

Consider the initial state in Eq. (5.1.14) with $p_0 = 0$, and set $\Delta = 1$, $t' = 0$:

$$\psi(x, 0) = \frac{e^{-x^2/2}}{(\pi)^{1/4}}$$

Find $\psi(x, t)$ using Eq. (5.1.18) above and compare with Eq. (5.1.15).

Hints: (i) Write $\psi(x, 0)$ as a power series:

$$\psi(x, 0) = (\pi)^{-1/4} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n}}{n!(2)^n}$$

(ii) Find the action of a few terms

$$1, \quad \left(\frac{i\hbar t}{2m} \right) \frac{d^2}{dx^2}, \quad \frac{1}{2!} \left(\frac{i\hbar t}{2m} \right)^2 \frac{d^4}{dx^4}$$

etc., on this power series.

(iii) Collect terms with the same power of x .

(iv) Look for the following series expansion in the coefficient of x^{2n} :

$$\left(1 + \frac{i\hbar t}{m} \right)^{-n-1/2} = 1 - (n+1/2) \left(\frac{i\hbar t}{m} \right) + \frac{(n+1/2)(n+3/2)}{2!} \left(\frac{i\hbar t}{m} \right)^2 + \dots$$

(v) Juggle around till you get the answer.

Exercise 5.1.4: A Famous Counterexample. Consider the wave function

$$\psi(x, 0) = \sin\left(\frac{\pi x}{L}\right), \quad |x| \leq L/2 \\ = 0, \quad |x| > L/2$$

It is clear that when this function is differentiated any number of times we get another function confined to the interval $|x| \leq L/2$. Consequently the action of

$$U(t) = \exp\left[\frac{i}{\hbar} \left(\frac{\hbar^2 t}{2m} \right) \frac{d^2}{dx^2} \right]$$

on this function is to give a function confined to $|x| \leq L/2$. What about the spreading of the wave packet?

[Answer: Consider the derivatives at the boundary. We have here an example where the (exponential) operator power series doesn't converge. Notice that the convergence of an operator power series depends not just on the operator but also on the operand. So there is no paradox: if the function dies abruptly as above, so that there seems to be a paradox, the derivatives are singular at the boundary, while if it falls off continuously, the function will definitely leak out given enough time, no matter how rapid the falloff.]

Some General Features of Energy Eigenfunctions

Consider now the energy eigenfunctions in some potential $V(x)$. These obey

$$\psi'' = -\frac{2m(E - V)}{\hbar^2} \psi$$

where each prime denotes a spatial derivative. Let us ask what the continuity of $V(x)$ implies. Let us start at some point x_0 where ψ and ψ' have the values $\psi(x_0)$ and $\psi'(x_0)$. If we pretend that x is a time variable and that ψ is a particle coordinate, the problem of finding ψ everywhere else is like finding the trajectory of a particle (for all times past and future) given its position and velocity at some time and its acceleration as a function of its position and time. It is clear that if we integrate 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:

$$V(x) = 0, \quad |x| < L/2 \\ = \infty, \quad |x| \geq L/2 \quad (5.2.1)$$

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 $|x| < L/2$.

[†] 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.)

(iii) 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.

As a prelude to our study of the continuity equation in quantum mechanics, let us recall the analogous equation from electromagnetism. We know in this case that the total charge in the universe is a constant, that is

$$Q(t) = \text{const, independent of time } t \quad (5.3.1)$$

This is an example of a global conservation law, for it refers to the total charge in the universe. But charge is also conserved locally, a fact usually expressed in the form of the continuity equation

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j} \quad (5.3.2)$$

where ρ and $\mathbf{j}$ are the charge and current densities, respectively. By integrating this equation over a volume V bounded by a surface S_V we get, upon invoking Gauss' law,

$$\frac{d}{dt} \int_V \rho(\mathbf{r}, t) d^3\mathbf{r} = - \int_V \nabla \cdot \mathbf{j} d^3\mathbf{r} = - \int_{S_V} \mathbf{j} \cdot d\mathbf{S} \quad (5.3.3)$$

This equation states that any decrease in charge in the volume V is accounted for by the flow of charge out of it, that is to say, charge is not created or destroyed in any volume.

