CHAPTER 10

Quantum Mechanics

There are only a few problems in quantum mechanics that can be solved exactly, most notably the harmonic oscillator, a particle in a box, and the hydrogen atom. Nearly all other nontrivial quantum problems either have no known analytic solutions or can be attacked analytically only with extreme difficulty. This is why perturbation methods play such an important role in quantum theory and also why numerical methods are an attractive alternative. Indeed, an extremely wide variety of numerical methods have been developed for dealing with quantum problems. There are far too many such methods for us to even mention all of them in this chapter. Our goal instead will be to describe a few of the algorithms that have been developed with quantum mechanics in mind, and use them to treat several representative problems.[1] We also hope to find some enlightening overlap with problems and techniques we have encountered in earlier chapters.

This chapter opens with a brief review of the Schrödinger equation, and a few of the fundamental ingredients of quantum theory. We then consider several methods for treating time-independent problems. While we have dealt with partial differential equations in a number of previous settings, the problems associated with the Schrödinger equation involve extra complications associated with boundary conditions and require some extensions of the methods we have previously employed. We also describe how Monte Carlo methods can be teamed up with the variational principle to calculate wave functions and eigenvalues. In the second half of this chapter we turn to time-dependent problems and describe several numerical approaches. The goal, as usual, is to learn how to deal with problems that are difficult or impossible to treat analytically. However, we will find it useful to apply our numerical approaches to several exactly soluble problems, as this will allow us to test the methods and also illustrate some of the key themes of quantum theory.

10.1 TIME-INDEPENDENT SCHRÖDINGER EQUATION: SOME PRELIMINARIES

The time-independent Schrödinger equation for a particle in three dimensions is

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\,\psi = E\,\psi\,, \tag{10.1}$$

where $\hbar$ is Planck's constant, m is the mass of the particle, V is the potential energy, E is the energy of the particle, and ψ is the wave function. As is well known with quantum theory, it is much easier to write this equation down than to really understand it. The key quantity here is the wave function, which has no direct classical counterpart. In the most general case, ψ is a complex function

[1] It is not our intention that this chapter be a substitute for a first course in quantum mechanics, although we will review a few aspects of the theory in the next several pages.

of position and, when properly normalized, $\psi(\vec{r})^*\psi(\vec{r})$ is the probability per u volume that the particle will be found at $\vec{r}$. Here we use the usual notation in whi ψ^* is the complex conjugate of ψ.

The fact that ψ can be complex will complicate our numerical treatment However, another aspect of (10.1) will turn out to be much more important numerical attacks on this equation. This is a partial differential equation who form is not very different from the wave equation encountered in Chapter 6, wi one important exception. The energy E is *also* an unknown. A complete soluti involves determining both ψ and the corresponding energy. These are also know as the eigenfunction and eigenvalue of the equation.[3] An interesting property eigenvalue problems is that in many cases solutions exist only for certain speci values of the eigenvalue, in this case E. Mathematically, this is the origin of th discrete energy levels of quantum theory. It is useful to illustrate these points wi an example that can be solved analytically; we will revisit this problem shortly usin a numerical approach. Consider a particle moving in free space, that is, a region i which the potential is constant. Since we are free to shift the origin of the potenti energy scale, we will take $V = 0$ everywhere. For simplicity we also assume tha space is one-dimensional so that $\psi = \psi(x)$ and the ∇^2 operator in (10.1) reduces t the second derivative d^2/dx^2. The Schrödinger (time-independent) equation the becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\,\psi\,, \tag{10.2}$$

which has the general solution

$$\psi = A\,\exp(\imath kx)\,, \tag{10.3}$$

where $\imath \equiv \sqrt{-1}$, and A and k are constants. That this is indeed a solution to (10.2) can be verified by substitution, which yields

$$E = \frac{\hbar^2 k^2}{2m}\,. \tag{10.4}$$

The wave function (10.3) has the form of a plane wave with wave vector $k = 2\pi/\lambda$ where λ is the wavelength of the particle. k is also closely related to the particle's momentum, p, with $p = \hbar k$.

In this particular problem there is a solution to the Schrödinger equation for any value of k, and thus all nonnegative values of E are allowed. We do not have quantized energy levels in this example (at least not yet). The constant A is not determined directly by the Schrödinger equation. Our solution satisfies the wave equation (10.2) for any value of A, a fact we should have expected since the equation is linear. Constants such as A, which set the overall magnitude of the wave

[2]While the wave function may be complex, there are many cases in which its phase can be chosen so as to make ψ real. In fact, in our numerical work we will not encounter any situations that absolutely demand that ψ be complex until we deal with time-dependent problems.

[3]Equations in which an operator, such as the ∇^2 operator in (10.1), acting on a function is equal to a constant times the function are known as eigenvalue equations and arise in many other contexts, a few of which are described in Chapter 11. See also Appendix H. Griffiths (1995) and Schiff (1968) contain nice introductions to this topic in the context of quantum mechanics.

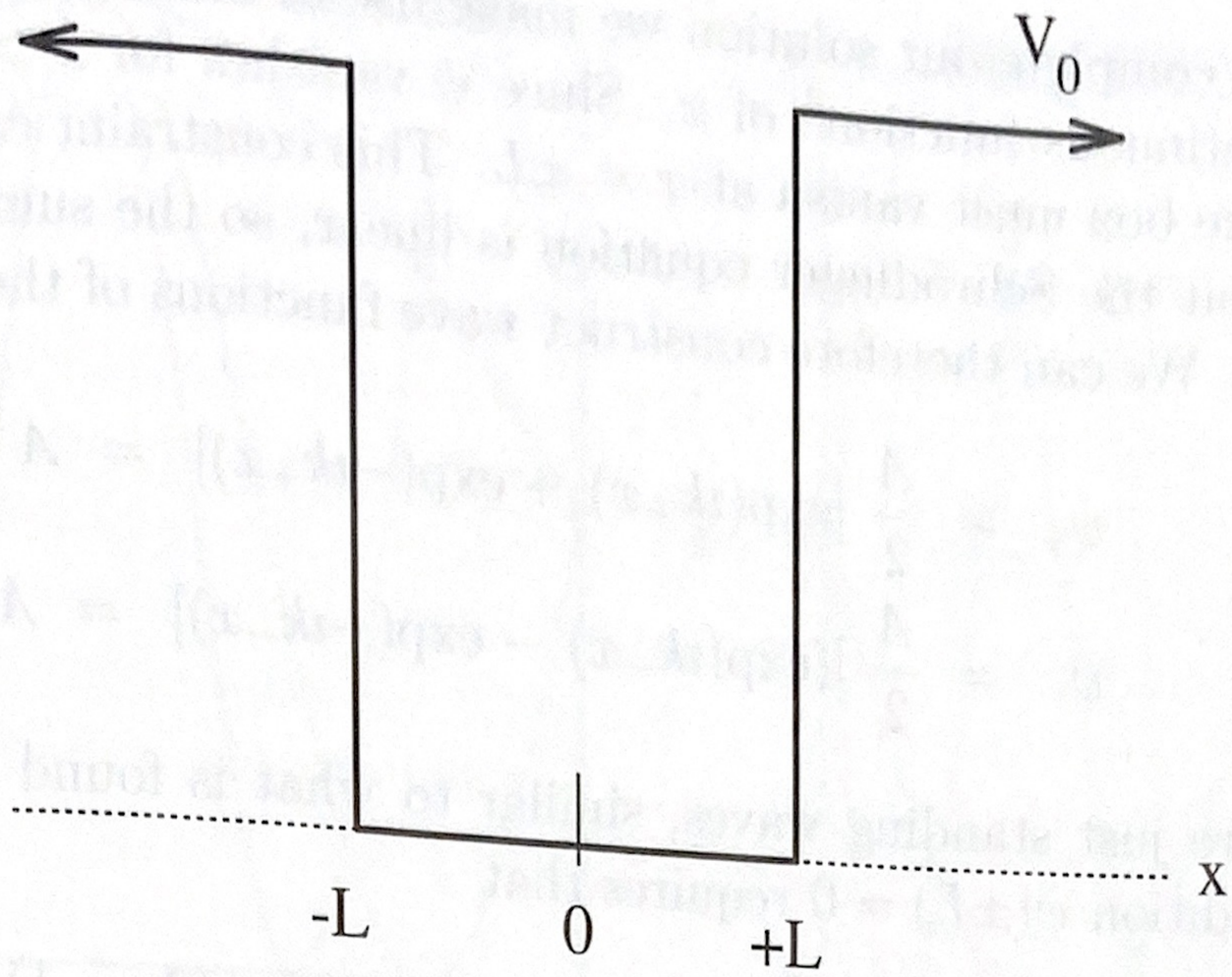

FIGURE 10.1: Potential energy for a particle in a box. The potential is $V = 0$ inside the box (i.e., for $|x| \leq L$) and V_0 outside. If $V_0 = \infty$, then the box is said to have "hard" walls, while if V_0 is finite, the walls are "soft."

function, are determined by the physical interpretation of ψ and its relation to the probability density. We already noted that the probability of finding the particle in a particular region of space is proportional to $\psi^*\psi$. For our one-dimensional case $\psi(x)^*\psi(x)dx$ is the probability of finding the particle within a region of length dx in the neighborhood of x. Since we are considering the behavior of a single particle, this probability must satisfy the normalization condition

$$\int \psi^*\psi \, dx = 1 \, . \tag{10.5}$$

In words, the total probability for finding the particle someplace must be unity. This condition can generally be used to set the overall magnitude of the wave function. However, applying it to our plane wave yields a minor difficulty. For the wave function (10.3) we have $\psi^*\psi = A^2$, so that $\int \psi^*\psi dx = A^2 \int dx$. If our particle is allowed to roam freely over an infinitely large region, we must make A infinitely small in order to preserve normalization.

It is convenient to deal with this situation by assuming that the particle is confined to a box that extends from $x = -L$ to $x = +L$. The plane wave (10.3) must then fit in this box. The corresponding potential is now $V = 0$ inside the box and very large outside, as sketched in Figure 10.1. Since $V(x)$ is a discontinuous function of position, it is simplest to solve for ψ separately in the regions $|x| \leq L$ (inside the box) and $|x| > L$ (outside the box). Inside we have $V = 0$, so ψ in this region is still given by (10.3). If we assume that the potential outside is $V = \infty$ and that the energy of the particle is not infinite, then the only way we can satisfy the Schrödinger equation in the outside region is if $\psi_{\text{outside}} = 0$. This implies that $d^2\psi_{\text{outside}}/dx^2 = 0$ also, so both sides of (10.2) are zero. Physically this result should not be surprising. A particle with a finite energy will have no chance of being found in a region where $V = \infty$, so the probability amplitude ψ must vanish.

To complete our solution we make use of one more constraint on ψ; it must be a continuous function[4] of x. Since ψ vanishes for $x > \pm L$, the solution for ψ inside the box must vanish at $x = \pm L$. This constraint can be satisfied by noting again that the Schrödinger equation is linear, so the sum of two solutions is also solution. We can therefore construct wave functions of the form

$$\begin{aligned} \psi_+ &= \frac{A}{2}\left[\exp(\imath k_+ x) + \exp(-\imath k_+ x)\right] = A\cos(k_+ x)\,, \\ \psi_- &= \frac{A}{2}\left[(\exp(\imath k_- x) - \exp(-\imath k_- x)\right] = A\sin(k_- x)\,. \end{aligned} \tag{10.6}$$

These are just standing waves, similar to what is found with a vibrating string. The condition $\psi(\pm L) = 0$ requires that

$$k_+ = \frac{\pi}{2L}, \frac{3\pi}{2L}, \ldots = \frac{(2n-1)\pi}{2L} \tag{10.7}$$

$$k_- = \frac{\pi}{L}, \frac{2\pi}{L}, \ldots = \frac{n\pi}{L}\,. \tag{10.8}$$

This constraint on k means that we now have discrete energy levels. Only certain special values of the wave vector are allowed. These values are those yielding standing waves that satisfy the boundary conditions on ψ at the walls of the box, as shown in Figure 10.2. Quantization of k also implies quantization of the energy since $E = \hbar^2 k^2/2m$. Constraints such as these boundary conditions generally lead to quantized levels. We will find that they play a major role in constructing numerical solutions to the Schrödinger equation.

