LAB 6: NUMERICAL SOLUTION OF SCHRÖDINGER'S EQUATION

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LEARNING OBJECTIVES

This is a computational lab without any experimental parts. You will:

- Gain experience with numerical methods and spreadsheet calculations.
- Explore solutions to Schrödinger's equation for the finite square well and simple harmonic oscillator.
- Compare their solutions to textbook diagrams and other similar potential functions.

PRE-LAB

For convenience, we are typing u instead of ψ in this document for the wavefunction. It's just easier to type.

0) READING.
   - Read this lab
   - Read the associated homework problem (on Guide 7). This problem is due with your problem set.
   - Read the Excel tips on page 5.
1) *Practice* one or more of the **Excel tips** 1 through 5 from pages 5-6.
   - *Report back* about which one you practiced and what you think of it.
   - Will it speed up your process?
2) Write **your own derivation of Eq. (2),** starting from two facts:
   - the Schrödinger equation in the form

   $-\frac{d^2u}{dy^2} + Wu = \mathrm{E}u$

   and
   - the definition of a derivative.

   Hint: The entire derivation is in this lab handout.

3) **Write Eq. (2) in Excel format**. That is, write it as a formula that you could enter directly into an excel cell.
   - It may help you if you refer to Figure 1. Give the formula for cell G4.
   - Hint helpful? Viva suggests this video, especially 2:00 to 3:00 https://www.youtube.com/watch?v=-kNiQGgTYK4

If you wish to use your own computer, please have Excel installed and bring your power cord.

INTRODUCTION

In class, we have seen solutions to Schrödinger's equation. Three canonical one-dimensional cases include the infinite square well, the finite square well, and the simple harmonic oscillator. In three-dimensions, the hydrogen atom is of particular importance. There are one or two other special cases that we can solve by analytic means, but even some extremely simple looking potentials *cannot* be solved analytically.

However, we can always find solutions to differential equations by ***numerical methods***. In this lab you will explore the finite square well and harmonic oscillator potentials through numerical solutions in Excel.

This lab might give you new insights into some important math and physics concepts:

1) Math: What is a limit? Why is the derivative defined with a limit?
2) Physics: Why do bound states have discrete energies?

The Method of Finite Differences: a computational approximation

At the heart of the numerical methods that we will examine is the replacement of the continuous position variable x by a discrete array of (usually equally spaced) points. Replacing with a discrete set requires converting differential operators (derivatives) into their finite approximations.

Let us start with some notation. We will call the spatial part of the wave function $u(x)$, because it is a lot easier to type than ψ, and the continuous space variable x. We will have a discrete set of equally spaced points

$$x_i = x_0 + \Delta x * i$$

where Δx is a conventional name for the grid spacing and i is an index, usually a series of integers. For the discrete approximation, we will replace the continuous wavefunction $u(x)$ by the set of values $u_i=u(x_i)$.

Now, we need to replace the derivatives by their finite approximations. The definition of the derivative is

$$\frac{d}{dx}u(x) = \lim_{\Delta x \to 0} \frac{u(x+\Delta x) - u(x)}{\Delta x}$$

We are going to replace the derivative by an approximation since we can't take a limit on a discrete grid. We actually have at least three choices

$$\frac{du}{dx} \approx \frac{u_i - u_{i-1}}{\Delta x}, \qquad \frac{du}{dx} \approx \frac{u_{i+1} - u_i}{\Delta x}, \quad \text{and} \quad \frac{du}{dx} \approx \frac{u_{i+1} - u_{i-1}}{2\Delta x}$$

which are called backward differences, forward differences, and central differences, respectively. We cannot make Δx zero but the smaller we make it, the more accurate our discrete approximation will be. If we repeat this process, then we can make second derivatives as well. The second derivative uses the same definition,

$$\frac{d^2u}{dx^2} = \lim_{\Delta x \to 0} \frac{u'(x+\Delta x) - u'(x)}{\Delta x} = \lim_{\Delta x \to 0} \frac{[u(x+2\Delta x) - u(x+\Delta x)] - [u(x+\Delta x) - u(x)]}{(\Delta x)^2},$$

