Quantum Bound States

Today we will study the quantum mechanical bound states corresponding to two potential wells. Instead of solving this problem using the shooting or matching method, as was done last week, we will treat the situation as an eigenvalue problem and use Python to solve it. This is a much more robust way to solve this kind of problem. The general form of the one-dimensional, time-independent Schrödinger's equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \tag{1}$$

[2] where $V(x)$ is the potential experienced by the particle(s) in question. Let's consider the problem of a particle in a one-dimensional harmonic oscillator well ($V(x) = \frac{1}{2}kx^2$). Schrödinger's equation for this situation is:

[2] This is the time-independent Schrödinger equation. To determine how a particle behaves over time requires a solution to the time-dependent version.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \tag{2}$$

with boundary conditions $\psi = 0$ at $x = \pm\infty$. A full analytic solution (paper and pencil solution) to this problem would take the discussion too far astray. We'll just need to remember that the allowed energies for this potential are given by

$$E_n = (n + \frac{1}{2})\hbar\sqrt{\frac{k}{m}} \tag{3}$$

Later when we obtain the numerical results we'll want to compare them to the well-know exact answer here.

A numerical solution

For now we'll start down the path of solving this equation numerically. First, notice that the numbers involved in equation (2) are extremely small ($\hbar = 1.054 \times 10^{-34}$ m^2 kg/ s, $m_{\text{electron}} = 9.109 \times 10^{-31}$ kg, etc) and the typical grid sizes that we have been using (2,5,10, etc) will most certainly not be appropriate for this problem (10^{-10} m). We could just set $\hbar$, m, and k to 1, but then we would lose all information about the specific physical situation being studied. Instead of trying to shrink our domain down to appropriate atomic scales, a better approach is to rescale the differential equation so that all of the small numbers go away. This also makes the problem more general, allowing the obtained results to work for any values of m and k.

P1.1 This probably seems a little nebulous(unclear), so follow the recipe below to see how to rescale equation (2) (write it out on paper).

1. In equation (2) use the substitution $x = a\xi$, where a has units of length and ξ is dimensionless. After making this substitution put Schrödinger's equation in the following form (Note: Think carefully about changing $\frac{d^2\psi}{dx^2} \rightarrow \frac{d^2\psi}{d\xi^2}$. The chain rule will be your friend!)

$$C\left(-\frac{D}{2}\frac{d^2\psi}{d\xi^2} + \frac{1}{2}\xi^2\psi\right) = E\psi \tag{4}$$

   where C and D involve the factors $\hbar$, m, k, and a.

2. Make the differential operator inside the parenthesis $(\ldots)$ on the left be as simple as possible by choosing $D = 1$. This choice will allow you to write down a relationship between the characteristic length a and $\hbar$, m, and k. Once you have determined a in this way, check that it has units of length. You should find that

$$a = \left(\frac{\hbar^2}{km}\right)^{1/4} = \sqrt{\frac{\hbar}{m\omega}} \quad \text{where} \quad \omega = \sqrt{\frac{k}{m}} \tag{5}$$

3. Now rescale the energy by writing $E = \epsilon\bar{E}$ where $\bar{E}$ has units of energy and ϵ is unitless. Show that if you choose $\bar{E} = C$ that (2) becomes the following dimensionless equation

$$-\frac{1}{2}\frac{d^2\psi}{d\xi^2} + \frac{1}{2}\xi^2\psi = \epsilon\psi \tag{6}$$

   You should find that

$$\bar{E} = \hbar\sqrt{\frac{k}{m}} \tag{7}$$

   Verify that $\bar{E}$ has units of energy.

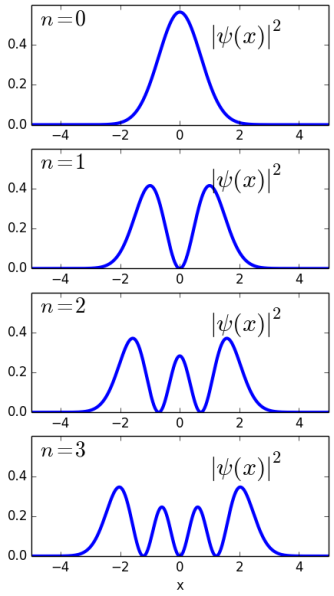

Figure 1: The probability distribution for the ground state and the first three excited states of of the harmonic oscillator.