It is interesting to notice that the wave functions (10.6) all have a definite parity; they are either even $\psi(+x) = \psi(-x)$, or odd $\psi(+x) = -\psi(-x)$, with respect x. This property can be traced to the potential energy. Whenever the potential is an even function of x, the wave functions can always be written so as to have a definite parity. This will prove useful in developing a numerical approach in the next section. Note also that the wave functions (10.6) can be properly normalized without coefficients that are infinitely small. The normalization condition (10.5) can be used to determine the value of A for these functions, yielding $A = L^{-1/2}$.

Two other features of the wave functions (10.6) will turn out to be very useful later in this chapter. The forms of these functions may remind you of the sines and cosines encountered in connection with Fourier transforms in Chapter 6 and Appendix C. It is thus not surprising that these wave functions form an complete set of orthogonal functions over the interval $|x| \leq L$. The term "orthogonal" means that $\int \psi_1^* \psi_2 dx = 0$ unless ψ_1 and ψ_2 refer to the same eigenstate. The term "complete set" means that any function[5] in this interval that vanishes at $x = \pm L$ can be written as a sum of these wave functions with suitably chosen coefficients. The orthogonality property makes this expansion, that is, the set of coefficients, unique. Such a collection of functions is usually referred to as a *basis set*. The similarity to Fourier transforms, in which the basis set is also composed of sines

[4]This condition is required to make quantities such as the momentum physically well behaved.
[5]We will not worry about pathological functions here.

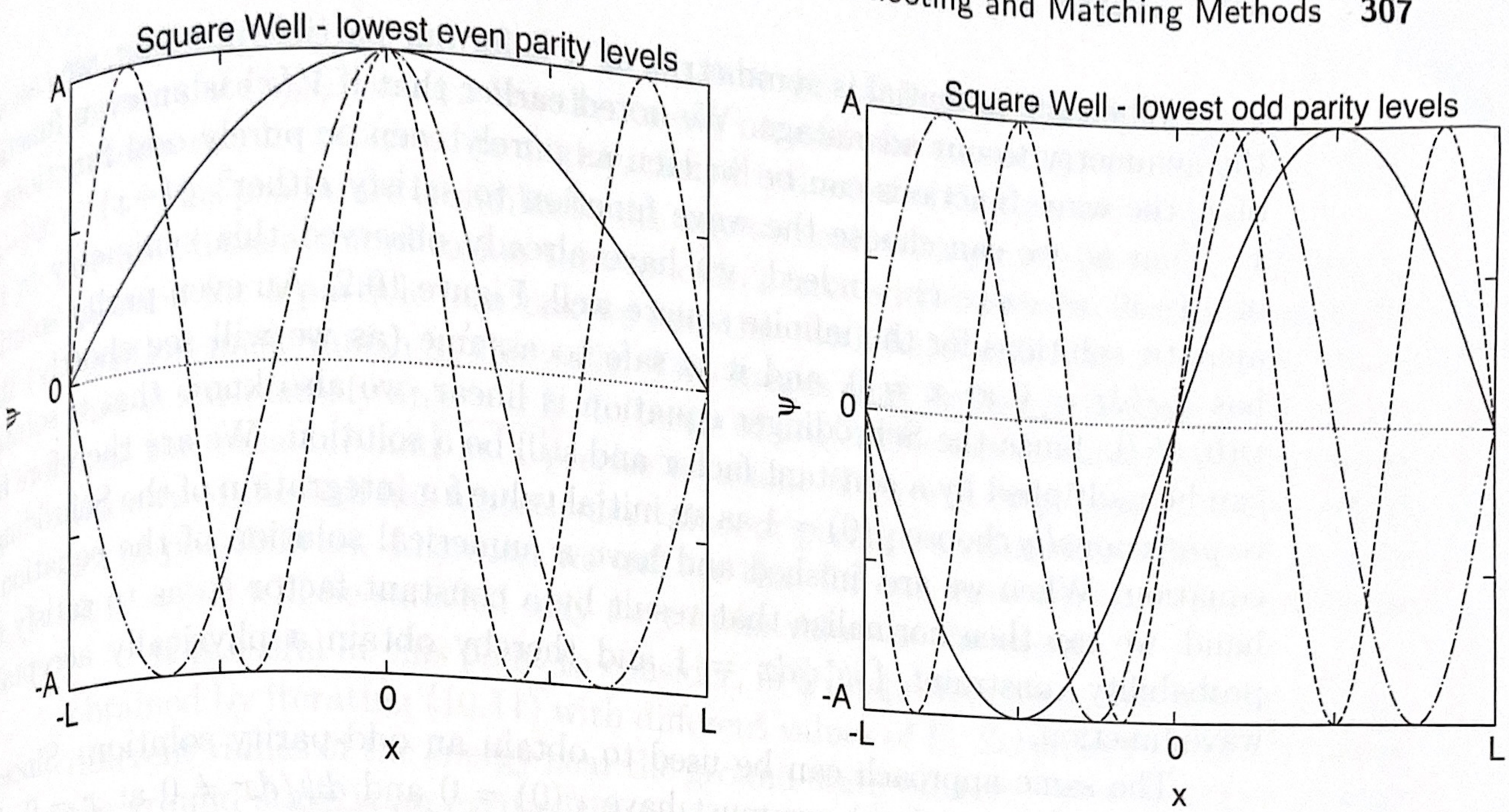

FIGURE 10.2: Wave functions for the lowest six eigenstates for a particle in a box. These are the standing waves in (10.6). The figure on the left shows the cosine-like (even parity) standing waves, while the sine-like (odd parity) wave functions are shown at right. In each case the solid curve is the lowest energy state (of that parity). Note that $A = L^{-1/2}$ is required for the wave functions to be properly normalized.

and cosines, should be evident. However, a basis set need not be this simple, as we will see in an example later in this chapter.

10.2 ONE DIMENSION: SHOOTING AND MATCHING METHODS

We next consider how we can solve numerically the time-independent Schrödinger equation in one dimension, using methods similar to those we have previously developed in connection with ordinary differential equations. We begin with the particle-in-a-box problem, as this will allow us to compare with the analytic solution obtained above. We will then consider several problems for which analytic solutions are not available.

The Schrödinger equation in one dimension (10.2) is very similar in form to the equations of motion we encountered in connection with projectiles in Chapter 2. In those cases we had a differential equation involving the position x, as a function of time. Starting with initial values for x and dx/dt we were able to numerically integrate forward in time to obtain $x(t)$. Now we have a differential equation for ψ as a function of x and we want to use a similar approach. To do this we need the values of ψ and $d\psi/dx$ at some location so that we can begin the integration. These "initial conditions" for the wave function and its derivative are analogous to the initial conditions in a projectile problem. For a projectile these conditions are determined by how the object is struck or thrown, etc. The initial conditions for a wave function are obtained in a somewhat different manner.

When the potential is symmetric, as it is for our particle in a box, we can use the symmetry to our advantage. We noted earlier that if $V(x)$ is an even function of x, the wave functions can be written as purely even or purely odd functions of x. That is, we can choose the wave function to satisfy either[6] $\psi(+x) = \psi(-x)$, or $\psi(+x) = -\psi(-x)$. Indeed, we have already observed this symmetry in the analytic solutions for the infinite square well, Figure 10.2. An even parity solution has $d\psi/dx = 0$ at $x = 0$, and it is safe to assume (as we will see shortly) that $\psi(0) \neq 0$. Since the Schrödinger equation is linear, we also know that a solution can be multiplied by a constant factor and still be a solution. We are therefore free to *provisionally* choose $\psi(0) = 1$ as an initial value for integration of the Schrödinger equation. When we are finished and have a numerical solution of the equation in hand, we can then normalize that result by a constant factor so as to satisfy the probability constraint $\int \psi^* \psi dx = 1$ and thereby obtain a physically acceptable wave function.

The same approach can be used to obtain an odd-parity solution. Since in this case $\psi(x) = -\psi(-x)$, we must have $\psi(0) = 0$ and $d\psi/dx \neq 0$ at $x = 0$. We are again free to pick the scale of ψ, as long as we normalize it at the completion of the calculation, so we can use $\psi(0) = 0$ and $d\psi/dx = 1$ as initial conditions.

By exploiting the symmetry we have thus obtained values for ψ and $d\psi/dx$ at $x = 0$. These are the initial conditions for our integration. The next step is to rewrite (10.2) in finite-difference form. In most of our previous examples we have written such second-order differential equations as two separate first-order equations. Here, since we aren't interested in the derivative $d\psi/dx$, we will take a slightly different approach (which may remind you of the Verlet method). As usual, we discretize space in steps of size Δx and write $\psi_n \equiv \psi(n\Delta x)$. The second derivative in (10.2) can be written in the usual finite-difference form

$$\frac{d^2\psi}{dx^2} \approx \frac{\psi_{n+1} + \psi_{n-1} - 2\,\psi_n}{(\Delta x)^2}\,, \tag{10.9}$$

which is similar to the expression we encountered in connection with the wave equation in Chapter 6. Inserting this into (10.2) we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} \approx -\frac{\hbar^2}{2m}\left[\frac{\psi_{n+1} + \psi_{n-1} - 2\,\psi_n}{(\Delta x)^2}\right] \approx (\mathrm{E} - \mathrm{V}_n)\,\psi_n\,, \tag{10.10}$$

where we have written $V_n = V(n\Delta x)$ and have used the $\approx$ signs to emphasize that this is only an approximation to the original differential equation. This can be rearranged to obtain ψ_{n+1} in terms of ψ_n and ψ_{n-1}. For convenience we will now follow the usual convention for such problems and employ units in which $\hbar = 1$ and $m = 1$, which leads to

$$\psi_{n+1} = 2\,\psi_n - \psi_{n-1} - 2\,(\Delta x)^2\,(\mathrm{E} - \mathrm{V}_n)\,\psi_n\,. \tag{10.11}$$

Let us first consider the even-parity solutions. We have already argued that we can take $\psi(0) = 1$, so we will first apply (10.11) at $n = 0$ (i.e., $x = 0$). Since

[6] If, in addition, the eigenvalue E is non-degenerate (i.e., if there is only one linearly independent solution with this value of E), then the eigenfunction $\psi(x)$ for E *must* possess a definite parity.

we also have $d\psi/dx = 0$ at $x = 0$, we take $\psi_{-1} = 1$ as well, so we can use (10.11) to calculate $\psi_{n+1} = \psi_1$. We then move on and use ψ_0 and ψ_1 to obtain ψ_2. The process can be repeated to find ψ_n for all values of n that are of interest.

This procedure is similar to the way we dealt with projectile motion. However, we now have a complication that we didn't have with baseballs. From the analytic solution for a particle in a box we saw that with hard walls ($V_0 = +\infty$) the wave function must vanish at the walls. This means that we have a boundary condition that ψ must satisfy at $x = \pm L$. In terms of projectiles this is analogous to requiring that the baseball land at a precise location. This will only happen if the initial velocity of the ball has a particular value, or perhaps a value chosen from a discrete set of possibilities. Likewise, we will see that for our wave function the conditions at $x = \pm L$ will be satisfied only for certain values of the energy.

It is useful at this point to consider, in a qualitative sense, the behavior of ψ_n obtained by iterating (10.11) with different values of E. Schematic results for three different values of the energy near the ground-state value E_G (you should recall that the ground state is an even-parity solution) are shown in Figure 10.3. We already know E_G from the analytic results. For the units we have chosen here ($\hbar = 1$, $m = 1$, and a box with $L = 1$), the ground state has an energy[7] of $E_G = \pi^2/8 = 1.2337\ldots$. If we were to use (10.11) to calculate ψ for a value of E that is smaller than this, we would find that ψ is greater than zero when we reach $x = L$ and then diverges to $+\infty$ at larger x, so the boundary condition is *not* satisfied. This is illustrated by the top curve in Figure 10.3. While this function is a solution of (10.2), it cannot be normalized and thus cannot be made to yield a physically acceptable probability density. It is therefore not an allowed wave function for our particle. On the other hand, if we were to perform this calculation with a value of E that is slightly larger than E_G, we would find that ψ drops too quickly with x, so that it is negative when we reach $x = L$ and diverges to $-\infty$ at larger x, as illustrated in Figure 10.3. Only if E has *precisely* the value E_G will the wave function reach zero at precisely $x = L$ and remain zero at larger values of x. This wave function is normalizable and is the ground state ψ for our particle in a box.

