Lab 19

Numerical Determination of Energy Levels

Continuing Objectives

6. Be able to make a good graph, either in your notebook or with a computer, including labels, scales, units, dependent, and independent variables.

9. Use a computer to simulate physical systems using numerical methods.

Introduction

Quantum mechanics predicts that the allowable energy levels in any bound system are quantized. A particle is said to be bound in a region if, for a given energy E of the particle, the total energy E (kinetic + potential) is greater than the potential energy $U(x)$ in that region, and that region is surrounded by regions where the total energy is less than the potential energy (see Figure 19.1). The quantized energies can be determined by finding the energies E for which (i) the wavefunction approaches 0 as x approaches $\pm\infty$; and (ii) the wavefunction satisfies the Schrödinger equation,

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \Big[E - U(x)\Big]\psi(x) = 0. \tag{19.1}$$

Eq. (19.1) is the time-independent, one-dimensional, non-relativistic Schrödinger equation, where $U(x)$ is a potential energy function depending only on x. Solutions of this equation are functions $\psi(x)$ that satisfy the equation and obey the appropriate boundary conditions.

To see what form the boundary conditions might take, let us consider the physical interpretation of $\psi(x)$. The wavefunction $\psi(x)$ is a quantum mechanical amplitude.

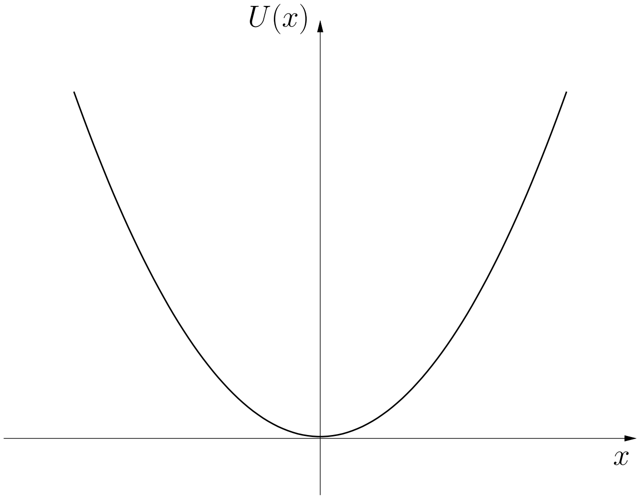

Figure 19.1: The potential energy function for a harmonic oscillator.

Therefore, the square of $\psi(x)$ is related to probability; $|\psi(x)|^2\,dx$ is the *probability* that the particle described by $\psi(x)$ is located between x and $x+dx$. Since the particle must be somewhere, we must have

$$\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1. \tag{19.2}$$

Eq. (19.2) is called a *normalization condition.* For our problem, this condition means that we accept only those solutions that do not become infinite as $x \to \pm\infty$.

One of the nice things about a numerical method like the one we will use in this lab is that it can be applied to any system with any potential, not just the "easy" examples. For the first part of this lab, we will study a harmonic oscillator (the quantum version of a mass on a spring), with potential energy given by

$$U(x) = \frac{1}{2}Kx^2, \tag{19.3}$$

(see Figure 19.1). Here, K is the spring constant.

Calculation of Wavefunctions

We first rewrite Eq. (19.1), multiplying and dividing by c^2 in the first term:

$$\frac{\hbar^2 c^2}{2mc^2}\frac{d^2\psi(x)}{dx^2} + \Big[E - U(x)\Big]\psi(x) = 0. \tag{19.4}$$

Then we solve for $\frac{d^2\psi}{dx^2}$, putting in the particular potential energy function we're interested in:

$$\frac{d^2\psi}{dx^2} = -\frac{2mc^2}{\hbar^2 c^2}\left(E - \frac{1}{2}Kx^2\right)\psi. \tag{19.5}$$

We will use units of electron volts (eV) and nanometers (nm), and study the motion of an electron in this potential. Therefore

$$mc^2 = 511 \times 10^3\,\mathrm{eV}$$

and

$$\hbar c = 197\,\mathrm{eV}\cdot\mathrm{nm}.$$

It will be useful to write the energies in terms of $\hbar\omega_0$, where $\omega_0 = \sqrt{K/m}$ is the classical frequency of the harmonic oscillator. Notice that

$$\hbar\omega_0 = \hbar c\sqrt{\frac{K}{mc^2}}. \tag{19.6}$$

Next, for finding values of $\psi(x)$ at equal increments of x (i.e., $x = 0$, Δx, $2\Delta x$, $3\Delta x$, $\ldots$) we will use the same algorithm that was introduced in Chapter 1 of the PHYS 211 Supplementary Reading pamphlet, and used in PHYS 211 lab in Experiment 6, *Numerical Solution: Air Drag on a Falling Object*. In Experiment 6 we determined successively $t, y(t), v_y(t)$ (and $a_y(t)$) by using

$$\begin{aligned} t_{\text{new}} &= t_{\text{old}} + \Delta t, & (19.7)\\ x_{\text{new}} &= x_{\text{old}} + v_{\text{old}}\,\Delta t, & (19.8)\\ \text{and}\quad v_{\text{new}} &= v_{\text{old}} + a_{\text{old}}\,\Delta t. & (19.9)\end{aligned}$$

