```
         call color( white )
         call line(x_fixed,y_fixed,x_bob,y_bob)
          ...
*        < Do another time step?  or else?  >
          ...
```

Note that a line is displayed on the screen while a new `theta` is being calculated. Then, in quick succession, the old line is redrawn with the background color (hence erasing it) and the new line is drawn with the color set to white. For the animation to simulate the motion of the pendulum accurately, we would need to ensure that the lines are redrawn/drawn at a constant rate, perhaps by adding a timing loop to the code. But for purposes of illustration, it's sufficient to modify the code to use a fixed step size (in time). This time step should be small enough to maintain the accuracy of the calculation. If you find that the animation proceeds too rapidly, you can further decrease the step size and update the display only after several steps have been taken.

EXERCISE 5.13

Animate your pendulum.

Another Little Quantum Mechanics Problem

Way back in Chapter 2 we discussed the one-dimensional Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\,{}^{\psi(x)}_{\wedge} = E\psi(x), \tag{5.68}$$

and found solutions for the problem of an electron in a finite square well. Those solutions were facilitated by knowing the analytic solutions for the different regions of the potential. Well, that was then, and this is now!

Let's imagine a different physical problem, that of an electron bound in the anharmonic potential

$$V(x) = \alpha x^2 + \beta x^4, \tag{5.69}$$

where α and β are constants. In a qualitative sense, the solutions to this problem must be similar to those for the finite square well; that is, an oscillatory solution between the classical turning points, and a decaying solution as you move into the forbidden region. The sought-for solution should look something like Figure 5.7.

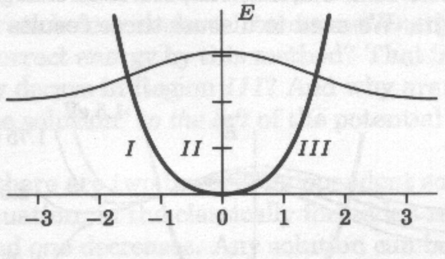


FIGURE 5.7 The anharmonic potential $V(x) = 0.5x^2 + 0.25x^4$, and its least energetic eigenfunction.

The computer code you presently have should work just fine, except for one small problem: what are the initial conditions? In this problem, you don't have them! Rather, you have *boundary conditions*. That is, instead of knowing ψ and $d\psi/dx$ at some specific point, you know how ψ should behave as $x \to \pm\infty$. That's a little different, and takes some getting used to.

There are various ways this difficulty can be overcome, or at least circumvented. For the immediate problem, we can simply *guess* initial conditions and observe their consequences. Deep in Region I, we know that ψ should be small but increasing as x increases; let's guess that

$$\psi(x_0) = 0,$$

and

$$\psi'(x_0) = \psi'_0, \tag{5.70}$$

where ψ'_0 is a positive number. We can then make an initial guess for the energy E, and "solve" the differential equation using the Runge–Kutta–Fehlberg integrator. Plotting the solution, we can see how good our guess for the energy was.

Before we can do the calculation, however, we need specific values for the constants. As noted earlier, the computer deals with pure numbers only, and not units, so that we need to exercise some care. Using an appropriate system of units is extremely advantageous. For example, the mass of the electron is 9.11×10^{-31} kilograms, but it's far more convenient, and less prone to error, to use a system of units in which the mass of the electron is defined as being 1. Using electron volts for energy and Angstroms for distance, we have

$$\hbar^2 = 7.6199682\, m_e\, \mathrm{eV}\, \mathrm{\AA}^2. \tag{5.71}$$

We'll take $\alpha = 0.5\ \mathrm{eV}\,\mathrm{\AA}^{-2}$, and $\beta = 0.25\ \mathrm{eV}\,\mathrm{\AA}^{-4}$. And to start the integration, we'll take $x_0 = -5\ \mathrm{\AA}$, $\psi'_0 = 1 \times 10^{-5}$, and let `EPSILON` $= 1 \times 10^{-5}$. Figure 5.8

contains the results of such calculations, for trial energies of 1.5, 1.75, 2.0, and 2.25 electron volts. We need to discuss these results in some detail.

