# Experiment 5:
# Numerical and Semiclassical Approaches to Bound States

## 1 Introduction

In the coordinate representation, the energy eigenvalue equation for a one-dimensional system reads

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

where $\varphi_n(x) = \langle x|E_n\rangle$ are the coordinate-space **eigenfunctions** of the Hamiltonian operator $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$. Sometimes, Eq. (1) is called the "time-independent Schrödinger equation," but this obscures the fact that it's just a representation of the energy eigenvalue equation. We refer to the "time-dependent Schrödinger equation,"

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t), \tag{2}$$

as the coordinate-space representation of the **Schrödinger equation**. The fundamental problem in quantum mechanics is to predict the probabilities of each possible outcome of an experiment (i.e., a measurement) given initial information about the system. As we have seen, an observable is represented by a Hermitian operator $\hat{A}$. Its eigenvalues represent the possible outcomes of measurements. The probability associated with a measurement that returns $a$ is obtained from the overlap of the corresponding eigenvector $|a\rangle$ with the state $|\psi(t)\rangle$. In the coordinate representation, this overlap takes the form

$$\langle a|\psi(t)\rangle = \int_{-\infty}^{\infty} a^*(x)\psi(x,t)dx, \tag{3}$$

where $a(x) \equiv \langle x|a\rangle$. Thus, we need the time-evolved wave function $\psi(x,t)$ which satisfies the Schrödinger equation. The general solution to Eq. (2) is

$$\psi(x,t) = \sum_n c_n\varphi_n(x)e^{-iE_nt/\hbar}, \tag{4}$$

where

$$c_n = \int_{-\infty}^{\infty} \varphi_n^*(x)\psi(x,0)dx. \tag{5}$$

That is, if we know the energy eigenfunctions $\varphi_n(x)$, the full solution $\psi(x,t)$ can be computed immediately. For this reason, much of a first course in quantum mechanics is devoted to solving for eigenfunctions $\varphi_n(x)$

for various choices of potential energy $V(x)$. The *only* reason for this is that the eigenfunctions play a pivotal role in the general solution of $\psi(x,t)$. Conceptually, this is the *boring* part of the calculation, but it's easy to get bogged down in the details. The eigenvalue equation for two-level systems $\hat{H}\left|E_n\right\rangle = E_n\left|E_n\right\rangle$ is solved by simple matrix diagonalization. For position-dependent **bound states**, we must confront the differential equation in Eq. (1), and the mathematics becomes *much* more complicated. In this numerical exploration, I hope to convince you that the process is conceptually no different from the case of discrete systems. As a controllable approximation, we will represent eigenfunctions by discrete vectors and differential operators by matrices. The dimension will be much larger than $n = 2$, but we have NUMPY to help with the heavy lifting.

## 2 Discretization of space

The *complication* that arises with bound states is that the basis $|x\rangle$ corresponds to an operator $\hat{x}$ whose eigenvalues form a continuous spectrum. For a particle confined to $0 \le x \le L$, we don't speak of a probability of finding the particle at a particular value of $x$, but rather in a range $a \le x \le b$. Instead of eigenvectors, we deal with eigenfunctions which are continuous functions of $x$. In this section you will see that differential operators (which act on functions) are the **continuum limit** of matrices (which act on vectors). The basic idea is to consider discretized space $x \to x_j$ for $j = 1, \cdots, N$. For a region $0 \le x \le L$ we could define $x_j = jL/N \equiv j\delta x$. Functions of $x$ are then *sampled* at these discrete locations, resulting in a finite set of values

$$\psi_j \equiv \psi(x_j). \tag{6}$$

While operators like $\frac{d}{dx}$ can act on continuous functions, they don't make sense on discrete samples of functions since the limit $\delta x \to 0$ must be taken,

$$\frac{df}{dx} \equiv \lim_{\delta x \to 0} \frac{f(x+\delta x) - f(x)}{\delta x}. \tag{7}$$