but the most common second derivative (the "centered difference") is made by combining one forward and one backward step to give a central formulation, so I'll replace every x with an $x - \Delta x$:

$$\frac{d^2u}{dx^2} = \lim_{\Delta x \to 0} \frac{[u(x+\Delta x) - u(x)] - [u(x) - u(x-\Delta x)]}{(\Delta x)^2} = \lim_{\Delta x \to 0} \frac{u(x+\Delta x) - 2u(x) + u(x-\Delta x)}{(\Delta x)^2}$$

$$\frac{d^2u}{dx^2} \approx \frac{u_{i+1} + u_{i-1} - 2u_i}{(\Delta x)^2} \tag{1}$$

We can use this discrete approximation to convert a differential equation into a sequential formula for finding the values of u, one at a time. In the problem in Guide 7, you transformed the time independent Schrödinger Equation for a finite depth potential well of length L into dimensionless units, which takes the form

$$-\frac{d^2u}{dy^2} + Wu = E'u,$$

where $W = \frac{2mL^2V}{\hbar^2} = \begin{cases} 0, & 0 \le x < 1 \\ W_o, & \text{elsewhere} \end{cases}$ and $E' = \frac{2mL^2E}{\hbar^2}$. Doing so we have used the natural scales of the problem to express our physical quantities. This means that our step size Δx will capture the relevant behavior of the wavefunction. This also allows us to express the Schrödinger Equation in a more basic form to focus on the shape of the wavefunctions and the relationship between energy values. So, let's move ahead with the 1-D Schrödinger equation in dimensionless units, as shown below (where we once again use x instead of y, making a change of variable – from now on x is not the same x as it was before – and similarly for $W \to V$ and $E' \to E$):

$$-\frac{d^2u}{dx^2} + V(x)u = Eu$$

The finite difference approximation of the Schrödinger equation will first involve replacing the function $V(x)$ by the set of discrete values

$$V_i = V(x_i)$$

and then substituting in our difference formula, Eq. (1), to get

$$-\frac{u_{i+1} + u_{i-1} - 2u_i}{(\Delta x)^2} + V_i u_i = Eu_i$$

First, we reorganize this slightly, getting

$$\frac{u_{i+1} + u_{i-1} - 2u_i}{(\Delta x)^2} = -(E - V_i)u_i$$

which we can re-write as a formula to find a new value of the wavefunction u given two old ones

$$\boxed{u_{i+1} = 2u_i - u_{i-1} - (\Delta x)^2(E - V_i)u_i} \tag{2}$$

This is the approach that we will use in our method. Note, this boxed equation IS the Schrödinger equation. But now it's in a form that is ideal for implementation in a spreadsheet. This form is called a recurrence relation. Recursion is very important in computer calculations. We can put the values of x_i, V_i, and u_i in columns in the spreadsheet and put the values of fixed parameters such as Δx and the energy E in cells that are referenced absolutely. We will need to supply the first two values of u_i to get the process going, but then Excel can do the rest.

PROCEDURE

Exercise #1: Finite square well

Explore the energies and wavefunctions of the finite square well potential:

$$V(x) = \begin{cases} 100 & x \leqslant 0 \\ 0 & 0 < x < 1 \\ 100 & x \geqslant 1 \end{cases} \tag{3}$$

The potential is already in dimensionless form, to plug straight into the finite difference equation, Eq. (2):

$$u_{i+1} = 2u_i - u_{i-1} - (\Delta x)^2 (E - V_i) u_i$$

Your objective is to determine the first four energy eigenvalues for this square well potential. You must verify that the solutions are viable by graphing the wavefunction, u(x) vs. x. You are also welcome to graph the probability density, $u^2(x)$ vs. x. Valid eigen-solutions must obey the boundary condition that the value of u must go to zero as x gets large. You must adjust the energy E by hand to make this happen, and may need to adjust the width of the solution region as the energy gets larger.