This approach for solving a differential equation that has boundary conditions that must be satisfied at *both* ends of an interval is known as the *shooting method*. The method is analogous to trying to throw a baseball or shoot a cannon shell so as to hit a specified target. Only for certain special conditions, in this case the value of E, will the function satisfy the required boundary conditions (that is, will the ball land at the desired spot). In the present case the boundary conditions[8] are such that the wave function must vanish at two particular locations ($x = \pm L$). This was a result of choosing the potential outside the box to be infinitely large. We will see in a moment how to handle cases in which the potential energy varies more slowly with position, such as a box with "soft" walls or a harmonic oscillator.

Let us next consider how to construct a program that implements this approach. The basic plan is to use (10.11) to calculate $\psi(x)$ for different values of the energy, and choose the result that comes closest to satisfying the boundary

[7] This can be verified from the results for k_+ (10.7) in the previous section.
[8] Because of the symmetry, we in effect have boundary conditions at $x = 0$ and $x = L$.

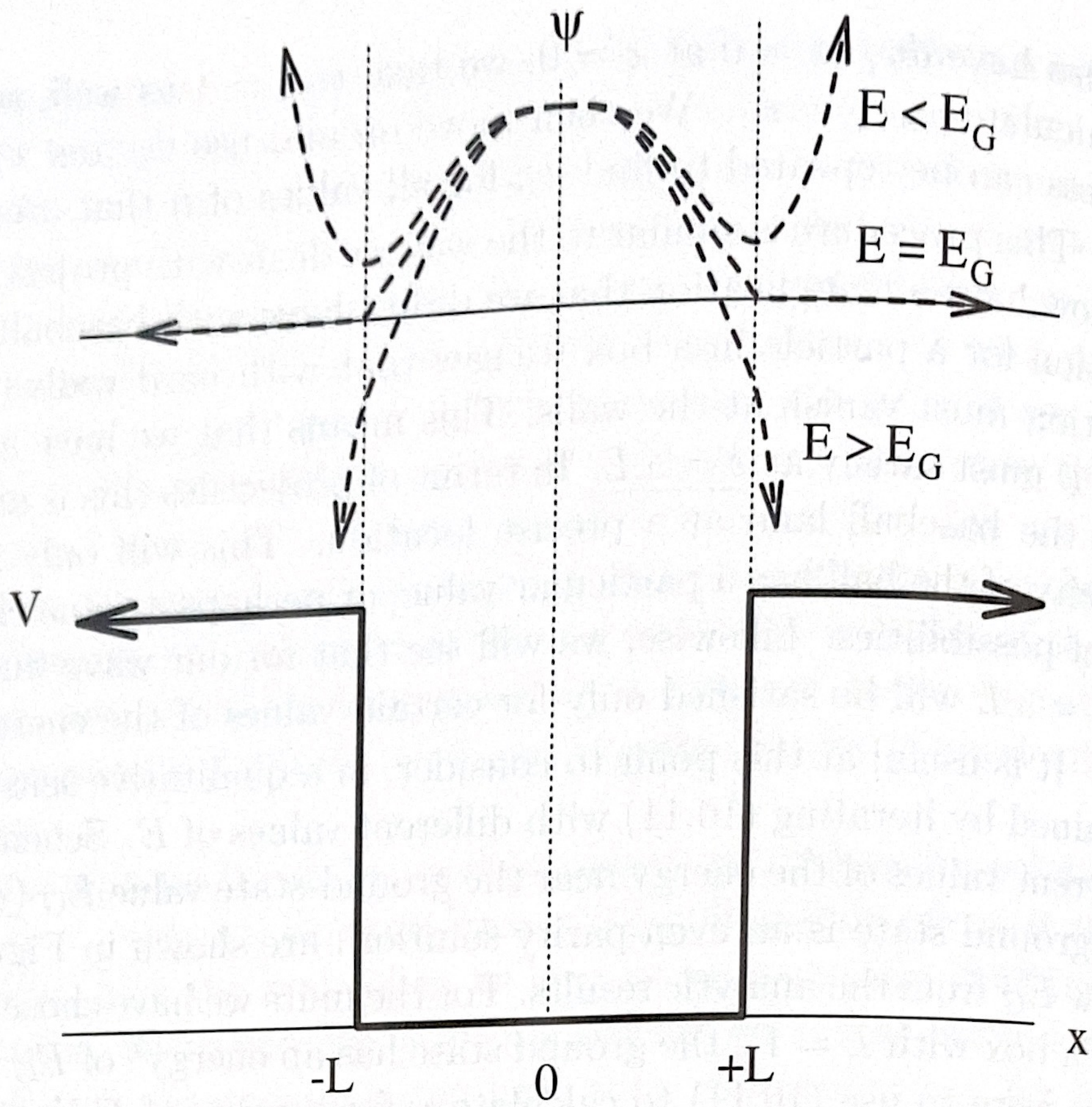

FIGURE 10.3: Schematic results for ψ calculated from (10.11) for several values of E. Top: behavior for the even-parity solution with E near the ground-state energy, E_G. Bottom: corresponding potential energy. The potential outside the box ($|x| > L$) is assumed to be very large.

conditions at the walls of the box. This procedure will yield *both* the wave function and the corresponding energy. We will actually design our program to search systematically for the proper value of E and thereby approach the correct value very closely. The routine sketched below uses the shooting method to integrate starting from $x = 0$ (we again assume $L = 1$), beginning with $\psi_{-1} = \psi_0 = 1$ corresponding to an even-parity solution.[9] After initializing variables such as the spatial step size Δx and the initial estimate for the energy E, the subroutine `calculate` is called. This routine integrates from `i=0` (which corresponds to $x = 0$) to larger values of `i`, stopping when the wave function ψ begins to diverge. At this point the loop is exited and the results for ψ can be displayed. From Figure 10.3 we know that if E is not precisely equal to one of the eigenvalues, the value of the energy should now be adjusted either up or down depending on which direction ψ last diverged. Our routine adds an amount ΔE to E, giving a new estimate for the energy, and the integration is repeated. Let us suppose that E has just been increased ($\Delta E > 0$). If in the next trial ψ diverges in the *same* direction as in the previous case, this means that we did not change the energy enough.[10] The

[9] We will leave it to the exercises to modify this routine to deal with the odd-parity solutions.

[10] This assumes that the last variation in E was made in the *correct* direction. Once the procedure starts to home in on a particular eigenvalue, having reversed the sign of ΔE once or more, this assumption is always true. However, initially, before the sign of ΔE is reversed the first time, it may not be true and the procedure may run away looking for an eigenvalue lower than the ground state energy E, or else home in on an eigenvalue different from the one we are after.

routine would then increase E again and repeat the integration. However, if ψ now diverges in the opposite direction, that means we have changed E by too much and have *overshot* the correct value of the energy. The `calculate` routine then cuts the value of ΔE in half, changes its *sign*, and adds it to E, so that we now proceed back toward the solution. We thus hunt down the correct value of the energy with ever-decreasing values of $|\Delta E|$.

EXAMPLE 10.1 Interactive shooting method routine `calculate`

- Input are the number N and the size Δx of the spatial grids, the initial guess for the energy E and increment ΔE, and the cutoff parameter b (see below).
- Implement $\psi'(0) = 0$ for an even parity solution by setting $\psi_0 = \psi_{-1} = 0$.
- Initialize variable *last_diverge* (which keeps track of the direction of the diverging trend) to zero (since we do not know this direction *à priori*). If the subsequent calculations to evaluate ψ for a given value of E exits by detecting a diverging trend, the sign of the last value of ψ evaluated indicates the direction.
- Main loop in which we iterate and home-in to a valid eigenvalue E:
  - ▷ For the current value of E, loop through the index $i = 0, 1, ..., N-1$ to successively compute the wave function $\{\psi_i\}$.
    - Calculate ψ_{i+1} from ψ_i and ψ_{i-1} using $\psi_{i+1} = 2\psi_i - \psi_{i-1} - 2(E - V(x_i))(\Delta x)^2\psi_i$.
    - Check if $|\psi_{i+1}| > b$ for a suitable cutoff value b.
      - ▷ If yes, assume that ψ is diverging. Exit the loop over i and display the computed ψ.
      - ▷ Otherwise, continue the loop with the next value i.
  - ▷ Display the computed ψ and current value of ΔE, and wait for key input to see if we should continue further.
    - If ΔE is small enough, we may conclude that the current E is acceptable (if the displayed ψ looks good), or reject this calculation (if it is not). Exit the subroutine.
    - If further iteration is indicated, continue.
  - ▷ If the last value of ψ evaluated ($\psi(i+1)$) and *last_diverge* are of different signs, turn around the direction of varying E and halve its magnitude by assigning $\Delta E = -\Delta E/2$.
  - ▷ Update the trial value of E to $E + \Delta E$.
  - ▷ Replace *last_diverge* by the sign of $\psi(i+1)$.
  - ▷ Go back to the beginning of the homing-in process and iterate.

In the `calculate` routine it is convenient to employ a user-defined function[11] for $V(x)$. Using a custom function in this way makes `calculate` easier to read and understand and also makes it simpler to modify the program to deal with other potential functions without modifying any other parts of the program. The cutoff parameter b is used to judge whether $\psi(x)$ is diverging (with no hope of return); the appropriate value of b depends on the eigenvalue E as well as the type of potential $V(x)$. For the the square-well problem treated here and the choice of $\psi(0)$ (or $\psi'(0)$ for the odd solutions), a value of $b \approx 2$ works well, but you need to experiment with it for other situations.

Also to be noted is the interactive nature of this routine. When $\psi(x)$ for some trial value of E has been computed (or when $|\psi_{i+1}| > b$ for some i), it is useful to display the current $\psi(x)$ and asks the user whether to continue. This is an optimization problem (similar to the one we discussed in connection with estimating the launch angle that maximizes a cannon range in Chapter 2, for example), and a visual evaluation of how good (or bad) the current wave function is can be valuable, particularly at initial stages of exploring possible solutions. Most programming languages allow some kind of interactive polling from the keyboard. On the other hand, it is not hard to convert this program into an automatic mode, in which case one needs to set a stopping criterion; setting a limit on the magnitude of ΔE is usually a good approach.

Some results from this program are shown in Figure 10.4 where we plot ψ calculated for several values of E near the exact value for the lowest energy level, $E_G = 1.2337\ldots$. Here we have taken $V = 0$ inside the box and $V = V_0 = 1000$ outside. This behavior is just like the schematic illustrations in Figure 10.3, with ψ diverging to either $+\infty$ or $-\infty$, depending on whether E is above or below the energy that best satisfies the boundary conditions. As the search routine approached this value, the boundary condition $\psi(L) = 0$ was satisfied with increasing precision and the divergence of ψ was pushed to larger and larger values of x. The last value of E considered here was 1.1790; decreasing it by only 0.0001 caused ψ to diverge to $-\infty$. Hence, these two values of E closely bracket the "best" numerical value. You may notice that this is a few percent lower than the exact value for a box with infinitely hard walls. We will see in a moment that this difference is due (largely) to the value used for V outside the box. The exact value for E_G quoted above assumes $V_0 = +\infty$, while the calculation here used $V_0 = 1000$.

This procedure can be employed to find the other even-parity levels by beginning the search at higher values of E. Finally, we should point out that the wave functions given in Figure 10.4 are not properly normalized. To do this would require that ψ be rescaled by a constant factor so as to satisfy (10.5). Note that this rescaling should be done using the wave function for $|x| \leq L$ from Figure 10.4 (that is, the diverging part outside the box should not be included). We will leave this task to the reader.