We *could* define the discrete derivative by taking the lattice spacing $\delta x$ as the smallest difference, with $f'_j = \left(f_{j+1} - f_j\right)/\delta x$. Sometimes that's even good enough, but it isn't symmetric around the point $x_j$. Sometimes this is referred to as the "right" numerical derivative. There's a whole industry of cooking up so-called **stencils** which approximate derivatives in a discrete system, but to make matters worse we actually need the *second* derivative to model the energy eigenvalue equation. A beautiful shortcut is provided by considering the Taylor expansion of $f(x)$,

$$\begin{aligned} f(x \pm \delta x) &= f(x) + f'(x)(\pm\delta x) + \frac{f''(x)}{2!}(\pm\delta x)^2 + \frac{f'''(x)}{3!}(\pm\delta x)^3 + \frac{f^{(4)}(x)}{4!}(\pm\delta x)^4 + \cdots \\ &= f(x) \pm f'(x)\delta x + \frac{f''(x)}{2!}\delta x^2 \pm \frac{f'''(x)}{3!}\delta x^3 + \frac{f^{(4)}(x)}{4!}\delta x^4 + \cdots, \end{aligned} \tag{8}$$

where we employ the shorthand $f^{(n)}(x) \equiv \frac{d^n f}{dx^n}$. Now let $x \to x_j$ so that $x_j \pm \delta x = x_{j\pm1}$ and $f(x_{j\pm1}) = f_{j\pm1}$. If we choose $\delta x$ "small enough,"[1] we can neglect terms beyond second order, obtaining

$$f_{j\pm1} \simeq f_j \pm \delta x f'(x_j) + \frac{f''(x_j)}{2}\delta x^2. \tag{9}$$

[1] But *how* small? This is a good thing to ponder as you're trying to fall asleep.

In the sum $f_{j+1} + f_{j-1}$, the first-order terms (containing that awful $f'(x_j)$ we never tried to define) cancel, and we can *solve* for $f''(x_j)$ as

$$f''(x_j) \simeq \frac{f_{j+1} + f_{j-1} - 2f_j}{\delta x^2}. \tag{10}$$

Well that's *nice*, as it gives us a way to define the second derivative. We say this is approximation is **second order** in $\delta x$, as the error is[2] $\mathcal{O}(\delta x^3)$ since the terms proportional to $\delta x^3$ would be the largest ones neglected (provided $\delta x$ is "small"). This is actually enough to start solving some differential equations (even some PDEs!), but we're trying to make $\hat{H}$ look like a matrix. To this end, let

$$\mathbf{f} = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ \vdots \\ f_N \end{pmatrix}. \tag{11}$$

Then the (discrete) second derivative looks like

$$\mathbf{f}'' = \frac{1}{\delta x^2} \begin{pmatrix} f_0 + f_2 - 2f_1 \\ f_1 + f_3 - 2f_2 \\ f_2 + f_4 - 2f_3 \\ \vdots \\ f_{N-1} + f_{N+1} - 2f_N \end{pmatrix}. \tag{12}$$

The pieces $f_0$ and $f_{N+1}$ do not actually exist, but they would have to be *defined* in order for us to define the second derivative at these locations. In other words, we can't define the second derivative at the edges unless we know something about the **boundary conditions**. Let us assume **closed boundary conditions**[3] so that $f_0 = f_{N+1} = 0$. The column vector $\mathbf{f}''$ is made up of a *reshuffling* of the components of $\mathbf{f}$. But that sounds like the work of a *matrix* multiplying $\mathbf{f}$. Indeed, you can verify that

$$\mathbf{f}'' = \frac{1}{\delta x^2} \begin{pmatrix} -2 & 1 & 0 & 0 & \cdots & 0 & 0 \\ 1 & -2 & 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & -2 & 1 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 1 & -2 \end{pmatrix} \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ \vdots \\ f_N \end{pmatrix} \equiv \mathbf{D}_2 \mathbf{f}. \tag{13}$$