In order to keep the number of decimal places that you need from getting out of hand, you will need to limit the domain of your horizontal variable, x. You have to both make sure that the wavefunction has time to go smoothly to zero in the classically forbidden regions. For the potential well bounded by $0 < x < 1$, we suggest starting with a numerical solution that spans from $-1 < x < 2$.

Your task: find all bound solutions, both energy and wavefunction.

Setting up your spreadsheet

We recommend Excel rather than other spreadsheet software for this computational investigation. Excel offers an extension called SOLVER that you may wish to use. Google Sheets doesn't have SOLVER.

Figure 1 shows a suggestion for how you might setup your spreadsheet. (It does not need to look exactly like this.)

	A	B	C	D	E	F	G
1	dx	0.01		xi	Vi	E-Vi	ui
2	x0	-1		-1	100	-99	0
3	V0	100		-0.99	100	-99	0.001
4				-0.98	100	-99	0.00201
5	u0	0		-0.97	100	-99	0.00304
6	u1	0.001		-0.96	100	-99	0.0041
7				-0.95	100	-99	0.0052
8	E1	1		-0.94	100	-99	0.006352
9				-0.93	100	-99	0.007567
10				-0.92	100	-99	0.008857
11				-0.91	100	-99	0.010234
12				-0.9	100	-99	0.011713

Figure 1: Example spreadsheet organization

- The cells with blue backgrounds contain simple numbers that you set. These are your starting conditions. You will end up changing these as needed.
- The yellow cells contain formulae of the form "=<cell above>+dx" to create the regularly spaced x values.
- The magenta cells contain the finite difference formula, Eq (2).
- The green cell is your "guess" for the energy, E. You will be changing this cell by hand to try out different energy values.
- The cells with V and E-V both contain formulae as well.

Remember that, for this to be a good approximation, the step size, Δx or dx, must be "small." If we work in SI units then we may find it very difficult to say what small means. Unfortunately, there is no easy way to tell from the results whether we have a small enough value; the formula will always produce a sequence of values for u_i. If dx is small enough, then they will be a good approximation to the correct function. If dx is too large, they will not. By putting equation into dimensionless form, small means small compared to 1. In this example, we are trying dx=0.01.

To find the $n = 1$ solution, you will observe the graph of $u(x)$ vs. x from $-1 < x < 2$. This will capture the potential well $0 < x < 1$, and also a bit extra on either side, so that you can see the exponential decay toward $u = 0$.

There are a few different ways to fill the column of values for V.

1) **Excel tip #1**: A nice Excel trick to allow you to use adjustable limits for your domain, as we have with V(x), is to write the potential as an IF function. This takes 3 arguments, like this

   IF(<conditional expression>, <value if true>, <value if false>)

   Here, $V = 0$ while x is between 0 and 1, but it is 100 otherwise (Eq. (3)). Try out the IF function. If you can't get it working, you can always use brute force, by copy and pasting the value you want in certain cells.
2) **Excel tip #2**: relative vs. absolute cell referencing with dollar sign: When you enter an equation in Excel to calculate E-V, you can type, for instance, =B8-E4. But if you copy and paste this expression all the way through the E-V column, errors will abound. Why? When you copy and paste, Excel takes the next row down for both values. So now E-V = B9-E5. Oops! You do want the calculation to update your value of V, but you don't want it to change your energy E. To ensure that you reference for E does not change, enter the dollar $ for absolute cell referencing. If you type =B$8-E4, then the calculation will always reference row 8. If you want to copy and paste calculations across both rows and columns, best to use B8 to fix both row and columns. You can press **F4** at the top of your keyboard to put the $ symbol[1]. You could alternatively make an entire column for E, which has the benefit that you may then plot it with your potential graph.
3) **Excel tip #3**: Filling cells. If you click on the little square in the corner of the selected cell, you can drag down its formula[2]. For the next column over, you can double click the little square to fill all the cells below. (See Figure 2, top.)
4) **Excel tip #4**: Name Box for jumping around the spreadsheet. When your spreadsheet becomes very large, you might have to scroll a while to get from the top to the bottom. It's faster to type the cell you want to jump to into the Name Box. You can even name a cell: Right click on the cell and Define Name. (See Figure 2, bottom.)