The continuity equation forbids certain processes that obey global conservation, such as the sudden disappearance of charge from one region of space and its immediate reappearance in another.

In quantum mechanics the quantity that is globally conserved is the total probability for finding the particle anywhere in the universe. We get

this result by expressing the invariance of the norm in the coordinate basis: since

$$\langle \psi(t) | \psi(t) \rangle = \langle \psi(0) | U^\dagger(t) U(t) | \psi(0) \rangle = \langle \psi(0) | \psi(0) \rangle$$

then

$$\begin{aligned} \text{const} &= \langle \psi(t) | \psi(t) \rangle = \iiint \langle \psi(t) | x, y, z \rangle \langle x, y, z | \psi(t) \rangle dx dy dz \\ &= \iiint \langle \psi(t) | \mathbf{r} \rangle \langle \mathbf{r} | \psi(t) \rangle d^3\mathbf{r} \\ &= \iiint \psi^*(\mathbf{r}, t) \psi(\mathbf{r}, t) d^3\mathbf{r} \\ &= \iiint P(\mathbf{r}, t) d^3\mathbf{r} \end{aligned} \quad (5.3.4)$$

This global conservation law is the analog of Eq. (5.3.1). To get the analog of Eq. (5.3.2), we turn to the Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \quad (5.3.5)$$

and its conjugate

$$-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* \quad (5.3.6)$$

Note that V has to be real if H is to be Hermitian. Multiplying the first of these equations by ψ^* , the second by ψ , and taking the difference, we get

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} (\psi^* \psi) &= -\frac{\hbar^2}{2m} (\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*) \\ \frac{\partial P}{\partial t} &= -\frac{\hbar}{2mi} \nabla \cdot (\psi^* \nabla \psi - \psi \nabla \psi^*) \\ \frac{\partial P}{\partial t} &= -\nabla \cdot \mathbf{j} \end{aligned} \quad (5.3.7)$$

where

$$\mathbf{j} = \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*) \quad (5.3.8)$$

is the *probability current density*, that is to say, the probability flow per unit

† The range of integration will frequently be suppressed when obvious.

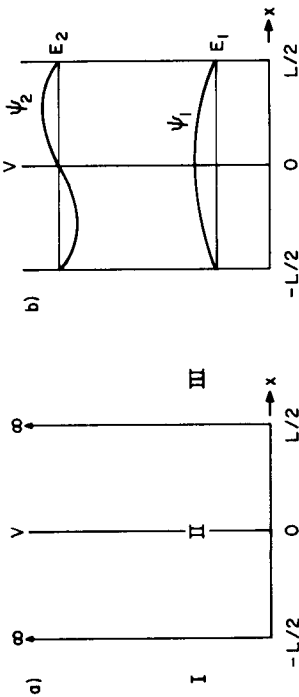


Fig. 5.1. (a) The box potential. (b) The first two levels and wave functions in the box.

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 Eq. (5.2.2) becomes

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

which is solved by

$$\psi_{III} = Ae^{-\kappa x} + Be^{\kappa x} \quad (5.2.4)$$

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 $Be^{\kappa x}$ blows up exponentially as $x \rightarrow \infty$ and such functions are not members of our Hilbert space. If we now let $V_0 \rightarrow \infty$, we see that

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

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

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

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

It therefore appears that the energy eigenvalues are once again continuous as in the free-particle case. This is not so, for $\psi_{II}(x) = \psi$ *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 II, respectively. In other words we require that

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

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

(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

$$Ae^{-ikL/2} + Be^{ikL/2} = 0 \quad (5.2.9a)$$

$$Ae^{ikL/2} + Be^{-ikL/2} = 0 \quad (5.2.9b)$$

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:

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

that is, only if

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

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

$$Ae^{-in\pi/2} + Be^{in\pi/2} = 0 \quad (5.2.13)$$

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):

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

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

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

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

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

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

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

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

We have here our first encounter with the quantization of a dynamical variable. Both the variables considered so far, X and P , had a continuous spectrum of eigenvalues from $-\infty$ to $+\infty$, which coincided with the allowed values in classical mechanics. In fact, so did the spectrum of the Hamiltonian in the free-particle case. The particle in the box is the simplest example of a situation that will be encountered again and again, wherein Schrödinger's equation, combined with appropriate boundary conditions, leads to the quantization of energy. These solutions are also examples of *bound states*, namely, states in which a potential prevents a particle from escaping to infinity. Bound states are thus characterized by

$$\psi(x) \xrightarrow{|x| \rightarrow \infty} 0$$

Bound states appear in quantum mechanics exactly where we expect them classically, namely, in situations where $V(\pm\infty)$ is greater than E .

