

10

Quantum Eigenvalues; Zero-Finding and Matching

10.1 PROBLEM: BINDING A QUANTUM PARTICLE

Your **problem** in this chapter is to determine whether the rules of quantum mechanics are applicable inside of a nucleus. More specifically, you are told that nuclei contain neutrons and protons (“nucleons”) with mass

$$mc^2 \simeq 940\text{MeV}, \quad (10.1)$$

and that a nucleus has a size of about 2 fm.¹ Your explicit **problem** is to see if these experimental facts are compatible, first, with quantum mechanics and, second, with the observation that there is a typical spacing of several million electron volts (MeV) between the ground and excited states in nuclei.

We will solve this problem in coordinate space. We start with a semi-analytic treatment and then search with an ODE solver. In §16.3, we discuss how to solve the equivalent momentum-space eigenvalue problem as a matrix problem. In Chapter 30, *Confined Electronic Wave Packets*, we study the related (but more complicated) problem of the motion of a quantum wave packet confined to a potential well. Further discussion of the numerical bound-state problem is found in [Schd 87] and [Koon 86]. To broaden your programming experiences, you may want to try out the sample programs on the diskette and the Web.

¹A fm, or fermi, equals 10^{-13} cm, and $\hbar c \simeq 197.32$ MeV fm.

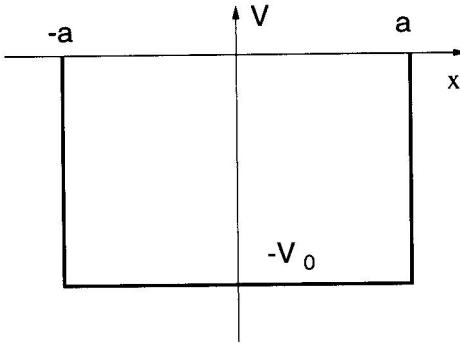


Fig. 10.1 A finite square well potential in one dimension. The depth is V_0 and the radius is a .

10.2 THEORY: QUANTUM WAVES

Quantum mechanics is the theory that describes phenomena at an atomic or subatomic scale of size (a nucleus is subatomic). It is a statistical theory in which the probability that a particle is located in the region of space from x to $x + dx$ is

$$\mathcal{P} = |\psi(x)|^2 dx, \quad (10.2)$$

where $\psi(x)$ is the *wave function*. When a particle is bound, it is in a *stationary state* with an $\exp(-iEt/\hbar)$ time dependence. In that case the wave function is determined by the time-independent form of the Schrödinger equation:²

$$\frac{-\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x), \quad (10.3)$$

where $V(x)$ is the potential experienced by the particle and E is its energy. This is the equation we must solve.

When a particle is bound, it is confined to some finite region of space. In quantum mechanics this means that the probability of finding the particle over all of space must be one,

$$\int_{-\infty}^{\infty} dx |\psi(x)|^2 = 1. \quad (10.4)$$

So, in addition to solving (10.3), we require that $\psi(x)$ also satisfies (10.4). This extra condition turns the quantum bound-state problem into an *eigenvalue problem* in which solutions (*eigenvectors*) exist only for a few values of E (*eigenvalues*).

²The time-dependent equation requires the solution of a partial differential equation, as discussed in Chapter 30, *Confined Electronic Wave Packets*.

10.3 MODEL: PARTICLE IN A BOX

The numerical methods we will be developing are able to handle the most realistic situations. Yet to make a connection with the standard textbook case, and to permit some analytic checking, we will use a simple model in which the potential $V(x)$ in (10.3) is the finite square well pictured in Fig. 10.1:

$$V(x) = \begin{cases} -V_0 = -83\text{MeV}, & \text{for } |x| \leq a = 2 \text{ fm}, \\ 0, & \text{for } |x| > a = 2 \text{ fm}. \end{cases} \quad (10.5)$$

A depth of 83 MeV and radius of 2 fm are typical for nuclei, and therefore this problem will be solved with energies in millions of electron volts and lengths in fermis. The Schrödinger equation (10.3) is now