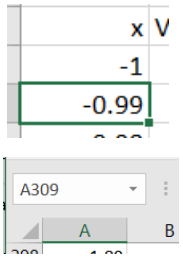


Figure 2: Excel tips

5) **Excel tip #5**: Another way to jump between top and bottom of a long spreadsheet: Use View -> Split. Then you have a split spreadsheet and you can scroll to different locations and see the top and bottom of your spreadsheet at once. (Solver can get a little annoying. You have to make sure you are clicking in the correct split section before you run Solver or else Solver will scroll away.)
6) **Physics and excel tip**: The overall height of the wavefunction is only set when you normalize it. **You don't have to normalize your wavefunctions today.** In Fig. 1, $u_2 = 0.001$. That second number u_2 sets the height of the wavefunction. If your wavefunction is annoyingly short or tall, you can change u_2 to scale it.

Create two graphs. One graph should be V(x) vs. x. This graph will show you the square well potential. Make sure it looks like what you expect. The other graph is the wavefunction u vs. x. For the infinite square well, you know that $u(x = 0)$ and $u(x = 1)$ must both be zero. For the finite square well, though, the wavefunction "leaks" through the well walls. However, u(x) must be zero "at infinity." Here, we graph from $-1 < x < 2$, which for practical purposes, is our infinity[3]. That is, $u(x = -1) = 0$ and $u(x = 2) = 0$. We set $u(x = -1) = 0$ in our initial setup. As you change the value of E, you will look for a graph where $u(x = 2) \to 0$.

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[1] professor-excel.com/insert-dollar-signs-to-different-existing-excel-formulas-simple-and-fast

[2] https://support.microsoft.com/en-us/office/fill-a-formula-down-into-adjacent-cells-041edfe2-05bc-40e6-b933-ef48c3f308c6

[3] Treating some reasonable number as infinity is an approximation. If you attempt to look too closely, you won't be able to see when you're successfully getting the wings to approach zero. But if you look too far along x, you will discover that this formula would only approach zero for one very particular energy out of all the real numbers – but to get that would require infinite digits. So, there is a distance along the x axis that is too far to look, but there is also a distance that is too close. If you aren't sure how to choose your min and max x for a given

What should I try?

Start with $E = 1$. You should see a graph that blows up to a large value at the $x = 2$ edge of the graph. Then try $E = 2$. It won't look much better (though if you monitor the value of $u(x = 2)$, you will see that it changes). Try stepping your guess for E by 1's. I promise, you won't have to go too far. [If the situation hasn't changed by $E = 10$, you have an error in your spreadsheet.]

Somewhere in the region $1 < E < 10$, you will find a solution that is bounded at zero on both ends. Keep guessing your value of E by trial and error to at least 4 significant figures[4]. i.e. you might confidently tell us that E_1=2.386 (it doesn't) and show us the u vs. x and/or u^2 vs. x graph to back it up. As you extend your guess to more and more significant figures, you graph is expected to look more and more like what you see in your textbook.

Once you have the first bound solution, E_1, the rest of the experiment is just guessing more energy solutions to find E_2, E_3, and E_4. No more hints; you will need to find these next ones yourself. For each new energy value hunt, I recommend creating a new tab in Excel that is a copy of your previous one (Figure 3). Then you won't lose your earlier work as you start to make tweaks to the spreadsheet. Along the way, you will need to expand your bounds from $-1 < x < 2$ to something like $-2 < x < 3$ or even wider, in order to allow the graph to slowly curve up or down at the boundary. Remember, we expect our solutions to exponentially decay toward zero.