The approximation becomes better as we take more samples, $N \to \infty$ and the spacing $\delta x = L/N \to 0$. Quite unsettlingly, this increases the dimension of the matrix. As the dimension grows, neighboring components of $\mathbf{f}$, say $f_j$ and $f_{j\pm1}$ become closer. In the true $N \to \infty$ limit, $\mathbf{f}$ becomes a continuously infinite "vector," or a *function* of the continuous index $j \to x$. The matrix $\mathbf{D}_2$ grows and appears to blow up as $\delta x \to 0$. But its action is to look at a "balanced" difference between a cluster of $f_j$ so the ratio of this difference to $\delta x$ actually remains finite and $\mathbf{D}_2 \to \frac{d^2}{dx^2}$. This limit is somewhat subtle, so it will be helpful to *use* this approximation and simply look at its predictions.

[2] That's read "error is of order $\delta x^3$.

[3] There are also **periodic boundary conditions** where $f_0 \equiv f_N$ and $f_{N+1} = f_1$ so that the system is actually a ring where the left edge is tied around to connect to the right edge. Another popular choice is $f_0 = f_2$, $f_{N+1} = f_{N-1}$ so that the numerical first derivative vanishes. Physics typically dictates boundary choices, and the made-up samples $j = 0, N+1$ are sometimes called **ghost cells**.

## 3 Discrete energy eigenfunctions

We're now able to write out an approximate (finite-dimensional) representation of the energy eigenvalue equation. We let $\psi(x) \to \psi_j \equiv \psi(x_j)$ and $V(x) \to V_j \equiv V(x_j)$. The term $V(x)\psi(x)$ can be represented by

$$V_j\psi_j \quad = \quad \begin{pmatrix} V_1 & 0 & 0 & 0 & \cdots & 0 \\ 0 & V_2 & 0 & 0 & \cdots & 0 \\ 0 & 0 & V_3 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & V_N \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_n \end{pmatrix} \quad = \quad \mathbf{V}\boldsymbol{\psi}. \tag{14}$$

Then the energy eigenvalue equation can be written

$$\hat{H}\varphi_n \quad \to \quad \left[-\frac{\hbar^2}{2m}\mathbf{D}_2 + \mathbf{V}\right]\boldsymbol{\psi}^{(n)} \quad \equiv \quad \mathbf{H}\boldsymbol{\psi}^{(n)} \quad = E_n\boldsymbol{\psi}^{(n)}. \tag{15}$$

That is, the matrix $\mathbf{H}$ has eigenvectors $\boldsymbol{\psi}^{(n)}$ and eigenvalues $E_n$ which correspond to the eigenfunctions and eigenvalues, respectively, of the original operator $\hat{H}$. The differential equation is thus reduced (approximately) to the diagonalization of a finite-dimensional matrix. That's a win!

This is really all the theory we need. The following snippet of code is sufficient to obtain approximate solutions to $\hat{H}\left|E_n\right\rangle = E_n\left|E_n\right\rangle$ for a variety of one-dimensional potentials $V(x)$:

```
from pylab import *

N = 1000
H = zeros((N,N))
x = linspace(0.0,1.0,N)
a = 1.0 #(a = hbar^2/(2m dx^2))

V = zeros(N) #replace with f(x) for other potential

for i in range(0,N):
    if (i<N-1):
        H[i,i+1] = -a

    if (i>0):
        H[i,i-1] = -a

    H[i,i] = 2*a + V[i]

w,v = eigh(H)
```

Most of this script is necessary to *define* the matrix representation of $\hat{H}$. You are free to change $N$. Loosely, we get a "better" approximation for larger values of $N$ since the continuum limit is obtained with $N \to \infty$. We'll explore this subtle point (and what "better" means) in more detail.