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E + V_0)\psi(x) = 0, \quad \text{for } |x| \leq a, \quad (10.6)$$

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\psi(x) = 0, \quad \text{for } |x| > a. \quad (10.7)$$

We write the constants in (10.6) with c^2 inserted in both the numerator and the denominator [L 96, Appendix A.1]:

$$\frac{2m}{\hbar^2} = \frac{2mc^2}{(\hbar c)^2} = \frac{2 \times 940\text{MeV}}{(197.32\text{MeV fm})^2} = 0.4829\text{MeV}^{-1}\text{fm}^{-2}. \quad (10.8)$$

10.4 SOLUTION: SEMIANALYTIC

For a general case we would solve (10.6) as an ordinary differential equation (ODE) eigenvalue problem. Before we do that in §10.6, we make connections with the standard textbook treatment of bound states in a square well, and introduce the *bisection algorithm*, which will be useful later.

The general form of the solution in the $|x| > a$ region (the “outer” wave function) depends on the sign of the energy E . If $E > 0$, the outer solution is a trigonometric function. Because a trigonometric function is not normalizable, it cannot meet the confinement requirements we have set on a bound-state wave function, and so there cannot be any $E > 0$ bound states.

If $E < 0$, the possible outer solutions are proportional to $\exp(\pm\beta x)$. Because a decaying exponential can be normalized, we use it to form³ an accept-

³The form of the wave function given in (10.9) corresponds to choosing a positive-parity

able bound-state solution:

$$\psi(x) = \begin{cases} Ce^{\beta x}, & \text{for } -\infty < x < -a, \\ B \cos \alpha x, & \text{for } -a < x < a, \\ Ce^{-\beta x}, & \text{for } a < x < +\infty, \end{cases} \quad (10.9)$$

where

$$\beta = \sqrt{\frac{-2mE}{\hbar^2}} = \sqrt{-0.4829E}, \quad (10.10)$$

$$\alpha = \sqrt{\frac{2m(E + V_0)}{\hbar^2}} = \sqrt{0.4829(E + 83)}, \quad (10.11)$$

and where energies are in MeV and are negative for bound states.

One way to solve our problem is to forget about a possible negative x solution and construct ψ to be symmetric about $x = 0$. We do not impose that symmetry externally, but rather solve for the wave function for both positive and negative x values, and then use the symmetry as a check.

In order for probability and current to be continuous at the edge of the well $x = \pm a$, the wave function and its first derivative must be continuous there. This demands that

$$B \cos \alpha a = Ce^{-\beta a}, \quad (10.12)$$

$$-\alpha B \sin \alpha a = -\beta C e^{-\beta a}. \quad (10.13)$$

We remove the dependence on the normalization constants B and C by dividing these equations by each other:

$$\alpha a \tan \alpha a - \beta a = 0. \quad (10.14)$$

If we substitute for α and β , it becomes clear that (10.14) is a transcendental equation in the variable E :

$$\sqrt{2m(E + V_0)} \tan \sqrt{\frac{2m(E + V_0)}{\hbar^2}} a - \sqrt{-2mE} = 0. \quad (10.15)$$

The transcendental equation (10.15) has solutions only for certain values of E , the eigenvalues. In general, it can be solved only by numerical techniques. A classic way of finding solutions of (10.15) starts by converting it to an

wave function; that is, one that is symmetric about the origin. We make that choice because we are interested in the lowest energy states and they are usually the ones with the fewest wiggles.

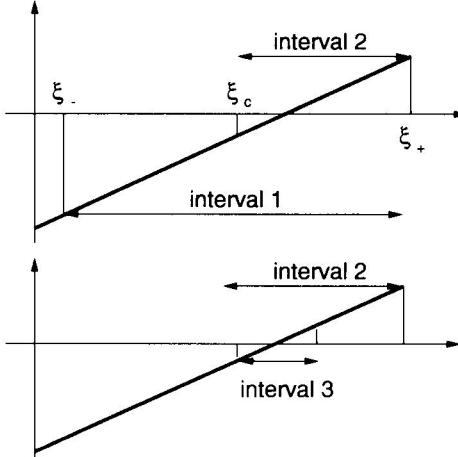


Fig. 10.2 The approximate behavior of the function $f(\xi)$ near its zero. The center point ξ_c is the approximate value of the root. The figure assumes that $f(\xi_+) > 0$ and that $f(\xi_-) < 0$, but only the relative sign matters. Observe how interval 3, resulting from the second iteration, is smaller than interval 2, resulting from the first iteration.