Next we consider the calculation of the odd-parity levels. We will leave this job mainly to the exercises, although we will show a few results here. As we

[11] By this we mean a function that is constructed by the user as opposed to being built into the language (or its libraries).

have already mentioned, the odd-parity wave functions are the solutions to (10.2) for which $\psi(+x) = -\psi(-x)$. Applying this condition at $x = 0$ requires that $\psi(0) = 0$. Since, as we have argued above, the overall magnitude of ψ at this stage is arbitrary,[12] we take $d\psi/dx = 1$ at $x = 0$. Hence, the `calculate` routine can again be used to obtain $\psi(x)$ by integration, the only difference being that we must employ the initial values $\psi_{-1} = -\Delta x$ and $\psi_0 = 0$. The rest of the calculation proceeds as before, as our routine hunts down the value of E that best satisfies the boundary conditions at $x = \pm L$. Some results for several different values of E are shown in Figure 10.5; the value we find for the energy of the lowest odd-parity level is ≈ 4.670, which is about 5 percent below the exact value for a box with infinitely high walls ($\pi^2/2 = 4.934\ldots$). As with the ground-state energy, this difference is due mainly to the fact that the potential outside the box is not infinitely large.

If you were to examine Figures 10.4 and 10.5 with very high resolution, you would notice that while the wave function at the walls of the box is small, it is not quite zero, even for the best values of E. You may recall that we obtained the boundary condition $\psi = 0$ at the walls of the box under the assumption that the potential is infinite outside the box. Actually, in our computations we have used a slightly different criteria for choosing the best wave function. This criteria involved the divergence of the wave function at large x and is a more general approach since it can be applied to a wide variety of potentials (as we will see in a moment). For a box with infinitely hard walls, that is, if the potential outside the box is truly infinite,

[12] We can once again adjust the magnitude of $\psi(x)$ at the end of the calculation so as to satisfy the normalization condition $\int \psi^* \psi dx = 1$.

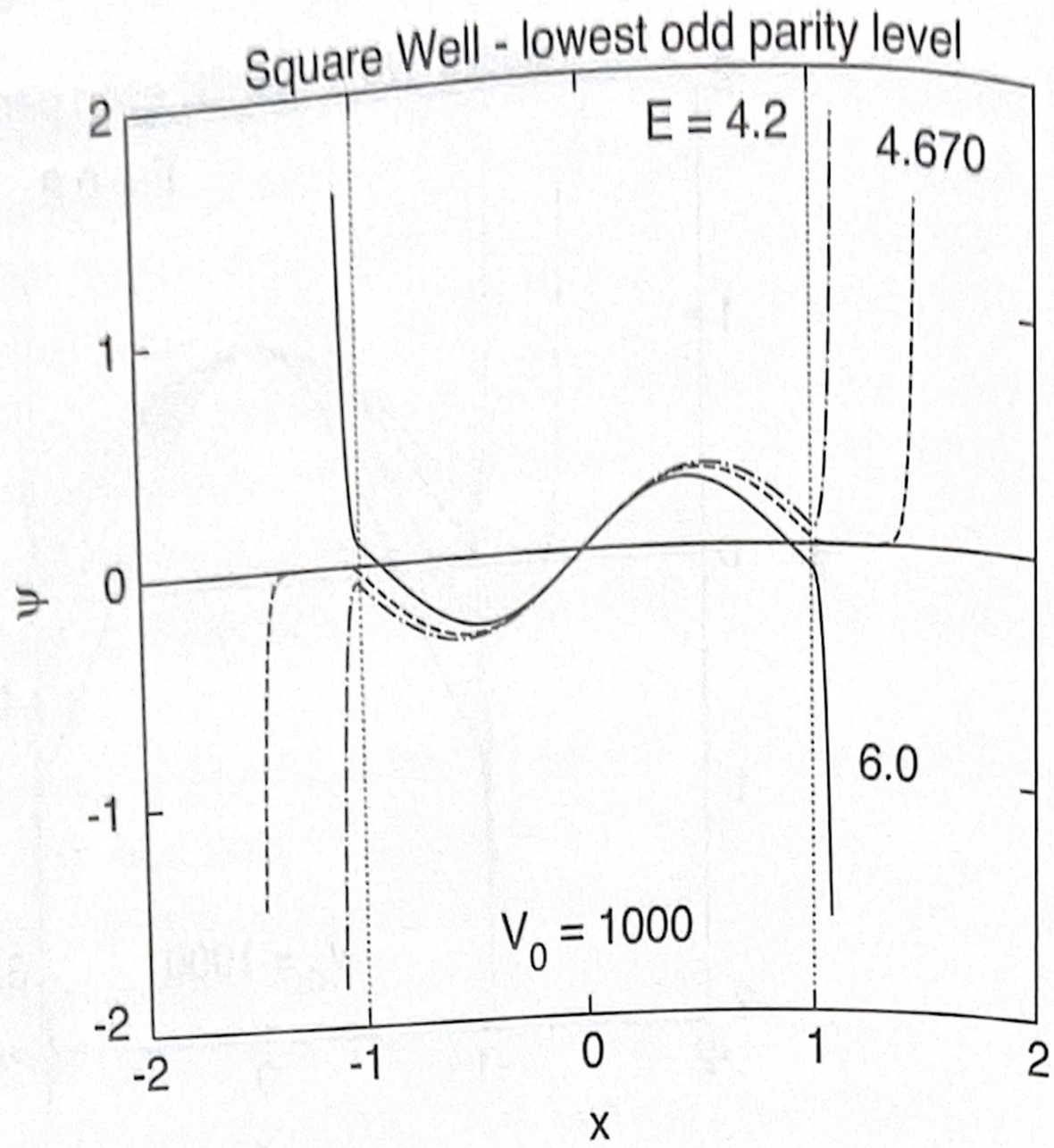

FIGURE 10.5: Trial wave functions for a square well with $V_0 = 1000$. All of the parameters are the same as in Figure 10.4, except that here we consider the lowest odd-parity level.

this divergence criteria is equivalent to the boundary condition that ψ vanish at the edges of the box. However, for a box with soft walls the wave function will be small, but nonzero, in the region beyond the walls. This is a well-known result of quantum theory, which is not found in classical physics.

According to classical theory, a particle cannot venture into a region where V is larger than its total energy. This would require that the classical kinetic energy be negative, which is not allowed. However, quantum theory places no such restriction on the particle. There is a small, but nonzero, chance of finding the particle *anywhere* in space so long as the potential energy is not infinite. This leads to a variety of interesting and important effects such as tunneling, which we will explore shortly. For the particle in a box problem it means that ψ need not go completely to zero at the walls of the box. It turns out that when $V > E$ the wave function decays exponentially with distance as we go farther and farther outside the box. This decay becomes more rapid as $V_{\text{outside}} \equiv V_0$ is made larger, as illustrated in Figure 10.6. Here we show the wave function for the lowest energy level with different values of V_0. In all three cases E is within ± 0.0001 of the ground-state energy for that particular value of V_0. We see that the magnitude of ψ at the wall increases as V_0 is reduced. In addition, the rate at which ψ diverges as $|x|$ is increased beyond the walls (at $x = \pm 1$) also increases greatly as V_0 is made larger. We will explore this behavior further in the exercises and in some other examples below.

The shooting method is a convenient way to deal with boundary-value problems in one dimension. However, it is limited to situations in which values of ψ and $d\psi/dx$ at some initial location can somehow be determined. In our particle-in-a-box problem the symmetry of the potential was essential for obtaining ψ and its deriva-

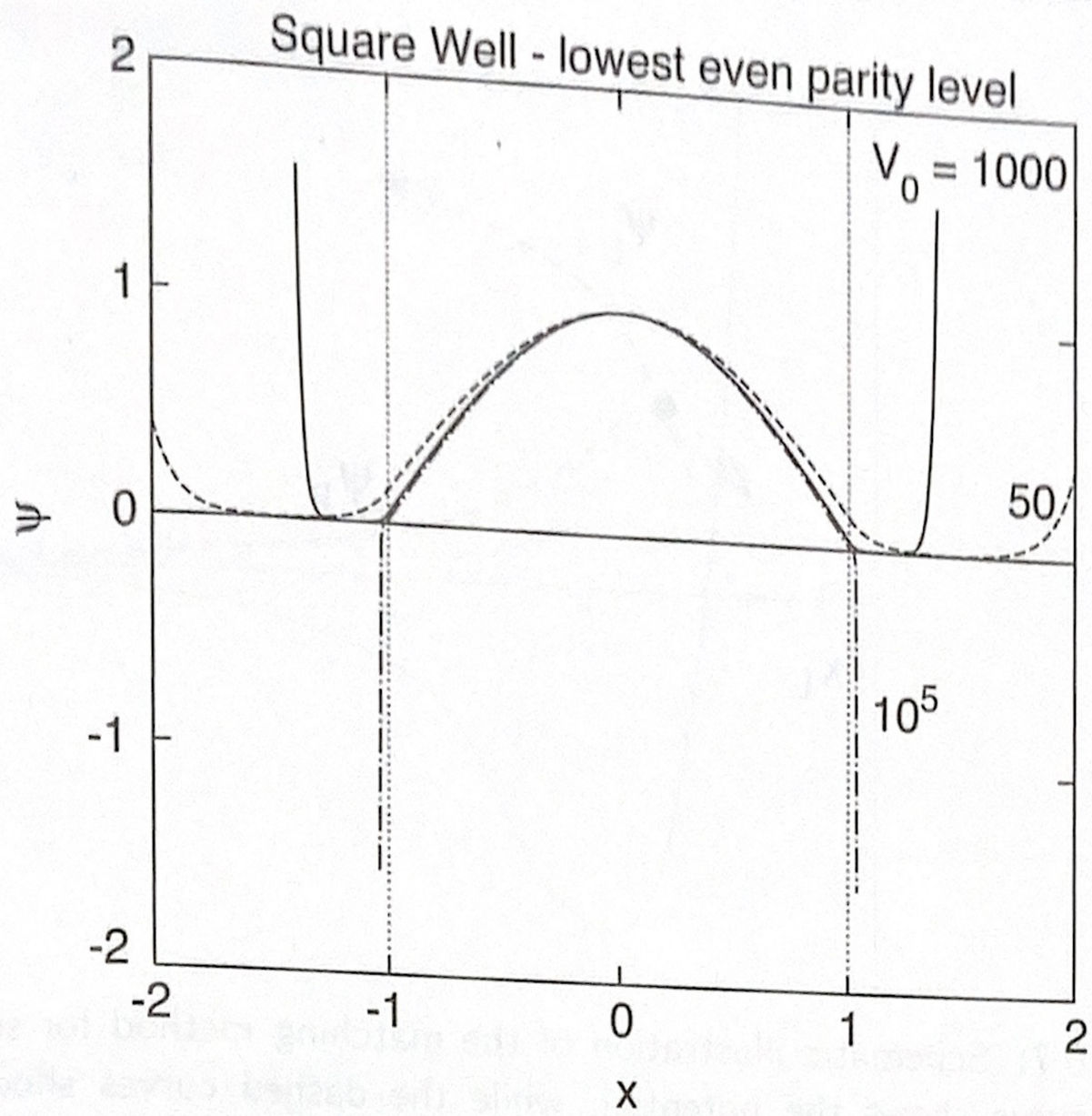

FIGURE 10.6: Ground-state wave function (unnormalized) calculated using the shooting method for a square well with different values of the potential outside the box, V_0. The walls of the box are at $x = \pm 1$. The ground-state energies here are 1.019, 1.179, and 1.221 for $V_0 = 50$, 10^3, and 10^5. The spatial step size was $\Delta x = 0.01$.

tive at the center of the box. In situations involving a nonsymmetric potential, the wave functions will not have a definite parity; thus we cannot obtain initial values of ψ and $d\psi/dx$ from symmetry arguments. In such cases a different approach that relies on the continuity of ψ can be employed. Consider the nonsymmetric potential shown schematically in Figure 10.7. This has a form much like the Lennard-Jones potential we encountered in our molecular dynamics work in Chapter 9 and is similar to what we might find for a system involving two atoms, with one located[13] at $x = 0$. Note, however, that in this example we restrict things to one dimension, so we are not yet treating the full three-dimensional Schrödinger equation. We expect on physical grounds to find a bound state in which the atom has a large probability of being found near the minimum of the potential. The wave function for this state will vanish at both large and small x and be significantly different from zero only in the region where V is large in magnitude and negative.