The energy levels of bound states are always quantized. Let us gain some insight into how this happens. In the problem of the particle in a box, quantization resulted from the requirement that ψ_{II} completed an integral number of half-cycles within the box so that it smoothly joined its counterparts ψ_I and ψ_{III} which vanished identically. Consider next a particle bound by a finite well, i.e., by a potential that jumps from 0 to V_0 at $|x| = L/2$. We have already seen [Eq. (5.2.4)] that in the classically forbidden region ($E < V_0$, $|x| \geq L/2$) ψ is a sum of rising and falling exponentials (as $|x| \rightarrow \infty$) and that we must choose the coefficient of the rising exponential to be zero to get an admissible solution. In the classically allowed region ($|x| \leq L/2$) ψ is a sum of a sine and cosine. Since V is everywhere finite,

we demand that ψ and ψ' be continuous at $x = \pm L/2$. Thus we impose four conditions on ψ , which has only three free parameters. (It may seem that there are four—the coefficients of the two falling exponentials, the sine, and the cosine. However, the overall scale of ψ is irrelevant both in the eigenvalue equation and the continuity conditions, these being *linear* in ψ and ψ' . Thus if say, ψ' does not satisfy the continuity condition at $x = L/2$, an overall rescaling of ψ and ψ' will not help.) Clearly, the continuity conditions cannot be fulfilled except possibly at certain special energies. (See Exercise 5.2.6 for details). This is the origin of energy quantization here.

Consider now a general potential $V(x)$ which tends to limits $V_{\pm}$ as $x \rightarrow \pm\infty$ and which binds a particle of energy E (less than both $V_{\pm}$.) We argue once again that we have one more constraint than we have parameters, as follows. Let us divide space into tiny intervals such that in each interval $V(x)$ is essentially constant. As $x \rightarrow \pm\infty$, these intervals can be made longer and longer since V is stabilizing at its asymptotic values $V_{\pm}$. The right- and leftmost intervals can be made infinitely wide, since by assumption V has a definite limit as $x \rightarrow \pm\infty$. Now in all the finite intervals, ψ has two parameters: these will be the coefficients of the sine/cosine if $E > V$ or growing/falling exponential if $E < V$. (The rising exponential is not disallowed, since it doesn't blow up within the finite intervals.) Only in the left- and rightmost intervals does ψ have just one parameter, for in these infinite intervals, the growing exponential can blow up. All these parameters are constrained by the continuity of ψ and ψ' at each interface between adjacent regions. To see that we have one more constraint than we have parameters, observe that every extra interval brings with it two free parameters and one new interface, i.e., two new constraints. Thus as we go from three intervals in the finite well to the infinite number of intervals in the arbitrary potential, *the constraints are always one more than the free parameters*. Thus only at special energies can we expect an allowed solution.

[Later we will study the oscillator potential, $V = \frac{1}{2}m\omega^2 x^2$, which grows without limit as $|x| \rightarrow \infty$. How do we understand energy quantization here? Clearly, any *allowed* ψ will vanish even more rapidly than before as $|x| \rightarrow \infty$, since $V - E$, instead of being a constant, grows quadratically, so that the particle is “even more forbidden than before” from escaping to infinity. If E is an allowed energy,[†] we expect ψ to fall off rapidly as we cross the classical turning points $x_0 = \pm(2E/m\omega^2)^{1/2}$. To a particle in such a state, it shouldn't matter if we flatten out the potential to some constant at distances much greater than $|x_0|$, i.e., the *allowed* levels and eigenfunctions

[†] We are not assuming E is quantized.

must be same in the two potentials which differ only in a region that the particle is so strongly inhibited from going to. Since the flattened-out potential has the asymptotic behavior we discussed earlier, we can understand energy quantization as we did before.[†]