equation in dimensionless variables:

$$\xi \tan \xi - \eta = 0, \quad (10.16)$$

where

$$\xi = \alpha a, \quad \eta = \beta a, \quad (10.17)$$

$$\xi^2 + \eta^2 = \frac{2mV_0a^2}{\hbar^2} = 16.083. \quad (10.18)$$

We then look for a zero or root of the function $f(\xi)$:

$$f(\xi) = \xi \tan \xi - \eta = 0. \quad (10.19)$$

If $\xi \tan \xi$ and η are plotted as functions of ξ , the solutions of (10.19) are the intersections of the two curves. Alternatively, one can sit down with a calculator, evaluate $f(\xi = 0)$, and increase ξ in small steps until $f(\xi)$ is found to change signs. The locations of the sign changes are the zeros. In this way we found the approximate eigenvalues $\xi \approx 1.25$, and $\xi \approx 3.6$. You may check these with your calculator. To determine the eigenvalues more precisely, we use the bisection algorithm described next.

10.5 METHOD: FINDING ZERO VIA THE BISECTION ALGORITHM

The bisection algorithm, illustrated in Fig. 10.2, is a simple and reliable way to find a root of the equation $f(\xi) = 0$; it may also be the slowest. We assume that we have an interval, $\xi_- < \xi < \xi_+$, in which $f(\xi)$ changes sign; that is, for which

$$f(\xi_-)f(\xi_+) < 0. \quad (10.20)$$

The bisection algorithm keeps checking that the condition (10.20) is satisfied for ever closer values of ξ_- and ξ_+ , and quits when the difference in ξ_- and ξ_+ is smaller than some tolerance ϵ . At that point we say that we have a solution. (The intermediate-value theorem of calculus guarantees that a solution must exist in the interval.) Explicitly, we define the center of the interval

$$\xi_c = \frac{1}{2}(\xi_- + \xi_+), \quad (10.21)$$

and use ξ_c as a trial root:

$$\text{if } f(\xi_c)f(\xi_+) < 0, \quad \begin{cases} \text{then } \xi_- = \xi_c, \\ \text{else } \xi_+ = \xi_c. \end{cases} \quad (10.22)$$

The process is continued, dividing the interval in half and analyzing which side the root is on until $|\xi_- - \xi_+| < \epsilon$.

10.6 METHOD: EIGENVALUES FROM AN ODE SOLVER

For more realistic potentials we would not be able to analytically solve the Schrödinger equation, but instead we would have to use an ODE solver to obtain a numerical wave function. In that case we would start with a guess for the energy. Then, as shown in Fig. 10.3, see how well the inner and outer wave functions match, and then guess a new energy. After two guesses for the energy we would use the bisection algorithm to predict an energy at which the wave functions match. The process continues until the difference in energy falls within some tolerance.

Generally, as discussed in Chapter 9, *Differential Equations and Oscillations*, we recommend the fourth-order Runge–Kutta method for solving ODEs. For the present eigenvalue problem we will use the *Numerov method* that is specialized for those ODEs not containing any first derivatives (the Schrödinger equation is such an equation). This algorithm provides one order more of accuracy than fourth-order Runge–Kutta, and does so with fewer computations (no partial steps). Nonetheless, it is not as general.