Let us therefore consider calculating ψ using (10.11), with integrations beginning in the regions where ψ is very small (i.e., at large x and small x) and proceeding toward the middle. That is, we now perform two integrations. One starts from a point on the far left in Figure 10.7, at the point $x = x_L$. At this location we set $\psi = 0$ and give the derivative $d\psi/dx$ a very small value. We then use (10.11) to obtain ψ at $x_L + \Delta x$, $x_L + 2\Delta x$, etc., and thus determine ψ at ever-increasing values of x. We call this function ψ_L, since it is obtained by integrating in from the

[13] For simplicity we can imagine that the atom at $x = 0$ is much more massive than the other so that it can be taken as fixed in space, and we need worry only about the wave function of the light atom.

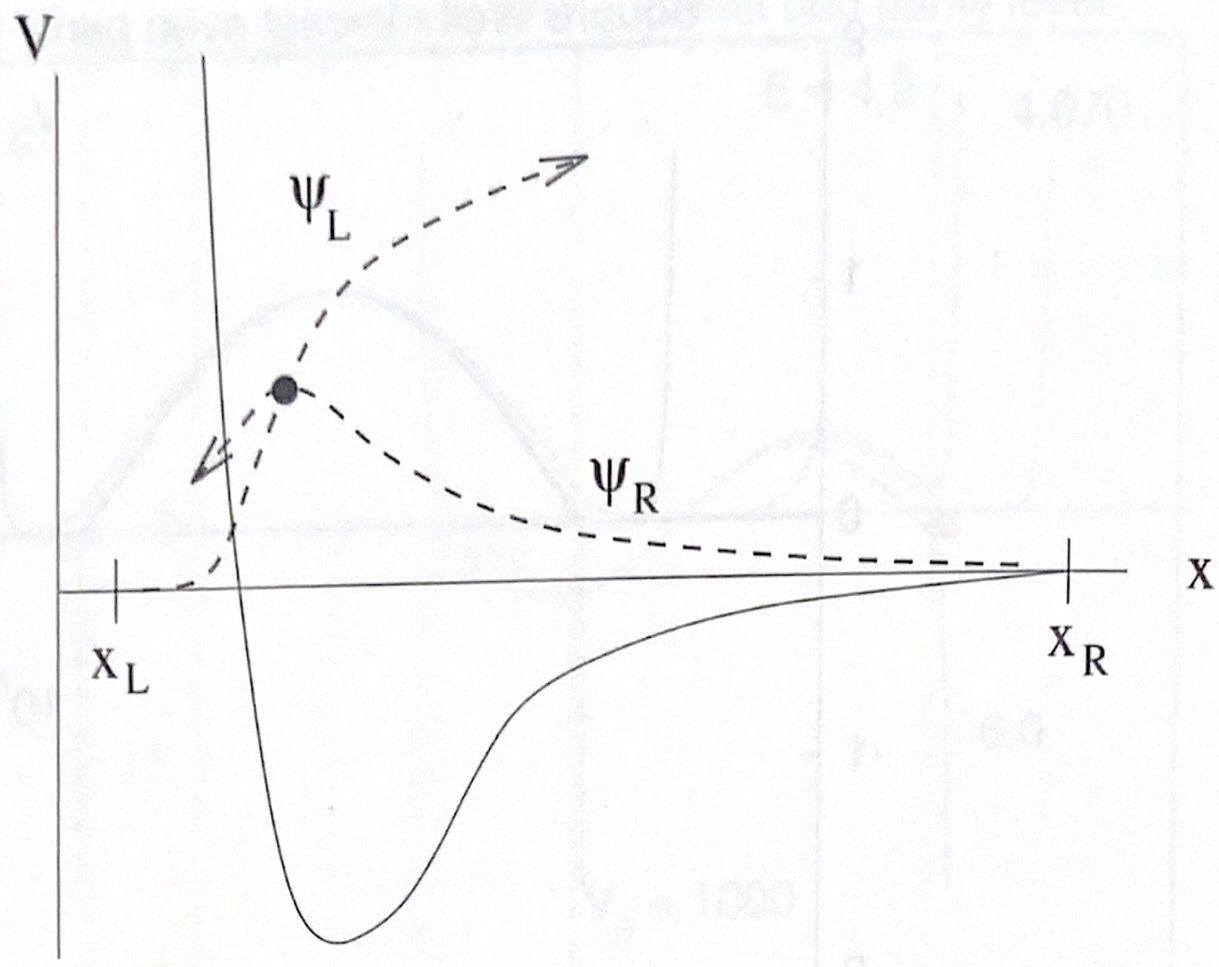

FIGURE 10.7: Schematic illustration of the matching method for solving the Schrödinger equation. The solid curve shows the potential, while the dashed curves show (hypothetical) wave functions calculated using (10.11), starting the integration from the left (ψ_L) and from the right (ψ_R). In this case the two trial functions do not match smoothly, and thus cannot be combined to give an acceptable solution of the Schrödinger equation.

left-most region. This procedure is then repeated starting from a point $x = x_R$, far to the right in Figure 10.7. At this location we set $\psi = 0$ and give $d\psi/dx$ a small value, in preparation for the application of (10.11). We then integrate toward smaller values of x, and obtain a function we call ψ_R. The plan is to combine the functions ψ_L and ψ_R to obtain the wave function over the entire range.

The correct wave function must be a smooth, continuous function. That is, ψ and its derivative must both be continuous.[14] This means that if a combination of our two functions ψ_L and ψ_R is to form an acceptable wave function, they must intersect somewhere (so that the wave function is continuous), and they must have the same slope at the intersection point (so that $d\psi/dx$ is continuous). We can always arrange for ψ_L and ψ_R to intersect since, as has already been noted several times, we can scale the calculated ψ by a constant factor and still obtain a solution to the Schrödinger equation. It is usually convenient and numerically advisable, to pick a location somewhere near the minimum of the potential as the matching point since the wave function will be large there, and then scale either ψ_L or ψ_R or both so that their values are equal at that point.[15] This still leaves us with the requirement that the derivatives be equal at the matching point. The only remaining adjustable parameter in the computation is the energy. For most values of E we find the situation depicted in Figure 10.7, where the derivatives $d\psi_L/dx$ and $d\psi_R/dx$ do *not* match. However, it is usually possible to adjust the value of E so as to make these derivatives match. When this occurs, the combination of ψ_L and ψ_R gives the wave function, and the associated value of E is the energy of the level.

This approach is often called the *matching method*, for obvious reasons. It

[14] This assumes that the potential is a smooth function.

[15] This is equivalent to scaling the derivatives at x_L and x_R so as to make $\psi_L = \psi_R$ at the matching point.

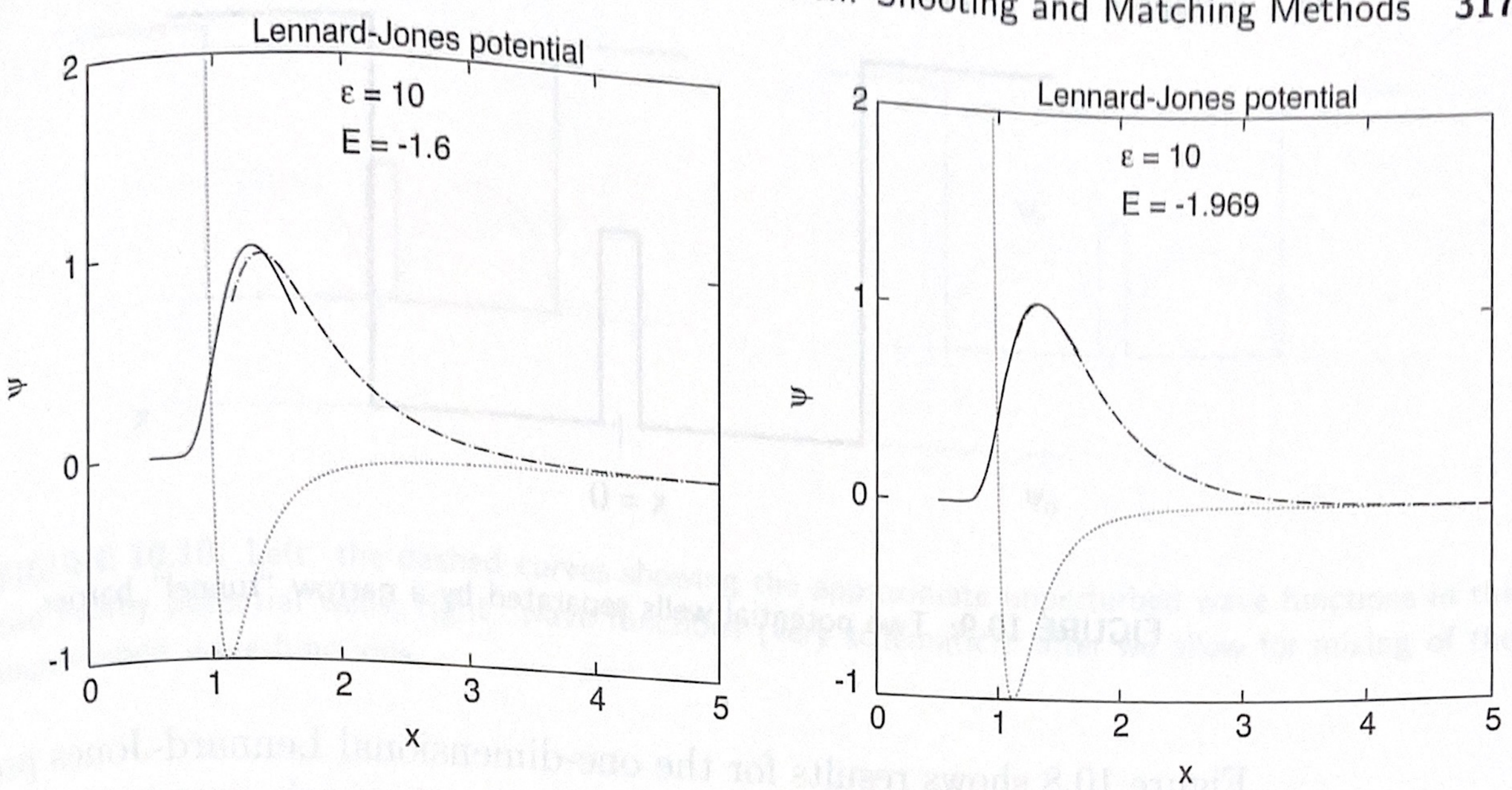

FIGURE 10.8: Solution for the ground state of the Lennard-Jones potential [(10.12) with $\epsilon = 10$ and $\sigma = 1$] constructed using the matching method. The integrations were started at $x_L = 0.5$ (on the left) and $x_R = 5$ (on the right) with $\Delta x = 0.01$. The two trial functions are shown by the solid (ψ_L) and dot-dashed (ψ_R) curves, and the potential is shown by the dotted curve (the scales for ψ and $V(x)$ are not the same). Left: for $E = -1.6$ the derivatives of ψ_L and ψ_R are not equal at the matching point ($x = 1.4$). Right: for $E = -1.969$ the derivatives match fairly well, so this is an acceptable approximation for the wave function. Note that this wave function is not normalized.

can be implemented numerically by modifying the `calculate` routine we developed for the shooting algorithm. A search routine can again be used to obtain an ever more accurate match of the derivatives $d\psi_L/dx$ and $d\psi_R/dx$, and thus better and better estimates for the wave function and energy. While we can use essentially the same structure as the `calculate` routine of the shooting method, the details differ considerably. First, since we are starting to compute $\psi(x)$ from both ends of the system, we must have initial values of the wave functions and their derivatives at both ends. That is, we need to start with $\psi_L(x_L - \Delta x)$, $\psi_L(x_L)$, $\psi_L(x_R + \Delta x)$, and $\psi_L(x_R)$, where the two values outside the interval (x_L, x_R) are needed to start the iteration of (10.11). These values are usually chosen so that the initial slopes are very small, e.g., $\psi_L(x_L - \Delta x) = -0.0001\Delta x$. For convenience we can choose the same value at both ends as they will be scaled differently to match the values of ψ_L and ψ_R at a central point anyway. Second and more importantly, we must have an efficient strategy to vary E so that the derivatives $d\psi_L/dx$ and $d\psi_R/dx$ approach each other. A valid approach here is to: (1) assign a value of ± 1 to a variable, say, *match*, depending on whether $d\psi_L/dx > d\psi_R/dx$ or vice-versa, and (2) if the sign of *match* is different from the corresponding quantity from the previous trial value of E, then (3) assign the new value $\Delta E = -\Delta E/2$ to the increment to use next. We leave it to the reader to confirm that this method works regardless of the signs of the derivatives and to construct a working program based on this strategy (of course, you are also welcome to design your own strategy!).