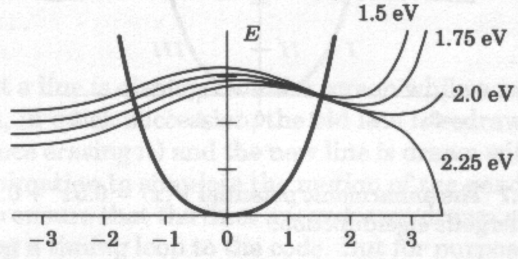


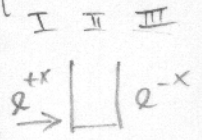
FIGURE 5.8 Numerical solutions of the anharmonic potential for trial energies of 1.5, 1.75, 2.0, and 2.25 electron volts. The numerical solution must satisfy the boundary conditions to be physically acceptable.

Consider the first trial energy attempted, 1.5 electron volts. In Region *I*, where the integration begins, the solution has the correct general shape, decreasing "exponentially" as it penetrates the barrier. In the classically allowed region the solution has a cosine-like behavior, as we would expect. But the behavior to the right of the well is clearly incorrect, with the solution becoming very large instead of very small. Recall that in this region there are two mathematically permitted solutions: one that is increasing, and one that is decreasing; it is on the basis of our *physical* understanding that only the decreasing one is permitted. But of course, our trial energy is not the correct energy, it's only a first guess, and a rather poor one at that, as evidenced by the poor behavior of the solution. Recall that we want to find that energy which leads to a strictly decaying solution in this region.

Let's try another energy, say, 1.75 electron volts. The behavior of the numerical solution is much as before, including a rapid increase to the right of the potential well. However, the onset of this rapid increase has been postponed until farther into the barrier, so that it is a better solution than we had previously. Let's try again: at 2.0 electron volts, the onset is delayed even further. We're coming closer and closer to the correct energy, finding solutions with smaller amounts of the increasing solution in them. So we try again, but as shown in the figure, we get a quite different behavior of the solution for 2.25 electron volts: instead of becoming very large and positive, it becomes very large and negative!

What has happened, of course, is that our trial energy has gotten too large. The correct energy, yielding a wavefunction that tends toward zero at large x, is between 2 and 2.25 electron volts, and we see a drastic change in behavior as we go from below to above the correct energy. But can we ever expect to find that correct energy by this method? That is, can we ever find a solution that strictly decays in Region III? And why aren't we seeing any of this "explosion of the solution" *to the left* of the potential well?

Recall that there are two linearly independent solutions to a second-order differential equation; in the classically forbidden region, one of the solutions increases, and one decreases. Any solution can be written as a linear combination of these two: what we want is that *specific* solution which has the coefficient of the increasing solution exactly equal to zero. As the trial energy comes closer to the correct energy, that coefficient decreases — but we saw that our numerical solution always "blew up" at some point. Why? Although the coefficient is small, it's multiplying a function that is *increasing* as x increases — no matter how small the coefficient, as long as it is not *exactly* zero, there will come a point where this coefficient times the increasing function will be larger than the desired function, which is *decreasing*, and the numerical solution will "explode"! Why wasn't this behavior seen in Region I? In that region, the sought-after solution was *increasing*, not decreasing — the contribution from the nonphysical function was *decreasing* as the integration proceeded out of the classically forbidden region. In Region I, we integrated in the direction such that the unwanted contribution vanished, while in Region III, we integrated in the direction such that the unwanted solution *overwhelmed* our desired one. ***We integrated in the wrong direction!***



Always propagate the numerical solution in the same direction as the physically meaningful solution increases.

The cure for our disease is obvious: we need always to begin the integration in a classically forbidden region, and integrate toward a classically allowed region. In the case of the potential well, we'll have two solutions, integrated from the left and right, and require that they match up properly in the middle. For symmetric potentials, such as the anharmonic potential we've been discussing, the situation is particularly simple since the solutions must be either even or odd: the even solutions have a zero derivative at $x = 0$, and the odd solutions must have the wavefunction zero at $x = 0$. It looks like we're almost ready to solve the problem.