Without loss of generality we're considering $0 < x < 1$. *Really* we're taking $0 < x < L$ for some arbitrary $L$ and measuring $x$ as a fraction of $L$ (e.g., $x = \frac{L}{2} \to \frac{1}{2}$). It is good numerical practice to keep the

numbers being manipulated as close to 1 as possible. When very large ($1/(\delta x)^2$) and very small ($\hbar$) numbers are combined numerically, excess roundoff error can occur. It is often possible to consider a dimensionless form of the equation with numbers of order unity. This is the computational equivalent of the theoretical physicist saying "let's work in units where $\hbar = c = 1$."

Lastly, note that we are considering "closed boundary conditions." This choice forces $\varphi_n(0) = \varphi_n(L) = 0$. These are precisely the boundary conditions for the infinite square well, so this system should give us an excellent playground to test the method. This choice will also limit us to localized potential wells where the wave function decays to (essentially) zero before hitting the boundaries.

1. Use the case $V(x) = 0$ with closed boundary conditions to obtain the eigenstates of the infinite square well. Plot a couple of eigenfunctions and include the analytic solutions on the same plot. For reference, these are

$$\varphi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \tag{16}$$

**Important note:** The numerical eigenvectors are normalized according to the sum rule

$$\sum_j \psi_j^* \psi_j = 1. \tag{17}$$

(Check this!) But this isn't the same thing as requiring $\int |\psi(x)|^2 dx = 1$. Numerically the integral is represented by

$$\int |\psi(x)|^2 \, dx = \sum_j \psi_j^* \psi_j \delta x = 1. \tag{18}$$

To compare the numerical eigenvectors with the analytic solutions for the eigenfunctions, you have to renormalize them according to this rule. This can be accomplished by letting $\psi_j \to \psi_j/\sqrt{\delta x}$. For example, for the first eigenvector you actually want to plot

```
plot(x,v[:,0]/sqrt(dx))
plot(x,sqrt(2)*sin(pi*x))
show()
```

Here `x = linspace(0.0,1.0,N)`.

2. You also have an analytic expression for the energy eigenvalues,

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}. \tag{19}$$

Plot the eigenvalues as a function of $n$ along with the theoretical values. Note we haven't set $\hbar = 1$. We've set the combination $a = \frac{\hbar^2}{2m\delta x^2} = 1$. Solve this for $\hbar^2$ for use in the analytic formula to make comparison. Here the factors of $2m$ should cancel, and $L = 1$. An easy way to set up the theoretical values is to define an array of $n$ values, say `xn`, and then calculate $E_n$ as

```
xn = linspace(1,N,N)
E = (hbar*pi*xn/L)**2

plot(xn,w)
plot(xn,E)
show()
```

How is the agreement? Can you think of a simple reason for why the numerical answer begins to deviate? Think about what happens to the eigenfunctions for large $n$ and what complications might arise when representing these eigenfunctions on *discrete* grid.

## 4 Bohr-Sommerfeld Quantization

We briefly discussed Bohr's slapdash quantization rule that leads to the hydrogen energy levels which amounted to quantizing angular momentum, $\ell = n\hbar$. These early quantum pioneers weren't dummies, but all they really knew was classical mechanics. So a lot of the early quantum theory was phrased in the language of advanced classical mechanics. Specifically, people thought in terms of **Hamiltonian dynamics**, which is essentially a fancier way of applying Newton's laws in terms of energy. Before the Schrödinger equation, attempts were made to generalize Bohr's trick for the hydrogen atom to obtain energy levels for other systems. The results were mixed, but one surprisingly robust trick was to quantize the following expression,

$$\frac{1}{2\pi}\oint p(x)dx = n\hbar. \tag{20}$$

The left-hand side is sometimes defined as the **action variable** $J$, but we won't use this enough to go into what that *means*.[4] But we should say something about how to evaluate the integral. We'll specialize to one-dimensional motion where things simplify a bit. The circle on the integral means that this integral is taken over a closed loop in the $(x, p)$ plane.[5] We apply this method to periodic systems in which the particle bounces back and forth (classically) between two points. For example, the particle in a box only has kinetic energy $E = \frac{p^2}{2m}$, so $p = \sqrt{2mE}$. Beginning at, say, the left wall ($x = 0$), it completes an oscillation after moving with momentum $p$ to the right wall ($x = L$), reflecting with momentum $-p$ and then coming back to $x = 0$. The integral then gives