We start by rewriting the Schrödinger equation (10.6) as

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi = 0, \quad (10.23)$$

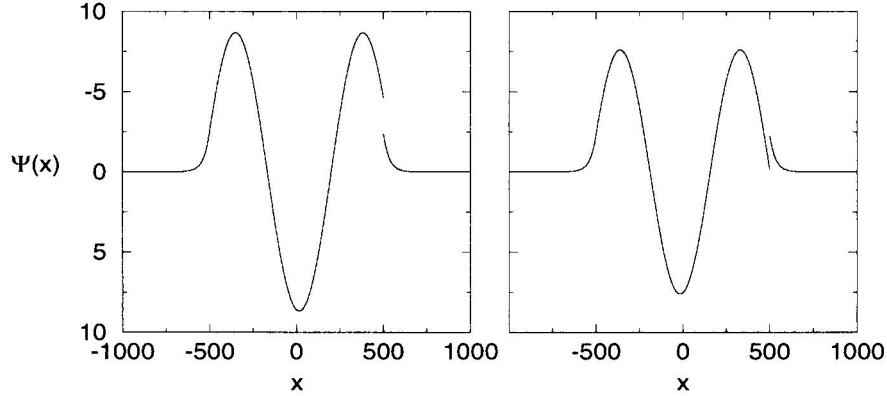


Fig. 10.3 (Left) A first guess at a wave function with an energy E that is 0.5% too low. We see that the left wave function does not vary rapidly enough to match the right one at $x = 500$. (Right) A second guess at a wave function with an energy E that is 0.5% too high. We see that, now, the left wave function varies too rapidly.

$$k^2(x) \stackrel{\text{def}}{=} \frac{2m}{\hbar^2} \begin{cases} E + V_0, & \text{for } |x| < a, \\ E, & \text{for } |x| > a. \end{cases} \quad (10.24)$$

We remind the student that $E < 0$ for bound states, and that in our units, $2m/\hbar^2 = 0.4829$. Observe that the present functional form for $k^2(x)$ (10.24) is for a square well, but it can be generalized for a realistic potential. As usual, the algorithm integrates (10.23) for a single interval $x \rightarrow x + h$, in which the potential is assumed constant. The process is repeated until a wave function throughout all of space is found.

The trick in the Numerov method is to get an extra order of precision in the second derivative. We start with the Taylor expansion of the wave function,

$$\psi(x+h) = \psi(x) + h\psi^{(1)}(x) + \frac{h^2}{2}\psi^{(2)}(x) + \frac{h^3}{3!}\psi^{(3)}(x) + \frac{h^4}{4!}\psi^{(4)}(x) + \dots, \quad (10.25)$$

where $\psi^{(n)}$ is used as shorthand for the n th derivative $d^n\psi/dx^n$. Because the corresponding Taylor expansion of $\psi(x-h)$ has odd powers of h appearing with negative signs, all odd powers cancel when we add $\psi(x+h)$ and $\psi(x-h)$:

$$\psi(h+h) + \psi(x-h) \simeq 2\psi(x) + h^2\psi^{(2)}(x) + \frac{h^4}{12}\psi^{(4)}(x) + \mathcal{O}(h^6). \quad (10.26)$$

We bring the $\psi^{(2)}$ term to the LHS to obtain a three-point algorithm for the second derivative:

$$\psi^{(2)}(x) \simeq \frac{\psi(x+h) + \psi(x-h) - 2\psi(x)}{h^2} - \frac{h^2}{12}\psi^{(4)}(x) + \mathcal{O}(h^6). \quad (10.27)$$

To eliminate fourth-derivative errors in the algorithm, we now apply the operator $1 + \frac{h^2}{12} \frac{d^2}{dx^2}$ to the Schrödinger equation (10.23) to obtain a modified Schrödinger equation:

$$\psi^{(2)}(x) + \frac{h^2}{12} \psi^{(4)}(x) + k^2(x)\psi + \frac{h^2}{12} \frac{d^2}{dx^2}[k^2(x)\psi^{(4)}(x)] = 0, \quad (10.28)$$

where the x dependence in $k^2(x)$ permits general potentials. Next we substitute the approximate expression for the second derivative (10.27) to obtain

$$\begin{aligned} & \frac{\psi(x+h) + \psi(x-h) - 2\psi(x)}{h^2} \\ & - \frac{h^2}{12} \psi^{(4)}(x) + \frac{h^2}{12} \psi^{(4)}(x) + k^2(x)\psi(x) + \frac{h^2}{12} \frac{d^2}{dx^2}[k^2(x)\psi(x)] \simeq 0. \end{aligned} \quad (10.29)$$

We see that the $\psi^{(4)}$ terms now cancel each other, which means that the error is $\mathcal{O}(h^6)$.