But there are a couple of loose ends remaining. What about the choice of ψ_0'? Doesn't that make any difference at all? Well it does, but not much. With a different numerical value of ψ_0' we would be lead to a different numerical solution, but one with exactly the same validity as the first, and only differing from it by an overall multiplicative factor. For example, if $\psi(x)$ is a solution, so is $5\,\psi(x)$. This ambiguity can be removed by normalizing the wavefunction, e.g., requiring that

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,dx = 1. \tag{5.72}$$

(We note that even then there remains an uncertainty in the overall phase of the wavefunction. That is, if ψ is a normalized solution, so is $i\psi$. For the bound state problem discussed here, however, the wavefunction can be taken to be real, and the complex conjugate indicated in the integral is unnecessary.) For our eigenvalue search, there's an even simpler approach. Since the *ratio* of ψ' to ψ eliminates any multiplicative factors, instead of searching for the zero of $\psi(0)$ we can search for the zero of the *logarithmic derivative*, and require

$$\left.\frac{\psi'(x,E)}{\psi(x,E)}\right|_{x=0} = 0 \tag{5.73}$$

for the eigenvalue E. (For the odd states, we'd want to find the zero of inverse of the logarithmic derivative, of course.)

Now, we're almost done; all that remains is to ensure that the calculation is accurate. If a (poor) choice of the tolerance yields 5 significant digits in the Runge–Kutta–Fehlberg integration, for example, then it's meaningless to try to find the root of the logarithmic derivative to 8 significant places. The overall accuracy can never be greater than the least accurate step in the calculation. We also need to verify that the x_0 is "deep enough" in the forbidden region that the eigenvalue doesn't depend upon its value.

EXERCISE 5.14

Find the lowest three eigenvalues, two even and one odd, of the anharmonic potential $V(x) = 0.5x^2 + 0.25x^4$, and plot the potential and the eigenfunctions. Discuss the measures you've taken to ensure 8-significant-digit accuracy in the eigenvalues.

We should not leave you with the impression that all the problems of quantum mechanics involve symmetric potentials — quite the contrary is true. Symmetry is a terrifically useful characteristic, and should be exploited whenever present. But the more usual situation is the one in which the potential is *not* symmetric. For example, let's consider the force between two atoms. When they are far apart, the electrons of one atom interact with the electrons and nucleus of the other atom, giving rise to an attractive force, the *van der Waals attraction*. But as the distance between the atoms becomes very small, the force becomes repulsive as the nuclei (or the ionic core in many-electron atoms) interact with one another. Thus the general shape of the potential must be repulsive at small distances and attractive at large ones, necessitating an energy minimum somewhere in the middle. As an example, the potential energy curve for the hydrogen molecule is presented in Figure 5.9.

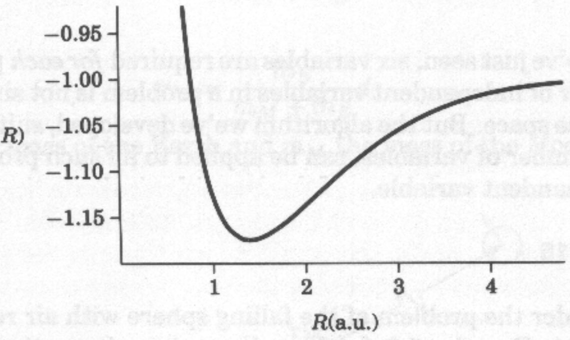


FIGURE 5.9 The ground state potential for molecular hydrogen. Energies are expressed in Hartree (≈ 27.2 eV) and distances in Bohr (≈ 0.529 Å). (Data taken from W. Kolos and L. Wolniewicz, "Potential-Energy Curves for the $X^1\Sigma_g^+$, $b^3\Sigma_u^+$, and $C^1\Pi_u$ States of the Hydrogen Molecule," *Journal of Chemical Physics* **43**, 2429, 1965.)

Clearly, the potential is not symmetric. And since it *is not* symmetric, the eigenfunctions *are not* purely even or odd functions. Still, the method of solution is essentially the same as before: choose a *matching point*, say, near the minimum of the potential well. Then, beginning far to the left, integrate to the matching point; beginning far to the right, integrate to the matching point; and compare the logarithmic derivatives at the matching point.

Several Dependent Variables

We've seen that the solution of a second-order differential equation can be transformed into the solution of two, first-order differential equations. Regarding these equations as components of a vector, we were able to develop a computer code to solve the problem. This code can easily be extended in another direction, to problems having several dependent variables.

For example, to describe the motion of a particle in space we need the