$$\begin{aligned}\frac{1}{2\pi}\oint p(x)dx &= \frac{1}{2\pi}\int_0^L \sqrt{2mE}dx + \frac{1}{2\pi}\int_L^0 (-\sqrt{2mE})dx \\ &= \frac{1}{\pi}\sqrt{2mE}L.\end{aligned} \tag{21}$$

Setting this equal to $n\hbar$ gives

$$\sqrt{2mE}L = \pi n\hbar \Rightarrow E = \frac{\pi^2 n^2 \hbar^2}{2mL^2}. \tag{22}$$

But *that* is just the expression for the energy levels of a particle confined to an infinite potential well of size $L$. For our purposes, we can get rid of the spooky "loop" definition and just write

$$\frac{1}{\pi}\int_{x_{\min}}^{x_{\max}} p(x)dx = n\hbar. \tag{23}$$

[4] Its conjugate variable $\theta$ is called the **angle variable**. Writing the equations of motion in terms of **action-angle variables** is a trick to make any quasi-periodic motion *look* like the math describing a set of harmonic oscillators (which are "easy").

[5] This space is called **configuration space** in Hamiltonian mechanics. It's subtly distinct from **phase space** $(x, \dot{x})$.

For a more general system where $E = \frac{p^2}{2m} + V(x)$, we have $p = \sqrt{2m(E - V(x))}$, so our one-dimensional quantization condition is

$$\frac{1}{\pi}\int_{x_{\min}}^{x_{\max}} \sqrt{2m(E - V(x))}dx \quad = \quad n\hbar. \tag{24}$$

And that's it! Pick a potential $V(x)$, and this formula gives you a way to calculate the energy levels from Bohr's semi-classical method. But it's not always right. It works reasonably well for "large $n$," but it's not guaranteed to give exact answers because it's not based on the full quantum theory. Still, if you have the stomach for dealing with some unpleasant integrals it's a really cheap way to get an approximate answer.[6] We're going to use our new numerical method to explore just how well it works.

Now there's a bit of a conundrum. The numerical method works best for *small n*, since the finite size of the lattice creeps in to distort the results when $n$ gets large. But Bohr's method works best for *large n*. In practice, parameters can usually be chosen so that there's a crossover regime where *both* methods agree. It's not a mathematical proof, but it provides some level of confidence that you're observing real physics when two approximate methods work.

First, we'll build up some intuition for a case where the full analytic solution is possible. But what's nice about these methods is that they give good results for where no analytic solution is known. These methods make you powerful!

3. **Harmonic oscillator:**

   (a) Use Eq. (24) to calculate the energy eigenvalues for the harmonic oscillator (i.e., spring) potential $V(x) = \frac{1}{2}m\omega^2 x^2$. The standard form given here assumes the well is centered at $x = 0$. Currently we have $0 \le x \le L$, so this should be modified as $V(x) \to \frac{1}{2}m\omega^2\left(x - \frac{L}{2}\right)^2$.[7] To do the integral, I recommend using a substitution like $x = A\cos\theta$ (or just letting WOLFRAM or Maple do it). The relationship between energy and amplitude $A$ is $E = \frac{1}{2}m\omega^2 A^2$. Here $x_{\min} = -A$ and $x_{\max} = +A$.

   (b) Use the numerical scheme to obtain the eigenvalues and eigenvectors of the corresponding discrete problem. Make a plot of eigenvalues as a function of $n$ and on the same graph, plot the theoretical eigenvalues. To make the comparison, you'll need to be careful. You should have definitions for $m$ and $\omega$, as they enter the formula for $V(x)$. We have actually set $\hbar$ *indirectly* by setting $a = \frac{\hbar^2}{2m\delta x^2} = 1$. Solve this expression for $\hbar$ in terms of the other constants, and use that expression for whenever $\hbar$ appears in your expression for $E_n$. Use a log-log graph to turn power-law dependence into straight lines: you can use `loglog(x,y)` instead of `plot(x,y)` to do this efficiently.