To handle the general x dependence of k^2 , we approximate⁴ the second derivative of $k^2(x)\psi(x)$ as

$$\begin{aligned} & \frac{d^2[k^2(x)\psi(x)]}{dx^2} \simeq \\ & \frac{[k^2(x+h)\psi(x+h) - k^2(x)\psi(x)] + [k^2(x-h)\psi(x-h) - k^2(x)\psi(x)]}{h^2}. \end{aligned} \quad (10.30)$$

After making a substitution, we obtain our algorithm:

$$\psi(x+h) \simeq \frac{2 \left[(1 - \frac{5}{12} h^2 k^2(x)) \psi(x) - \left(1 + \frac{h^2}{12} k^2(x-h) \right) \psi(x-h) \right]}{1 + \frac{h^2}{12} k^2(x+h)}. \quad (10.31)$$

This uses the values of ψ at two previous steps to move ψ forward one step (to step backward in x , we only need to reverse the sign of h). In terms of discrete indices, $x = ih$, the algorithm is simply

$$\psi_{i+1} \simeq \frac{2 \left(1 - \frac{5}{12} h^2 k_i^2 \right) \psi_i - \left(1 + \frac{h^2}{12} k_{i-1}^2 \right) \psi_{i-1}}{1 + \frac{h^2}{12} k_{i+1}^2}. \quad (10.32)$$

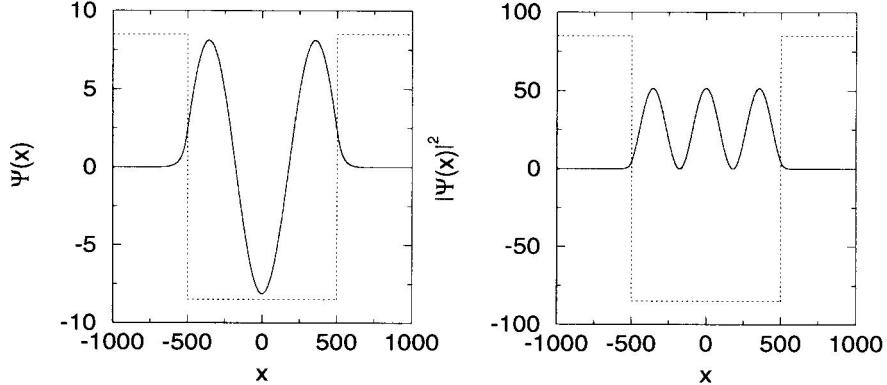


Fig. 10.4 (Left) The eigenfunction after the eigenenergy was found. The dashed curve shows the potential well. Observe the perfect symmetry. (Right) The probability density for this eigenfunction is clearly confined to the well.

10.6.1 Matching

The bound-state problem adds the extra requirement that the solution at large $|x|$ be the decaying exponential $\exp(-\beta|x|)$. We numerically impose that by integrating the ODE, starting at large positive x with $\psi = \exp(-\beta x)$, and then stepping inward (to the left) one h at a time. Next, we integrate the ODE, starting at large negative x with $\psi = \exp(\beta x)$, and step inward (to the right) one h at a time. At some arbitrary value of x , the *matching radius*, we test to see if the left and right values for ψ and $d\psi/dx$ agree and apply the bisection algorithm. When they agree, we have a solution.

Because the overall normalization of the wave function is arbitrary, there is really only one condition we must meet at the matching radius. Most usually, the normalization constraint is removed by requiring continuity of the logarithmic derivative ψ'/ψ . But in our case, we start with perfectly symmetric starting wave functions of the same magnitude on the right and left, and so we need to match only their magnitudes. If they do match, so will their derivatives.