Now that Schrödinger's equation is in a unitless form, it makes sense to choose a grid that goes from -5 to 5 , or some other similar pair of numbers. These numbers are suppose to approximate infinity in this problem, so make sure (by looking at the eigenfunctions) that they are large enough that the wave function goes to zero with zero slope at these locations.

Comparing equation (3) to equation (7) we see that our unitless energies are now given by:

$$\epsilon_n = n + \frac{1}{2} \tag{8}$$

[3]

With our attention now turned to solving equation (6), we need to write a finite-difference version of the second derivative. The centered-difference version is always the best choice and that's what we'll use here

[3] To undo the rescaling and arrive at the true eigenvalues, you can simply plug in chosen values for m and k into the rescaling equations (Eq. (7)).

$$\psi''(\xi) = \frac{\psi(\xi+h) - 2\psi(\xi) + \psi(\xi-h)}{h^2} \tag{9}$$

Inserting this equation into Eq. (6) gives:

$$-\frac{1}{2}\frac{\psi(\xi+h) - 2\psi(\xi) + \psi(\xi-h)}{h^2} + \frac{1}{2}\xi^2\psi(\xi) = \epsilon\psi(\xi) \tag{10}$$

simplify and switching to index notation

$$\frac{-\psi_{j+1} + 2\psi_j - \psi_{j-1}}{2h^2} + \frac{1}{2}\xi^2\psi_j = \epsilon\psi_j \tag{11}$$

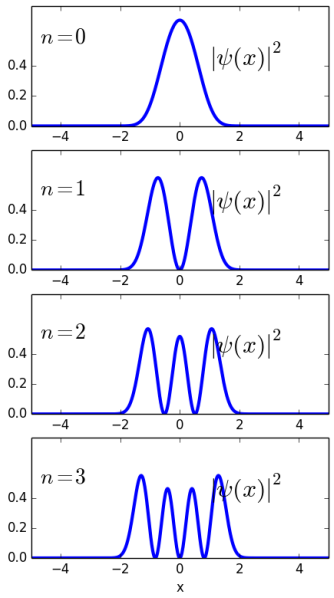

Figure 2: The probabililty distribution for the ground state and the first three excited states for the potential $V(x) = \mu x^4$.

P1.2 Notice that equation (11) is not a single equation but rather a family of equations. Read that last sentence again. If you need help understanding, call someone over to talk it out with you. Once you understand, write down an explanation that might help you if you ever need to remember this. Write down 2 or 3 of these equations. Here are two that I chose

$$-\frac{1}{2h^2}\psi_1 + (\frac{1}{h^2} + \frac{1}{2}\xi^2)\psi_2 - \frac{1}{2h^2}\psi_3 = \epsilon\psi_2 \tag{12}$$

$$-\frac{1}{2h^2}\psi_2 + (\frac{1}{h^2} + \frac{1}{2}\xi^2)\psi_3 - \frac{1}{2h^2}\psi_4 = \epsilon\psi_3 \tag{13}$$

In linear algebra you should have learned that a system of linear equations can be neatly expressed in matrix form. For this particular problem that would look like

$$\boldsymbol{A\psi} = \epsilon\boldsymbol{B\psi} \tag{14}$$

which is written out as

$$\begin{bmatrix} 1 & 0 & 0 & \dots & 0 & 0 \\ -\frac{1}{2h^2} & (\frac{1}{h^2}+\frac{1}{2}\xi^2) & -\frac{1}{2h^2} & \dots & 0 & 0 \\ 0 & -\frac{1}{2h^2} & (\frac{1}{h^2}+\frac{1}{2}\xi^2) & \dots & 0 & 0 \\ . & . & . & \dots & . & . \\ . & . & . & \dots & . & . \\ . & . & . & \dots & . & . \\ 0 & 0 & 0 & \dots & (\frac{1}{h^2}+\frac{1}{2}\xi^2) & -\frac{1}{2h^2} \\ 0 & 0 & 0 & \dots & 0 & 1 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ . \\ . \\ . \\ \psi_{N-1} \\ \psi_N \end{bmatrix} = \epsilon \begin{bmatrix} 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & 1 & 0 & \dots & 0 & 0 \\ 0 & 0 & 1 & \dots & 0 & 0 \\ . & . & . & \dots & . & . \\ . & . & . & \dots & . & . \\ . & . & . & \dots & . & . \\ 0 & 0 & 0 & \dots & 1 & 0 \\ 0 & 0 & 0 & \dots & 0 & 0 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ . \\ . \\ . \\ \psi_{N-1} \\ \psi_N \end{bmatrix}$$