Similarly we determine in today's lab in steps of Δx successively x, $\psi(x)$, $\psi'(x)$, and $\psi''(x)$ where we use the notation ψ' as shorthand for the first derivative $d\psi/dx$, and ψ'' for the second derivative $d^2\psi/dx^2$. Analogous to Eqs. (19.7)–(19.9) we use the following set of equations

$$\psi(x + \Delta x) \simeq \psi(x) + \Delta x\,\psi'(x), \tag{19.10}$$

and

$$\psi'(x + \Delta x) \simeq \psi'(x) + \Delta x\,\psi''(x). \tag{19.11}$$

And rewriting the Schrödinger Equation gives,

$$\psi''(x) = -\frac{2\,(mc^2)}{(\hbar c)^2}\left(E - \frac{1}{2}Kx^2\right)\psi(x). \tag{19.12}$$

According to this algorithm, if we know ψ and ψ' at one position x, then we can extrapolate ψ to a slightly different position, $x + \Delta x$. In this lab, you will choose an initial E value and use Eqs. (19.10)–(19.12) to calculate $\psi(x)$ in steps of Δx.

Getting Started

For a symmetric potential energy function such as that shown in Figure 19.1, there are two possible types of wavefunctions: odd and even. For even functions, the value of ψ at $x = 0$ can be chosen to be 1 (i.e., $\psi(0) = 1$) and we have $\psi'(0) = 0$. (Why?). For odd functions, $\psi(0) = 0$. Since for our purposes the value of ψ' is arbitrary, we can choose $\psi'(0) = 1$ for odd functions. To summarize, we have

Even Functions	Odd Functions
$\psi(0) = 1$	$\psi(0) = 0$
$\psi'(0) = 0$	$\psi'(0) = 1$

Once $\psi(0)$ and $\psi'(0)$ are chosen, the basic algorithm, Eqs. (19.12)–(19.11), gives $\psi(\Delta x)$, $\psi(2\Delta x)$, $\psi(3\Delta x)$, etc.

Criterion for a Well-Behaved Wavefunction

Only if E takes on certain well-defined values will the curve of $\psi(x)$ vs. x approach zero as x becomes large. If $\psi(x)$ starts to "blow up" (i.e., tends to values of $\pm\infty$) for large values of x, you can stop your numerical integration and try a new value of E.

However, since you are doing a numerical calculation, no matter how accurately you find E, your wavefunction will eventually blow up. Thus the goal is to find two slightly different values of E, one of which makes ψ approach $+\infty$ and one of which makes ψ approach $-\infty$. The true E will then be some place between these two values. This method is called the "shooting method" because you launch the wave function with better and better initial conditions until you come close to hitting your target.

Procedure

1. We will use for the K of the harmonic oscillator $K = 3\,\mathrm{eV/nm}^2$.
2. Open an Excel template file for this lab, as follows. Navigate to the `PHYS211_212 Lab` folder, open the folder `212Lab` and therein open the folder labeled `Numerical Determination of Energy Levels`
Double-click on `numericalELevels_HarmonicOsci_template.xls`
and `Save As` to your network space.
3. This template should help you to concentrate on the important aspects of this lab. Note that all constants (i.e. variables which are independent of x) are defined at the top (yellow cells). Fill in the yellow boxes. We will use $\Delta x = 0.003$. When you put in a value in cell `B9`, look at what happens to the values

in the x-column (cells `A18` and down). For cells `B10` and `B11`, begin with the even case, that means $\psi(0) = 1$ and $\psi'(0) = 0$. Note that cells `B17` and `C17` change appropriately. Finally, put in a trial value of $E = 0.1\,\text{eV}$.

4. Now, enter Eqs. (19.10)–(19.12) into the green cell, the blue cell, and the purple cell. Be sure to use absolute references to refer to any values that you filled in from the yellow cells above. All of the variables in the yellow cells also have names associated with them, which you can view in the top left corner of the main Excel ribbon when you click on a given cell. After you enter your formulas into the colored cells, you'll need to copy and paste your formulas into the columns beneath the colored cells. You can achieve this for example by clicking on `B18` and then moving the cursor to the bottom right corner of the cell until the white + turns into a black thin +, then double click.