The first two steps in the matching is shown in Fig. 10.3, and the final wave function is shown in Fig. 10.4. In this case, the wave function has a node, which means that it is an excited state rather than the ground state. To find the ground state, we lowered the energy at which we started the search.

10.7 IMPLEMENTATION: ODE EIGENVALUES, NUMEROV.C

1. Start with a step size $h = 0.04$. This means that there are 200 steps in the interval $x_{\min} = -4 \leq x \leq x_{\max} = 4$. Your ψ will be then an array of dimension 200, with the $i = 0, 1, \dots$ elements representing the wave function to the left ψ_l , and the $i = 200, 199, \dots$ elements representing ψ_r . (You will need to store separately the left and right values of the wave function at the matching radius.)
2. Write a subroutine which calculates the matching function

$$f(E, x) = \frac{\psi_l(x - h) - \psi_r(x - h)}{\psi_l(x)} \quad (10.33)$$

as a function of energy and matching radius. This subroutine will be called by the bisection algorithm program to search for the energy at which $f(E, x = 2)$ vanishes.

3. As a first guess, take

$$E \simeq \xi^2 \frac{\hbar^2 c^2}{2mc^2 a^2} \simeq (3.6)^2 \frac{(197.32 \text{MeV fm})^2}{2 \times 940 \text{MeV2(fm)}^2} \simeq 65 \text{MeV}. \quad (10.34)$$

4. Determine the left and right wave functions by integrating the Schrödinger equation and using the Numerov algorithm (10.32). Start with

$$\psi_l \equiv \psi_{i=0} = \psi(x_{\min}) = e^{\beta(-4)}, \quad \psi_1 = e^{\beta(-4+h)}, \quad (10.35)$$

$$\psi_r \equiv \psi_{200} = \psi(x_{\max}) = e^{\beta(-4)}, \quad \psi_{199} = e^{\beta(-4+h)}. \quad (10.36)$$

5. Continue the step-by-step integration to $x_m = -2$ where you will match wave functions.
6. Renormalize the wave function so the left and right values match at x_m .
7. Write a main program that calls your subroutine for different energies (say, within $\pm 15\%$ of your energy guess). Then use the bisection algorithm to zero in on the eigenenergy.
8. Print out the value of the energy for each iteration. This will give you a feel as to how well the procedure converges, as well as a measure of the precision obtained. Try different values for the tolerance until you are confident that you are obtaining three good decimal places in the energy.
9. Build in a limit to the number of energy iterations you permit, and print out (emphatically) when the iteration scheme fails.

10. Check that your computation is a solution of the transcendental equation (10.15).
11. Have you solved the **problem**? Is the spacing between levels on the order of MeV for a nucleon bound in a several-fm well?

10.8 ASSESSMENT: EXPLORATIONS

1. Check to see how well your search procedure works by using arbitrary values for the starting energy. For example, because no bound-state energies can lie below the bottom of the well, try $E = -V_0$ as well as some arbitrary fractions of V_0 . In every case examine the resulting wave function and check that it is both symmetric and continuous.
2. Increase the depth of your potential progressively until you have three or four bound states. Look at the wave function in each case and determine the relation between the number of nodes in the wave function and the position of the bound state in the well.
3. Explore how a bound-state energy changes as you change the depth V_0 of the well. In particular, as you keep decreasing the depth, watch the eigenenergy move closer to $E = 0$, and see if you can find the depth at which the bound state just exists.
4. For a fixed well depth V_0 , explore how the energy of a bound state changes as the well radius a is varied.
5. Conduct some explorations in which you discover different values of (V_0, a) that give the same ground-state energies. The existence of several different combinations means that knowledge of a ground-state energy is not enough to determine a unique depth of the well.
6. Modify the procedures to solve for the eigenvalue and eigenfunction for odd wave functions.
7. Solve for the wave function of a linear potential:

$$V(x) = -V_0 \begin{cases} |x|, & \text{for } |x| < a, \\ 0, & \text{for } |x| > a. \end{cases} \quad (10.37)$$

There is less potential than for a square well, so you may expect lower binding energies and a less-confined wave function. (There are no analytic results with which to compare.)