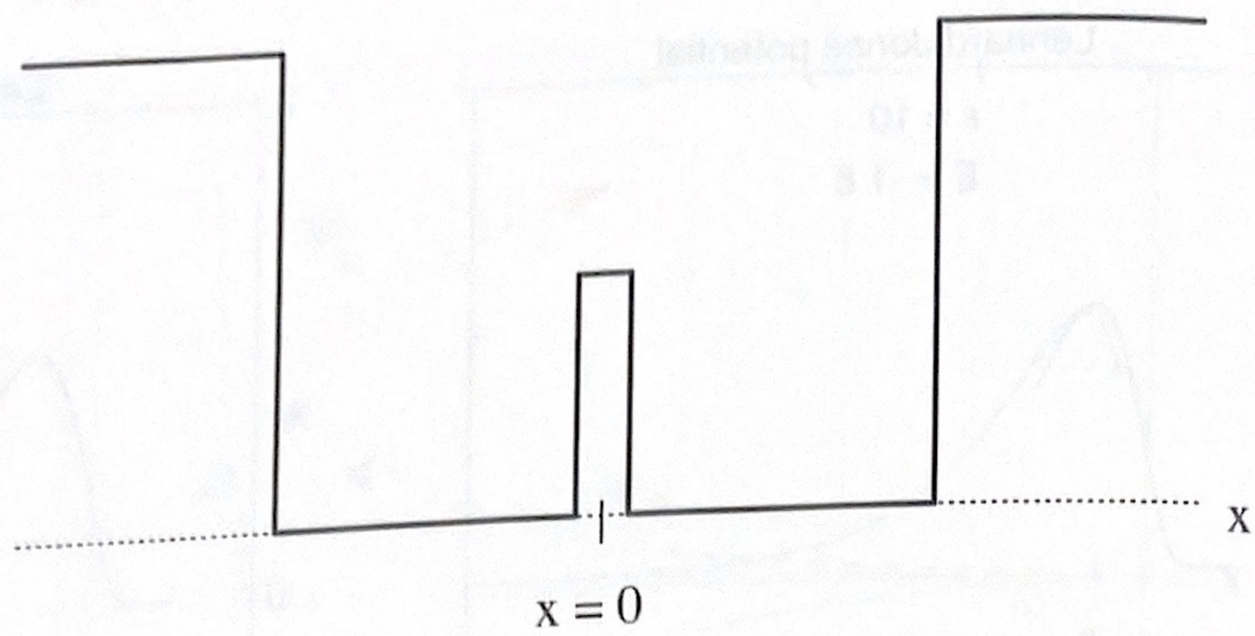

FIGURE 10.9: Two potential wells separated by a narrow "tunnel" barrier.

Figure 10.8 shows results for the one-dimensional Lennard-Jones problem[16]

$$V(x) = 4\epsilon\left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6}\right]. \tag{10.12}$$

Here we plot results for two values of E. In each case we have normalized both ψ_L and ψ_R to unity at the matching point $x_{\text{match}} = 1.4$. For the case on the left there was a sizable discontinuity in $d\psi/dx$ at the matching point, so this solution is not satisfactory. After letting the search routine iterate several times, we obtain the result on the right, where ψ_L and ψ_R join much more smoothly. By starting the search at other values of E we can obtain the wave functions for other energy levels. We will, as usual, leave this for the exercises.

While we introduced the matching strategy for dealing with nonsymmetric potentials, it is not limited to such cases. An interesting example is a square well containing a small potential barrier inside the well, shown schematically in Figure 10.9. This particular potential is actually symmetric, so we could use the shooting method here, starting from $x = 0$. However, there are many interesting variations on this problem; for example, we could move the small barrier off center or make the potential of the barrier vary with x. Such asymmetric potentials require the matching approach.

Before we construct the wave functions for the potential in Figure 10.9, it is worthwhile to anticipate some of the physics of the problem. This potential consists of two square wells, one to the left and one to the right of the barrier. If the barrier is large (very high or very wide or both), the two wells are effectively uncoupled, since the wave function in one will not penetrate far enough into the barrier to reach into the other well (compare with Figure 10.6). The wave functions in each well will therefore be unaffected by the presence of the other, and the solutions will be those we have already encountered in our work on the particle-in-a-box problem. The ground-state wave function for this case is shown schematically on the left side of Figure 10.10.

If, on the other hand, the barrier separating the two wells is not large, the unperturbed wave function from one side will be able to penetrate through to the

[16] You may recall that this is the potential we used in our molecular-dynamics calculations in Chapter 9.

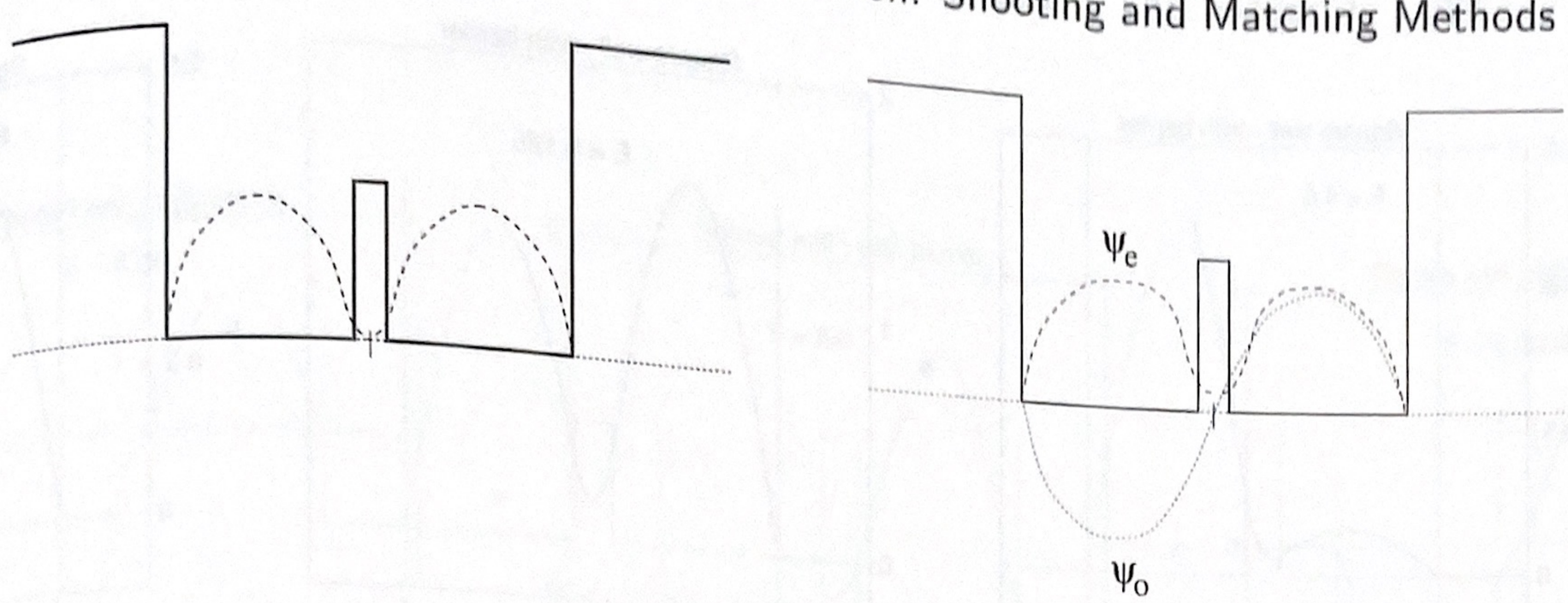

FIGURE 10.10: Left: the dashed curves showing the approximate unperturbed wave functions in the two nearby potential wells; right: wave functions (very schematic!) after we allow for mixing of the unperturbed wave functions.

other before it decays to a negligibly small value. Actually, the unperturbed wave functions from both wells will decay as they penetrate the barrier from opposite sides. These two wave functions must meet continuously in the center, just as we saw with ψ_L and ψ_R in the Lennard-Jones problem (Figure 10.8). This leads to what is usually referred to as *mixing* of the two, initial, unperturbed wave functions. If we denote the unperturbed wave functions as ψ_1 and ψ_2, then to a first approximation they will combine to form wave functions for the entire two-well system as either $\psi_e \sim \psi_1 + \psi_2$, or $\psi_o \sim \psi_1 - \psi_2$. That is, they can form either an even (ψ_e) or odd (ψ_o) combination.[17] These are sketched on the right side of Figure 10.10. Note that the wave functions we have sketched are derived (approximately) from the initial unperturbed wave functions in the two separate wells. Similar combinations are formed from the unperturbed excited-state wave functions.

The two wave functions ψ_e and ψ_o will have energies close to that of the initial unperturbed states. According to perturbation theory, the mixing of two such states leads to a small splitting of the energy levels, with the even level (ψ_e) being pushed to a lower energy and the odd level pushed higher. This can be illustrated nicely using the solutions obtained from the matching algorithm. The ground state has even parity and is considered in Figure 10.11. On the left we show the behavior for a value of E that is too low, and we see that ψ_L and ψ_R do not match smoothly. In the middle case E is slightly too large, although the derivatives of ψ_L and ψ_R match fairly well on the scale shown here. On the right we show results for a value of E that yields a slightly better match. It is interesting that even here the wave function is not quite symmetric; you can see this from the fact that the amplitudes of the two maxima are not quite the same. This is a result of the numerical errors that arise when integrating through a classically forbidden region (the tunnel barrier), as the solutions tend to be divergent in such regions (compare again with Figure 10.6). In this particular problem we could have obtained a better result by employing the shooting method, as this would preserve the symmetry inherent in the problem. However, using the matching method in this case gives a good impression of the strengths and weaknesses of that algorithm.

[17] The precise parity of the solutions in this case can be traced to the symmetry of the potential. When the potential is not symmetric the solutions will not have a definite parity, but there will still be two wave functions constructed (approximately) as the sum and difference of the two unperturbed wave functions.

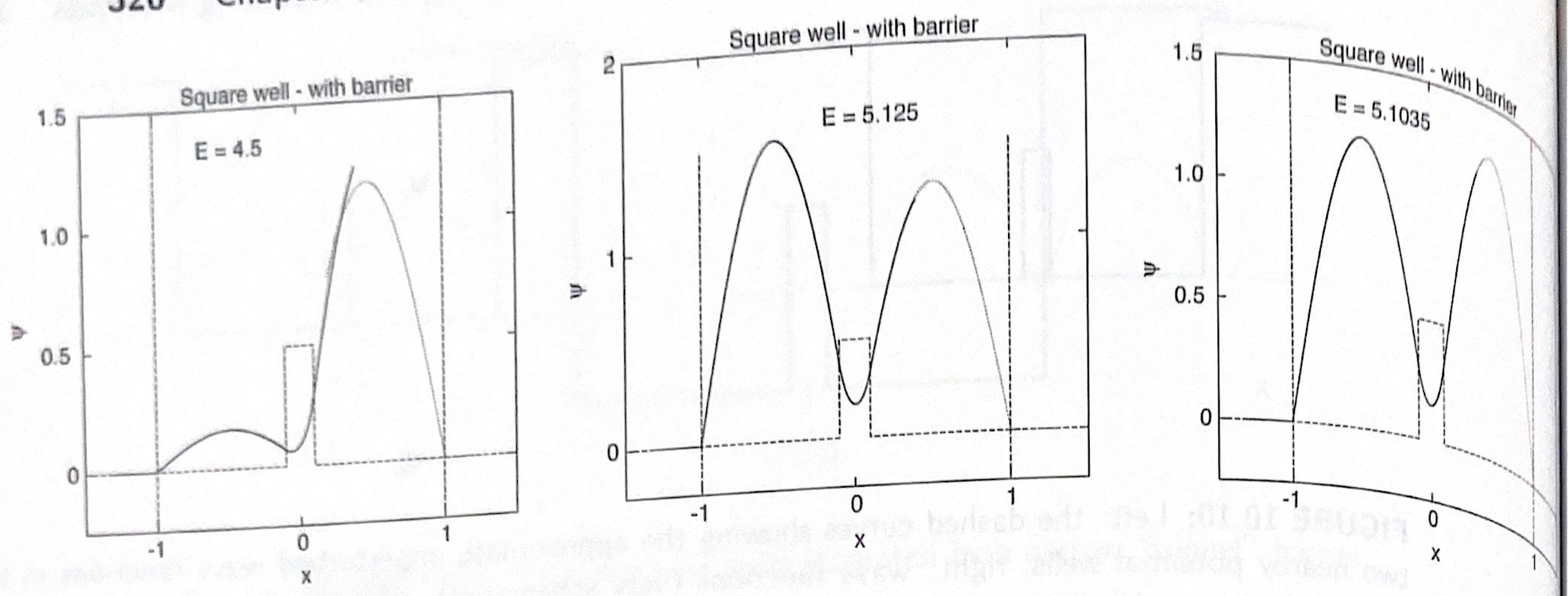

FIGURE 10.11: Results for ψ_L and ψ_R calculated with the matching method for the potential in Figure 10.9, for several values of E. The integrations were started at $x = \pm 1.3$, the step size was $\Delta x = 5 \times 10^{-4}$, and the matching was done at $x_{\text{match}} = 0.3$. The parameters associated with the potential were $V = 0$ inside each well, $V = 10^5$ for $|x| > 1$, and $V = 100$ for $|x| \leq 0.1$. The vertical dashed lines indicate the edges of the potential wells. Note that the scale for ψ varies from plot to plot.