   (c) Plot the first eigenstate $\phi_0(x_j)$ =`v[:,0]/sqrt(dx)` and compare to the analytic result that we'll derive in class,

$$\phi_0(x) \quad = \quad \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left[-\frac{m\omega}{2\hbar}\left(x - x_0\right)^2\right], \tag{25}$$

   where $x_0 = L/2$.

[6] Incidentally, this is good enough that it can be improved upon somewhat. The **Einstein-Brillouin-Keller (EBK)** quantization procedure does the same thing in a somewhat fancier way, obtaining a better semi-classical approximation. You can even get the relativistic expression (which is *hard* to get using full-blown QM) for the hydrogen atom to fall out in a few lines.

[7] Alternatively, you can change the $x$ values to $-\frac{L}{2} \le x \le \frac{L}{2}$ and leave $V(x) = \frac{1}{2}m\omega^2 x^2$.

4. Repeat the comparison of eigenvalues (semiclassical vs. numerical) for a **linear potential** which has an infinite wall on the left side:

$$V(x) \quad = \quad \begin{cases} \mathcal{F}x & (x > 0) \\ \infty & (x \leq 0) \end{cases} \tag{26}$$

Here, the particle goes between $x_{\text{min}} = 0$ and $x_{\text{max}}$ where the right-most position is defined by $p = 0$, so $E = \mathcal{F}x_{\text{max}}$ (all the energy is potential). You don't need to worry about incorporating the infinite potential for negative $x$ because the boundary conditions take care of this.

*Note:* The linear potential $V \propto x$ corresponds to a constant force $\mathcal{F}$, the simplest type of system considered in introductory mechanics. Interestingly, it's a *very* hard problem in quantum mechanics that can only be solved using special functions–the **Airy functions**, which are distant cousins of **Bessel functions**.

5. Repeat the eigenvalue comparison for **1D hydrogen** defined by the potential $V(x) = -\frac{\alpha}{x}$ for $\alpha > 0$ so the potential is negative. Again assume $V(x) = +\infty$ for $x < 0$ so that the same boundary conditions apply. You can assume $x_{\text{min}} = 0$ while $x_{\text{max}}$ is defined by $E = -\frac{\alpha}{x_{\text{max}}}$, corresponding to all the available energy going into potential energy. Also, feel free to try your hand at the integral. I couldn't do it without losing patience, but I'm weak. MATHEMATICA told me that

$$\int_0^{-\alpha/E} \sqrt{2m\left(E + \frac{\alpha}{x}\right)}dx \quad = \quad \pi\alpha\sqrt{\frac{-m}{2E}}, \tag{27}$$

for $\alpha > 0$ and $E < 0$. For numerical implementation, you'll run into trouble with $\alpha/x$ for $x = 0$. Feel free to be creative, but a quick fix that's fine for our purposes is to set `V = alpha/(x+0.0001)` (or using any small shift to avoid dividing by zero). Also, keep $\alpha \sim 0.01$ for best results (but feel free to explore). It's important to use logarithmic axes on this one because it's the most slippery of the examples considered. Since the eigenvalues are negative, you'll want to look at the logarithm of $-E$ which is positive (and thus has a well-defined logarithm).

*Note:* 1D hydrogen doesn't exist, but we don't yet possess the machinery required to tackle a three-dimensional problem. Interestingly, $E_n \propto n^{-2}$ for the one-dimensional model and the 3D (realistic) model, so some shred of reality survives the reduction of dimension. Actually, if you use $\alpha = \frac{e^2}{4\pi\epsilon_0}$ corresponding to the 3D Coulomb interaction, you find that this predicts the *same* eigenvalues as the 3D case for much less effort.