Let us restate the origin of energy quantization in another way. Consider the search for acceptable energy eigenfunctions, taking the finite well as an example. If we start with some arbitrary values $\psi(x_0)$ and $\psi'(x_0)$, at some point x_0 to the right of the well, we can integrate Schrödinger's equation numerically. (Recall the analogy with the problem of finding the trajectory of a particle given its initial position and velocity and the force on it.) As we integrate out to $x \rightarrow \infty$, ψ will surely blow up since ψ_{III} contains a growing exponential. Since $\psi(x_0)$ merely fixes the overall scale, we vary $\psi'(x_0)$ until the growing exponential is killed. [Since we can solve problem analytically in region III, we can even say what the desired value of $\psi'(x_0)$ is: it is given by $\psi'(x_0) = -\kappa\psi(x_0)$. Verify, starting with Eq. (5.2.4), that this implies $B = 0$.] We are now out of the fix as $x \rightarrow \infty$, but we are committed to whatever comes out as we integrate to the left of x_0 . We will find that ψ grows exponentially till we reach the well, whereupon it will oscillate. When we cross the well, ψ will again start to grow exponentially, for ψ_I also contains a growing exponential in general. Thus there will be no acceptable solution at some randomly chosen energy. It can, however, happen that for certain values of energy, ψ will be exponentially damped in both regions I and III. [At any point x'_0 in region I, there is a ratio $\psi'(x'_0)/\psi(x'_0)$ for which only the damped exponential survives. The ψ we get integrating from region III will not generally have this feature. At special energies, however, this can happen.] These are the allowed energies and the corresponding functions are the allowed eigenfunctions. Having found them, we can choose $\psi(x_0)$ such that they are normalized to unity. For a nice numerical analysis of this problem see the book by Eisberg and Resnick.[†]

It is clear how these arguments generalize to a particle bound by some arbitrary potential: if we try to keep ψ exponentially damped as $x \rightarrow -\infty$, it blows up as $x \rightarrow \infty$ (and vice versa), except at some special energies. It is also clear why there is no quantization of energy for unbound states: since the particle is classically allowed at infinity, ψ oscillates there and so we have two more parameters, one from each end (why?), and so two solutions (normalizable to $\delta(0)$) at any energy.

[†] R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles*, Wiley, New York (1974). See Section 5.7 and Appendix F.

Let us now return to the problem of the particle in a box and discuss the fact that the lowest energy is not zero (as it would be classically, corresponding to the particle at rest inside the well) but $\hbar^2\pi^2/2mL^2$. The reason behind it is the uncertainty principle, which prevents the particle, whose position (and hence ΔX) is bounded by $|x| \leq L/2$, from having a well-defined momentum of zero. This in turn leads to a lower bound on the energy, which we derive as follows. We begin with[†]

$$H = \frac{P^2}{2m} \quad (5.2.18)$$

so that

$$\langle H \rangle = \frac{\langle P^2 \rangle}{2m} \quad (5.2.19)$$

Now $\langle P \rangle = 0$ in any bound state for the following reason. Since a bound state is a stationary state, $\langle P \rangle$ is time independent. If this $\langle P \rangle \neq 0$, the particle must (in the average sense) drift either to the right or to the left and eventually escape to infinity, which cannot happen in a bound state.

Consequently we may rewrite Eq. (5.2.19) as

$$\langle H \rangle = \frac{\langle (P - \langle P \rangle)^2 \rangle}{2m} = \frac{(\Delta P)^2}{2m}$$

If we now use the uncertainty relation

$$\Delta P \cdot \Delta X \geq \hbar/2$$

we find

$$\langle H \rangle \geq \frac{\hbar^2}{8m(\Delta X)^2}$$

Since the variable x is constrained by $-L/2 \leq x \leq L/2$, its standard deviation ΔX cannot exceed $L/2$. Consequently

$$\langle H \rangle \geq \hbar^2/2mL^2$$

In an energy eigenstate, $\langle H \rangle = E$ so that

$$E \geq \hbar^2/2mL^2 \quad (5.2.20)$$

[†] We are suppressing the infinite potential due to the walls of the box. Instead we will restrict x to the range $|x| \leq L/2$.

The actual ground-state energy E_1 happens to be π^2 times as large as the lower 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

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

and calculate

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

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.

(i) 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.

(ii) 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.)