This is called a generalized eigenvalue problem[4] and it can be solved easily in python.You may be wondering about the first and last rows of matrix $\boldsymbol{A}$ as well as why we needed matrix $\boldsymbol{B}$ at all. First notice that equation (11) can't be written down when $j = 1$ or when $j = N$ because we would have to step off of the grid to the left or the right to evaluate equation (11). Equation (11) can only be written down for $1 < j < N$. Excluding those

[4] You should have seen this in Math 316

two points on our grid would make $N-2$ equations with N unknowns to solve for. In other words, there would be more unknowns than equations and the system wouldn't be solvable.[5] Luckily, we do have two more equations to add to the system: the boundary conditions. Remember that $\psi = 0$ for $x = \pm\infty$. Our grid does not extend to $\pm\infty$ but it should extend far enough that we expect ψ to be zero. The top and bottom row of matrix $\boldsymbol{A}$ as well as matrix $\boldsymbol{B}$ are used to enforce the boundary conditions.

[5] The linear algebra term for this situation is "underdetermined"

P1.3

1. Take a second to convince yourself that the matrix equation above is really the same thing as equation (11).
2. Look at the first and last row and convince yourself that they are enforcing the boundary conditions that $\psi(\pm\infty) = 0$. Can you see the need for matrix $\boldsymbol{B}$ now? What would those boundary conditions look like if $\boldsymbol{B}$ was not there? Take time to understand these questions and answer them in your lab notebook before moving on.

Now that all of the paper and pencil work is done, we are ready to build a program to solve this problem.

P1.4
(i)Start by initializing some variables that you'll need:

1. Number of grid points.
2. Domain end points. You may need to experiment with these. You'll want to make sure that your wave functions go to zero with zero slope at the domain boundaries. If they don't, you should extend them.
3. Step size. This can be calculated from the number of grid points and the domain definition defined above.
4. A list (or numpy array) that holds the location of the grid points. linspace is a good choice for this. After you create this array you'll want to ensure that your step size agrees with the actual spacing in your domain list. Print your domain list and your step size to verify and modify as needed.

(ii)Now load matrices $\boldsymbol{A}$ and $\boldsymbol{B}$. When you are done, print them off (to your screen) to verify that they are correct.
(iii)Once these arrays are loaded, python can easily solve the eigenvalue problem. Use the python code below to solve the eigenvalue problem and plot it.
You must put a descriptive comment next to each line of code below to get full credit.

```
self.vals, self.vecs = scipy.linalg.eig(self.A,self.B)
self.key = sorted(range(len(self.vals)), key=lambda k: self.vals[k])
vec = self.vecs[:,self.key[mode]]
normalization = sqrt(numpy.sum(vec * numpy.conjugate(vec) * self.dx))
plt.plot(self.domain,real(vec * numpy.conjugate(vec)/normalization**2))
plt.show()
```

P1.5 Now redo this entire problem, but with the harmonic potential replaced by

$$V(x) = \mu x^4 \tag{15}$$

making Schrödinger's equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \mu x^4 \psi = E\psi \tag{16}$$

With this new potential, you will need once again rescale this equation to eliminate small contants and make the equation unitless. Similar to with the harmonic oscillator, you're unitless version of this equation should become

$$-\frac{1}{2}\frac{d^2\psi}{dx^2} + \xi^4 \psi = \epsilon\psi \tag{17}$$

with

$$a = \left(\frac{\hbar^2}{m\mu}\right)^{1/6} \qquad \bar{E} = \left(\frac{\hbar^4\mu}{m^2}\right)^{1/3} \qquad E = \epsilon\bar{E} \tag{18}$$

Find the first four bound states by finding the lowest 4 eigenvalues and their corresponding eigenvectors.