The numerical difficulties associated with integrating through a classically forbidden region (where $V > E$) bring up a related issue. In all of our applications of the matching method we have started the integrations in such forbidden regions and integrated toward the regions where $V < E$, that is, the regions where we expect the wave function to be large. In principle we could have started at a location where $V < E$, and integrated toward the classically forbidden regions. However, the numerical problems and divergences are usually more severe in the latter case. As a general rule it is best to integrate away from classically forbidden regions, toward regions where ψ is large.

Figure 10.12 shows results for slightly higher values of E. The left and middle plots show behavior for values of E that are too low and too high and thus provide poor matches. The plot on the right shows a good match, and the wave function is seen to have odd parity, as expected from the discussion given above.

The shooting and matching methods described in this section are well suited for the time-independent Schrödinger equation in one dimension and similar types of boundary-value problems. We have only been able to consider a few examples here; the exercises explore these and several other cases in more detail.

EXERCISES

10.1. Use the shooting method to obtain the lowest six energy levels for a square well. This will require that you write a program that can deal with both even- and odd-parity solutions. Examine how the energy varies with level number and test your values against the exact results (10.7) and (10.8). Compare the wave functions (make sure that they are properly normalized!) with the exact solution (10.6). It is also instructive to examine the behavior as a function of the spatial step size Δx. Study how the value of the ground-state energy varies with the choice of step size; try $\Delta x = 0.05$, 0.01, and 0.005, for a box with walls at $x = \pm 1$.

10.2. Use the matching method to calculate the wave functions and energies of the

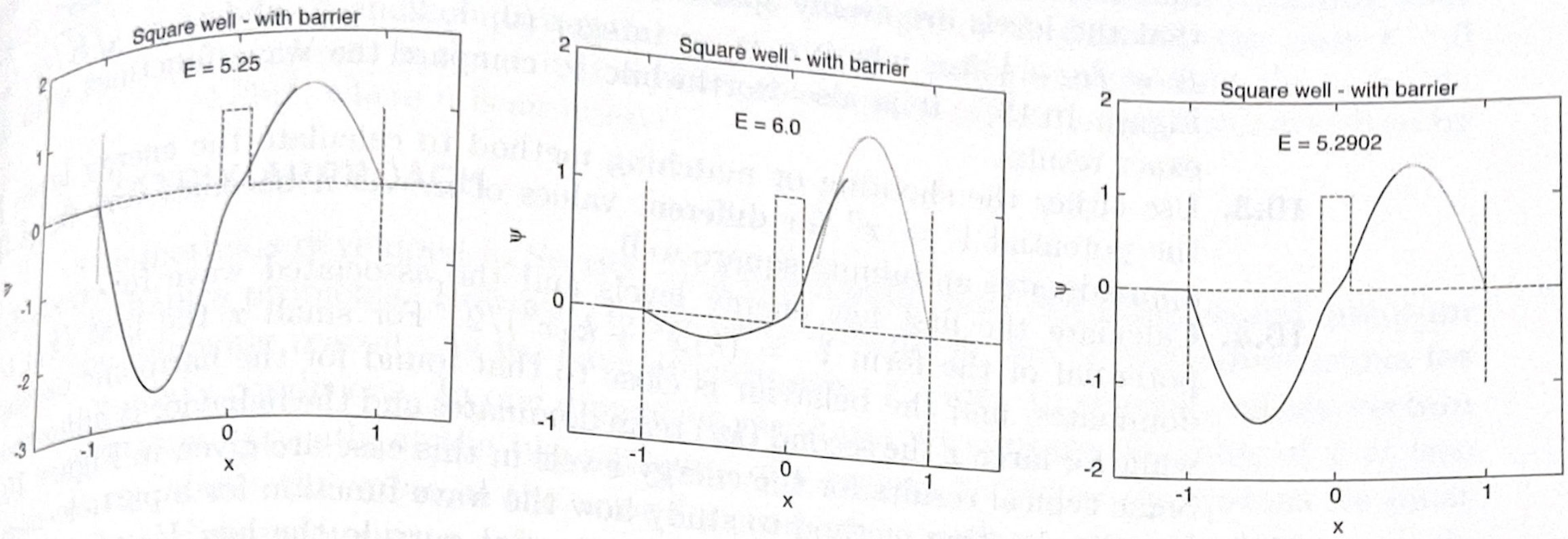

FIGURE 10.12: Results for ψ_L and ψ_R calculated with the matching method for the tunnel potential in Figure 10.9. Here we have used several values of E that are near the energy of the lowest odd-parity level. The other parameters were the same as in Figure 10.11.

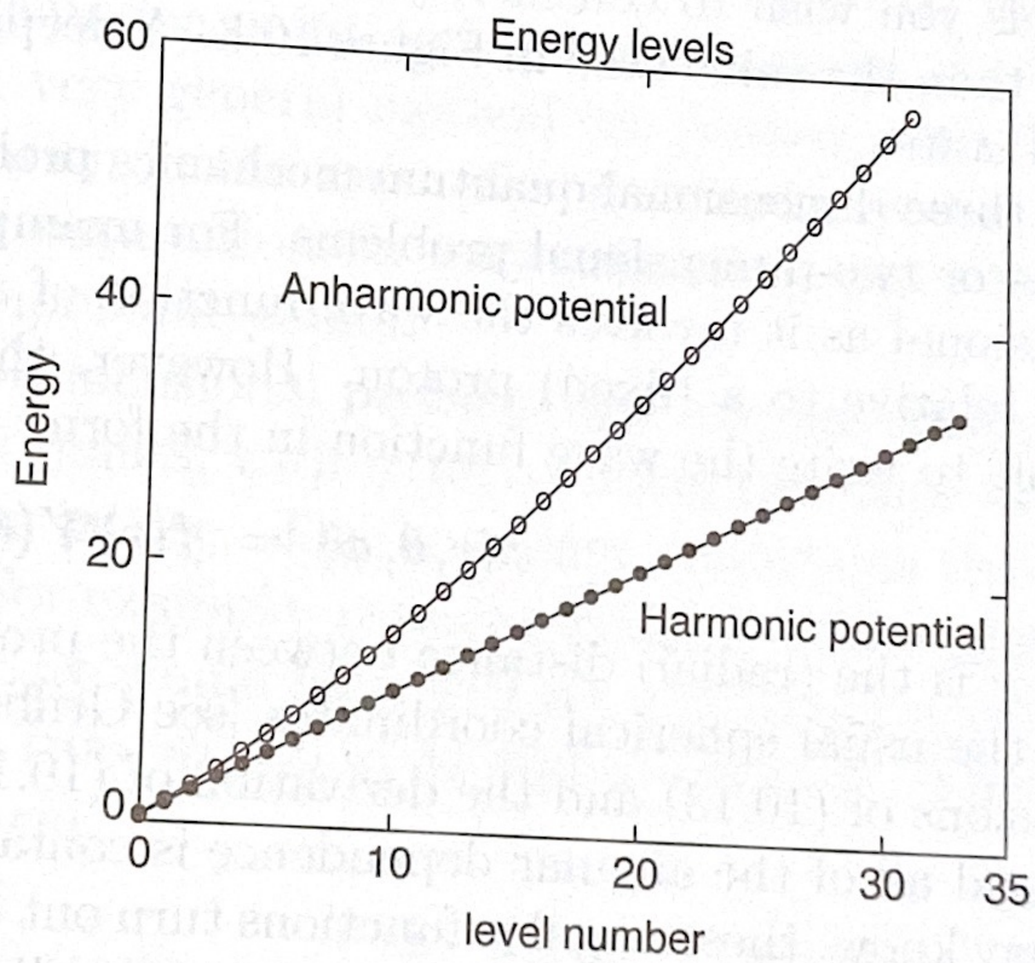

FIGURE 10.13: Lowest few energy levels for a harmonic oscillator ($V = Kx^2/2$ with $K = 1$) and an anharmonic oscillator [$V = (k_1x^2 + k_2x^4)/2$, with $k_1 = 1$ and $k_2 = 0.1$]. In both cases we have used our usual choice of units, for which $\hbar = m = 1$. Note that for the harmonic case the energy varies linearly with level number (which agrees with the well-known, analytic solution). For the anharmonic case the corresponding energies are shifted to progressively higher values. For the higher levels the wave function has more of its "weight" at larger values of x (classically speaking, the vibration amplitude is higher) where the potential is larger due to the anharmonic term, and this pushes the energy higher than in the harmonic case.

first few energy levels of the harmonic oscillator potential $V = Kx^2/2$. Show that the levels are evenly spaced in energy and compare with the exact result $E = (n + \frac{1}{2})\hbar\omega$, where n is an integer (0, 1, 2, ...) and $\omega = \sqrt{K/m}$ (see Figure 10.13). It is also worthwhile to compare the wave functions with the exact results.

10.3. Use either the shooting or matching method to calculate the energy levels for the potential $V = x^n$ for different values of n. As n becomes very large this approximates an infinite square well.

10.4. Calculate the first few energy levels and the associated wave functions for a potential of the form $V = (k_1x^2 + k_2x^4)/2$. For small x the first (k_1) term dominates, and the behavior is close to that found for the harmonic oscillator, while for large x the second (k_2) term dominates and the behavior is *anharmonic*. Some typical results for the energy levels in this case are given in Figure 10.13.

10.5. Use the shooting method to study how the wave function for a particle-in-a-box depends on the magnitude of the potential outside the box V_0. Examine the variation of ψ beyond the walls of the box and show that it decays exponentially with distance in this region. Study the decay length as a function of V_0 and compare the results for different energy levels. As the energy of the level approaches V_0 the decay length should become larger.

***10.6.** Use the matching method to obtain the wave functions for the first few states above the ground level for the one-dimensional Lennard-Jones potential. Compare the variation of the energy with level number with the results shown for the harmonic and anharmonic potentials in Figure 10.13. Depending on the number of levels you wish to consider, you may have to make the value of ϵ in (10.12) larger than the value used in Figure 10.8. A deeper potential well possesses more bound states.

