Problem 16.4 Bound state solutions of the time-independent Schrödinger equation

(a) Consider the potential energy function defined by

$$V(x) = \begin{cases} 0 & \text{for } -a \le x \le 0 \\ V_0 & \text{for } 0 < x \le a \\ \infty & \text{for } |x| > a. \end{cases} \tag{16.15}$$

As for the infinite square well, the eigenfunction is confined between infinite potential barriers at $x = \pm a$. In addition, there is a step potential at $x = 0$. Choose $a = 5$ and $V_0 = 1$ and run `SchroedingerApp` with an energy of $E = 0.15$. Repeat with an energy of $E = 0.16$. Why can you conclude that an energy eigenvalue is bracketed by these two values?

(b) Choose a strategy for determining the value of E such that the boundary conditions at $x = +a$ are satisfied. Determine the energy eigenvalue to four decimal places. Does your answer depend on the number of points at which the wave function is computed?

(c) Repeat the above procedure starting with energy values of 0.58 and 0.59 and find the energy eigenvalue of the second bound state. ■

If you were persistent in doing all of Problem 16.4, you would have discovered two energy eigenvalues, 0.1505 and 0.5857.

The procedure we used is known as the *shooting* algorithm. The allowed eigenvalues are imposed by the requirement that $\phi_n(x) \to 0$ at the boundaries. Although the shooting algorithm usually yields an eigenvalue solution, we often wish to find specific eigenvalues, such as the eigenvalue $E = 1.1195$ corresponding to the third excited state for the potential in (16.15). Because the energy of a wave function increases as the wavelength decreases, we can order the energy eigenvalues by counting the number of times the corresponding eigenstate crosses the x-axis, that is, by the number of nodes. The ground state eigenstate has no nodes. Why? Why can we order the eigenvalues by the number of nodes? The number of nodes can be used to narrow the energy bracket in the shooting algorithm. For example, if we are searching for the third energy eigenvalue and we observe 5 nodes, then the energy is too large. To find a specific quantum state, we automate the shooting method as follows:

1. Choose a value of the energy E and count the number of nodes.
2. Increase E and repeat step 1 until the number of nodes is equal to the desired number.
3. Decrease E and repeat step 1 until the number of nodes is one less than the desired number. The desired value of the energy eigenvalue is now bracketed. We can further narrow the energy by doing the following:
4. Set the energy to the bracket midpoint.
5. Initialize $\phi(x)$ at the left boundary and iterate $\phi(x)$ toward increasing x until ϕ diverges or until the right boundary is reached.
6. If the quantum number is even (odd) and the last value of $\phi(x)$ in step 4 is negative (positive), then the trial value of E is too large.
7. If the quantum number is even (odd) and the last value of $\phi(x)$ in step 4 is positive (negative), then the trial value of E is too small.

8. Repeat steps 2–7 until the wave function satisfies the right-hand boundary condition to an acceptable tolerance. This procedure is known as a binary search because every repetition decreases the energy bracket by a factor of two.

Problem 16.5 asks you to write a program that finds specific eigenvalues using this procedure.

Problem 16.5 Shooting algorithm

(a) Modify `SchroedingerApp` to find the eigenvalue associated with a given number of nodes. How is the number of nodes related to the quantum number? Test your program for the infinite square well. What is the value of Δx needed to determine E_1 to two decimal places? three decimal places?

(b) Add a method to normalize ϕ. Normalize and display the first five eigenstates.

(c) Find the first five eigenstates and eigenvalues for the potential in (16.15) with $a = 1$ and $V_0 = 1$.

(d) Does your result for E_1 depend on the starting value of $d\phi/dx$? ■

Problem 16.6 Perturbation of the infinite square well

(a) Determine the effect of a small perturbation on the eigenstates and eigenvalues of the infinite square well. Place a small rectangular bump of half-width b and height V_b symmetrically about $x = 0$ (see Figure 16.1). Choose $b \ll a$ and determine how the ground state energy and eigenstate change with V_b and b. What is the relative change in the ground state energy for $V_b = 10$, $b = 0.1$ and $V_b = 20$, $b = 0.1$ with $a = 1$? Let ϕ_0 denote the ground state eigenstate for $b = 0$ and let ϕ_b denote the ground state eigenstate for $b \neq 0$. Compute the value of the overlap integral

$$\int_0^a \phi_b(x)\phi_0(x)\,dx. \tag{16.16}$$

This integral would be unity if the perturbation was not present (and the eigenstate was properly normalized). How is the change in the overlap integral related to the relative change in the energy eigenvalue?

(b) Compute the ground state energy for $V_b = 20$ and $b = 0.05$. How does the value of E_1 compare to that found in part (a) for $V_b = 10$ and $b = 0.1$? ■

Because numerical solutions to the Schrödinger equation grow exponentially if $V(x) - E > 0$, it may not be possible to obtain a numerical solution for $\phi(x)$ that satisfies the boundary conditions if $V(x) - E$ is large over an extended region of space. The reason is that energy can be specified and ϕ can be computed only to finite accuracy. Problem 16.7 shows that we can sometimes solve this problem using simpler boundary conditions if the potential is symmetric. In this case,

$$V(x) = V(-x), \tag{16.17}$$

and $\phi(x)$ can be chosen to have definite parity. For even parity solutions, $\phi(-x) = \phi(x)$; odd parity solutions satisfy $\phi(-x) = -\phi(x)$. The definite parity of $\phi(x)$ allows us to specify