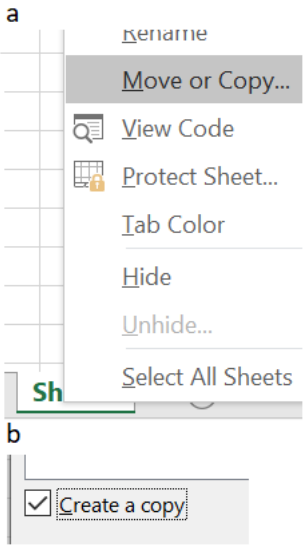


Figure 3: Steps a and b show how to copy an Excel tab

Do I really have to guess and check to find each energy value? Isn't there a better way?

There is. After you find the first one or two energy values by hand, you may wish to use SOLVER to help find subsequent energy values.

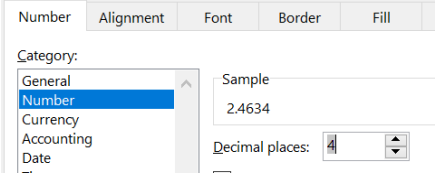
How do I know I have finished this exercise?

Do you have all four discrete values of energy, E, representing n=1, n=2, n=3, and n=4? Do you have four graphs of the wavefunction u(x) vs. x, where u smoothly decays toward zero at both extremes and the sinusoidal region contains the expected number of modes of vibration? Then you are done! Move on to Exercise #2.

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potential, talk to your lab instructor. This is part of the art of approximation that is so essential to how physicists use math. Later you can opt to calculate your truncation error.

[4] Another note on precision. I can imagine a student who tries to spend many minutes getting the 19th digit. Remember that this is only an approximation: we started with a finite difference formula (approximating the derivative as something without a full limit), so we don't wish to pretend to have false precision here. If you are a perfectionist and find yourself tempted to spend a lot of time to go beyond the decimal place that is significant, note that you can hide extra decimal places in the format menu. Unfortunately, Excel cannot count significant figures, only decimal places. If you aren't sure how to choose what decimal place is sufficient for a given potential geometry, talk to your lab instructor.



Exercise #2: Harmonic oscillator

Explore the energies and wavefunctions for the harmonic oscillator potential, $V(x) = kx^2/2$. The 1-D Schrödinger equation becomes

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dx^2} + \frac{1}{2}kx^2u = Eu$$

You are to find the lowest four eigen-solutions to this equation[5], which can be put into the dimensionless form:

$$-\frac{d^2u}{dx^2} + x^2u = \epsilon u$$

so that $V_i = x_i^2$. Here, we let $\hbar = m\omega$, $\epsilon = \frac{2E}{\hbar\omega}$ and made a change of variable for x to arrive at this dimensionless form.

- Obtain the first four energies and wavefunctions for the harmonic oscillator and compare your results to theory.
- You want at least 4 significant figures in your energy values.
- NOTE: We suggest that you limit your x-axis to the range -4 to $+4$. That will be wide enough to get good values but not so wide that it is hard to keep the wave functions on scale.

Expansions

- Go back to the finite square well and plot an un-bound wavefunction.
  - Estimate your uncertainty for the $n = 4$ state in the finite square well.
    - Estimate the discretization error of your energy eigenvalues by trying another value for dx.
      - You might try a larger (worse) dx to overestimate your uncertainty, or a smaller (better) dx to underestimate your uncertainty.
    - Estimate your truncation error of your energy eigenvalues by trying another pair of max and min x as your approximation for $\pm\infty$.
      - You might try a wider view to underestimate your uncertainty, or a narrower view to overestimate your uncertainty.
    - Estimate your overall uncertainty from the discretization error and truncation error.
    - Do your results agree with the expected energies, within uncertainty?
- Plot wavefunctions for any potential you like. Any fun shape! You are no longer limited by your ability to solve analytically!

[5] You certainly cannot expect to find every discrete solution to the harmonic potential today; we must cap it.