note that k and κ are related by

$$k^2 + \kappa^2 = 2mV_0/\hbar^2 \quad (5.2.25)$$

Verify that as V_0 tends to ∞ , we regain the levels in the box.

(2) Equations (5.2.23) and (5.2.24) must be solved graphically. In the ($\alpha = ka$, $\beta = \kappa a$) plane, imagine a circle that obeys Eq. (5.2.25). The bound states are then given by the intersection of the curve $\alpha \tan \alpha = \beta$ or $\alpha \cot \alpha = -\beta$ with the circle. (Remember α and β are positive.)

(3) Show that there is always one even solution and that there is no odd solution unless $V_0 \geq \hbar^2 \pi^2 / 8ma^2$. What is E when V_0 just meets this requirement? Note that the general result from Exercise 5.2.2b holds.

5.3. The Continuity Equation for Probability

We interrupt our discussion of one-dimensional problems to get acquainted with two concepts that will be used in the subsequent discussions, namely, those of the *probability current density* and the *continuity equation* it satisfies. Since the probability current concept will also be used in three-dimensional problems, we discuss here a particle in three dimensions.

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