***10.7.** Many three-dimensional quantum mechanics problems can be reduced effectively to one- or two-dimensional problems. For example, the hydrogen atom is three dimensional as it involves the wave function of an electron as a function of position relative to a (fixed) proton. However, the spherical symmetry makes it possible to write the wave function in the form

$$\psi(r, \theta, \phi) = f(r)\, Y(\theta, \phi) , \tag{10.13}$$

where r is the (radial) distance between the proton and the electron, and θ and ϕ are the usual spherical coordinates [see Griffiths (1995) and Schiff (1968) for discussions of (10.13) and the derivation of (10.14)]. Here $f(r)$ is a function of r only, and all of the angular dependence is contained in the function $Y(\theta, \phi)$. As you may know, these angular functions turn out to be the spherical harmonics. In this problem we will be concerned with the radial function, $f(r)$. When the form (10.13) is inserted into the three-dimensional Schrödinger equation we obtain a differential equation for $f(r)$. It is common practice at this point to deal instead with the related function $g(r) \equiv rf(r)$, which satisfies the equation

$$\frac{d^2g}{dr^2} = \left(2\,[V(r) - E] + \frac{\ell(\ell+1)}{r^2}\right) g , \tag{10.14}$$

where $V(r) = -1/r$ is the Coulomb potential[18] and ℓ is an integer associated with the angular momentum of the electron that arises from the solution for

[18] More precisely, this is the electric potential multiplied by the charge of the electron. We use units in which this charge is -1.

$Y(\theta, \phi)$. Employ the shooting method to solve (10.14) for $g(r)$ starting your integration at $r = 0$, with the initial value $g(0) = 0$. Consider the cases $\ell = 0$ and $\ell = 1$ and compare your results with the analytic solution for the hydrogen atom. *Hint:* In the units used here the energies of the bound states are given by $-1/2n^2$, where n is an integer.

10.3 A MATRIX APPROACH

The methods developed in Section 10.2 can handle most one-dimensional quantum mechanics problems. However, life is more difficult in two or three dimensions for the following reason. As we have already seen, ψ must, in general, satisfy certain boundary conditions. In one dimension these usually concern the value of ψ at two locations; typically at the two extremes of a region. In higher dimensions we must worry about the value of the wave function on a *surface*, which could be a circle in two dimensions or a sphere in three dimensions. In some cases the potential may have enough symmetry that the problem can be reduced to a differential equation involving only one variable. For example, we have seen in the exercises in Section 10.2 that with the hydrogen atom we can separate the radial and angular dependences of ψ and thereby reduce the radial dependence to a one-dimensional problem. In such cases the matching or shooting method can then be used. Many textbook problems are like this, for the simple reason that more complicated cases can almost never be solved analytically!

Shooting and matching methods are not well suited for satisfying boundary conditions at more than one point and therefore cannot (easily) be used in two or three dimensions. A very general method for dealing with these cases is to write the Schrödinger equation in the form of a matrix eigenvalue problem. While such an approach can be computationally very difficult to carry through, it is useful for illustrating several important points.

Consider a two-dimensional problem and assume that, as usual, we break up space into a lattice of points, with $\psi(m, n)$ being the value of the wave function at location (m, n) on the lattice. The boundary conditions then specify the value of ψ on the boundary. For example, ψ might vanish on the edges of the system; if the system is rectangular, we would have $\psi(0, n) = \psi(M, n) = \psi(m, 0) = \psi(m, N) = 0$, where the lattice runs from $m = 0$ to M and $n = 0$ to N. The Schrödinger equation (10.1) then has the form

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\,\psi &= -\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right] + V(\vec{r})\,\psi \\
&\approx -\frac{\hbar^2}{2m}\left[\frac{\psi(m+1,n) + \psi(m-1,n) - 2\psi(m,n)}{(\Delta x)^2}\right. \\
&\quad \left. + \frac{\psi(m,n+1) + \psi(m,n-1) - 2\psi(m,n)}{(\Delta y)^2}\right] + V(m,n)\,\psi(m,n) \\
&\approx E\,\psi(m,n)\,,
\end{aligned}
\tag{10.15}
$$

where the last several lines give the wave equation in finite-difference form. This is a system of algebraic equations for $\psi(m, n)$; there are (of order) $M \times N$ unknown values of $\psi(m, n)$ and the same number of equations.

If we define a column vector $\vec{\psi}$ whose elements are $\psi(m,n)$,

$$\vec{\psi} = \begin{pmatrix} \psi(0,0) \\ \psi(0,1) \\ \dots \end{pmatrix}, \tag{10.16}$$

and a square matrix $\mathcal{H}$ representing the Hamiltonian *operator*,

$$\mathcal{H} \equiv -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}), \tag{10.17}$$

then these equations can be written as a linear equation

$$\mathcal{H}\vec{\psi} = E\vec{\psi}, \tag{10.18}$$

where the Hamiltonian $\mathcal{H}$ is be represented by a matrix

$$\mathcal{H} = \begin{pmatrix} 4+V(0,0) & -1 & 0 & \dots \\ -1 & 4+V(0,1) & -1 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}. \tag{10.19}$$

Here we have taken the liberty to set $\Delta x = \Delta y$ and to absorb factors such as these as well as $\hbar$ and mass m into V and E.[19] The points we wish to make here depend on the general *form* of these equations, so we will avoid the notational distractions associated with specifying all of the factors precisely.

Equations (10.18) and (10.19) define an eigenvalue problem for the Hamiltonian matrix $\mathcal{H}$, which is one of the standard problems in linear algebra.[20] Efficient programs for obtaining the eigenvalues E and the associated eigenvectors $\vec{\psi}$ can be found in all serious packages of mathematical routines. Moreover, since $\mathcal{H}$ is usually *sparse*, that is, most of its entries are zeroes, a number of techniques are available to simplify such work.[21]

Focusing on the eigenvalues, these equations are sometimes put in the form

$$\begin{pmatrix} 4+V(0,0)-E & -1 & 0 & \dots \\ -1 & 4+V(0,1)-E & -1 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \psi(0,0) \\ \psi(0,1) \\ \dots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \dots \end{pmatrix}. \tag{10.20}$$

If we define a square matrix $\mathcal{M}(\mathrm{E})$ whose elements are shown as the left-most matrix in (10.20), this can be written as

$$\mathcal{M}(E)\,\vec{\psi} = \vec{0}, \tag{10.21}$$

[19] This procedure is equivalent to setting $\Delta x = \Delta y = 1$, $\hbar = 1$, and $m = 1/2$.

[20] The reader may note the similarities between this problem and the one encountered in Chapter 7 where we discussed the problem of diffusion on a disordered network as well as the one we will treat in Chapter 11 concerning the vibrations of a membrane. More on the numerical aspects of the linear problems are given in Appendix H.

[21] Nevertheless, computing the eigenvalues and eigenvectors of large matrices is usually a formidable task, which can require large amounts of computer time as we will detail later.

where $\vec{0}$ is a column vector whose elements are all zero. Here we have indicated explicitly the fact that the matrix $\mathcal{M}(E)$ is a function of E. In general there will be MN values of E for which this equation has a nontrivial solution.[22] Formally, these eigenvalues are the roots of the algebraic equation

$$\det\left[\mathcal{M}(E)\right] = 0 , \tag{10.22}$$

called the *secular equation*, where the function det[] denotes the determinant of a matrix. Each eigenvalue has an associated eigenvector, which is the wave function for that particular energy level.

This matrix approach is completely general and can be very useful, especially in formal arguments. However, it is often a very large computational task unless the Hamiltonian matrix has a special form that reduces the computational requirements. Since the column or row reduction of the determinant would require of the order of $(MN)!$ operations, a naive estimate of the number of required operations might appear to be an exponential function of the matrix size. Fortunately, there are efficient methods available to reduce it to $O([MN]^3)$ (or even lower if the matrix is of a special form such as *tridiagonal*). Sometimes, an approximate solution is sufficient, allowing us to substitute a matrix of a special form (and often a much smaller one as well), saving a large amount of computing resources. However, in general we are still faced with large computational requirements. For example, if there are 50 grid elements along both m and n in a two-dimensional problem, one must deal with a 2500×2500 matrix. In three dimensions the matrix would be $125{,}000 \times 125{,}000$. While such eigenvalue problems arise in many applications, and efficient programs for carrying out these computations do exist, computing the eigenvalues and eigenvectors of such large matrices is still a formidable task.[23]

We end this section by describing one particularly effective use of the matrix method. This is sometimes called the *power method*, one in which we do *not* explicitly solve for the eigenvalue or the eigenvector, but rely on the repeated application of the $n \times n$ matrix (say, $\mathbf{W}$) on an arbitrary starting trial vector $\vec{u}$ to weed out the contributions to $\vec{u}$ from all but the eigenvector $\vec{u}_1$ with the largest (i.e., "dominant") eigenvalue λ_1. First, let us assume that the eigenvalues are ordered so that $|\lambda_1| > |\lambda_2| \geq |\lambda_3| \geq \ldots \geq |\lambda_n|$, and assume also that the initial state $\vec{u}$ can be represented as a linear combination[24]

$$\vec{u} = \sum_{i=1}^{n} a_i \vec{u}_i , \tag{10.23}$$

where $a_1 \neq 0$ and $\vec{u}_i$ are the eigenvectors with eigenvalues λ_i, so that

$$\mathbf{W}\, \vec{u}_i = \lambda_i\, \vec{u}_i . \tag{10.24}$$

[22] A trivial solution is one for which all of the $\psi(m,n)$ are zero. Note also that because of the boundary conditions on $\vec{\psi}$, the number of solutions may be less than MN.

[23] However, it can be quite useful for quantum problems in which, for some reason, the size of the $\vec{\psi}$ vector (and hence the size of the Hamiltonian matrix) is not too large. Cases of this kind arise, for example, in magnetic problems in which the number of spin (or angular momentum) states is often of order 10 or less.

[24] This is known to be possible for Hermitian matrices such as those representing a physical Hamiltonian.

Applying $\mathbf{W}$ on $\vec{u}$ then gives

$$\mathbf{W}\,\vec{u} = \sum_{i=1}^{n} a_i\,\lambda_i\,\vec{u}_i\,, \tag{10.25}$$

and doing so k consecutive times gives

$$\mathbf{W}^k\,\vec{u} = \sum_{i=1}^{n} a_i\,\lambda_i^k\,\vec{u}_i = \lambda_1^k\left[a_1\vec{u}_1 + \sum_{i=2}^{n} a_i\,(\lambda_i/\lambda_1)^k\,\vec{u}_i\right]. \tag{10.26}$$

Since $|\lambda_i/\lambda_1| < 1$ for $i \neq 1$, all but the first term in the square brackets will decrease in magnitude relative to the first term as $k \to \infty$. Thus, for large k we eventually get

$$\mathbf{W}^k\,\vec{u} \approx a_1\lambda_1^k\vec{u}_1\,, \tag{10.27}$$

and hence $\vec{u}_1$ can be obtained by normalizing $\mathbf{W}^k\,\vec{u}$.

While this method targets the dominant eigenvalue, there are various extensions which are able to find states other than the one with the largest eigenvalue. For example, if we know that there is an upper bound Λ for the magnitudes of the eigenvalues, we can apply the power method to the modified (and shifted) matrix $\Lambda^2\mathbf{I} - \mathbf{W}^2$ and obtain the eigenstate with the eigenvalue of the smallest magnitude (say, the ground state wave function). Alternatively, we can also consider the application of the power method with $\mathbf{W}^{-1}$ if we are interested in the ground state. It turns out that this can be accomplished without actually inverting the matrix first. Similarly, it is possible to use the combinations of shifting and inversion to look for eigenstates with eigenvalues in a neighborhood of values of our choice. Moreover, once an eigenstate and its eigenvalue are obtained by such a method, it is possible to iteratively project out the linear space associated with such states and look for the next most dominant one, and so forth. We will not dwell any further on this method, but it can be a very effective way to obtain a specific state, such as the one with the largest (or the smallest) eigenvalue.

10.4 A VARIATIONAL APPROACH

The computational difficulties with a "direct" matrix approach to eigenvalue problems have motivated the development of a number of alternative schemes. We do not have space to discuss all of them here; the interested reader can explore some of them through the references. In this section we will introduce one of these schemes to give an example of how the Schrödinger equation can be attacked. The method we now describe involves a Monte Carlo approach, similar to that described in Chapter 8, coupled with the variational principle.

The variational principle of quantum mechanics can be expressed as follows. Let φ be a "trial" wave function. We imagine that we are searching for the ground-state solution to the Schrödinger equation for a particular problem and that φ is a proposed wave function, or perhaps our best numerical guess for the true wave function. We can calculate the "energy" corresponding to this trial function

$$E^* \equiv \frac{\int \varphi^*\,\mathcal{H}\,\varphi\,d\vec{r}}{\int \varphi^*\,\varphi\,d\vec{r}}\,, \tag{10.28}$$