5. Verify that your first four lines of your Excel table match the following table. If not, please call your instructor or TA over for assistance.

x (nm)	$\psi(x)$	$\psi'(x)$	$\psi''(x)$
0.000	1	0	-2.63340978
0.003	1	-0.00790023	-2.63305427
0.006	0.9999763	-0.01579939	-2.63192535
0.009	0.9999289	-0.02369517	-2.63002318

6. The graph should automatically plot. Once your Excel sheet is working properly, write down in your notebook the Excel versions of the formulas you typed into the colored cells.

7. Now you are ready to search for the first energy level. Look at the graph for $E = 0.1\,\text{eV}$, then try $E = 0.2\,\text{eV}$, $E = 0.3\,\text{eV}$, etc., until you see the asymptotic behavior of the wave function switch from blowing up to $+\infty$ to blowing up (down?) to $-\infty$. Note those two values of energy in your notebook.

8. Now, adjust between those two values, but this time only change the hundredths place. Repeat this loop until you have found two values of E, separated by no more than $0.0001\,\text{eV}$, such that one value off E makes ψ go to $+\infty$ while the other sends ψ to $-\infty$. Record these values of E.

9. Print the graph of your wave function $\psi(x)$ that corresponds to the best found E. (It may help to label the plot with your names to help distinguish them at the printer). The graph printed is for $-3.5\,\text{nm} < x < +3.5\,\text{nm}$. To fill in the $\psi(x)$ for $x < 0$, use that we are looking at an **even** case right now, so $\psi(-x) = \psi(x)$. Carefully draw this in by hand. On your plot, make sure to also sketch what the **ideal** (true) waveform would look like (that means if E is determined with infinite precision.) On the print out write down the two E values which specify the found energy (i.e. fill in the dots of $\ldots < E < \ldots$.)

10. Next print only the top of your EXCEL sheet (instead of 1000 lines of data points) and on the print out we also want the gridlines and column and row labels. To do so: In the top menu click on "Page Layout", click the boxes for "Print" for both "Gridlines" and for "Headings". Then highlight the area you would like to print and then click on "Print Area" and select "Set Print Area". Then you are ready to print as usual: `File` $\longrightarrow$ `Print` and choose the "Landscape Orientation".

11. After finding this energy and its corresponding wave function, the next energy level is ODD so, **begin again with the odd case, changing your initial conditions** in the table. Again adjust the values for energy (in steps of 0.100 eV as before until you see the asymptotic behavior of the wave function switch from blowing up to $+\infty$ to blowing up to $-\infty$). It might help to adjust the vertical scale of your plot. Calculate the wave function $\psi(x)$, repeating for different values of E until you have found a pair of values of E on either side of the true energy and differing by no more than 0.0001 eV. Print the graph of the wave function and add (hand drawn) the $\psi(x)$ for $x < 0$. Remember that now it is the odd case, so $\psi(-x) = -\psi(x)$. Again sketch $\psi(x)$ for the **ideal** solution and add to your print out the two energy values specifying your found energy level.

12. Repeat the last step in order to get the next energy level/wave function. **Make sure that you have switched back to the even case!** Again, it may help to adjust the vertical scale of your plot. As before, on the print out add the $\psi(x)$ for $x < 0$, specify the dots of $\ldots < E < \ldots$, and sketch $\psi(x)$ for the ideal solutions.

13. Repeat these steps for the next odd energy level/wave function so that you have a total of two even and two odd solutions.

14. In your notebook arrange the graphs of the four ideal wavefunctions (i.e. $\psi(x \to \pm\infty) = 0$) in order of increasing energy and add to each sketch the corresponding most accurate energy you obtained. Which patterns do you find?

15. Determine the energy differences between the first and second wavefunctions, second and third wavefunctions, and third and fourth wavefunctions. Do you notice a pattern? Use this pattern to predict the energy of the fifth level, and then verify your prediction with the numerical calculation in Excel. Note that it might not be exact because of numerical rounding.

16. Summarize ALL the observations and trends you have noticed for wavefunctions and corresponding energies of a harmonic oscillator potential. Compare your energies to $\hbar\omega_0$.

STOP Discuss your summary with your instructor or a TA.

Hydrogen Atom

Now that you've learned how to apply the shooting method to obtain energy levels, let's apply this technique to the hydrogen atom. We looked at this same element in the previous lab, where we determined the ground state energy experimentally using the emission spectrum. We therefore will be able to compare the previous lab result with our computational result for the hydrogen atom energy. We will also compare with the expected energy levels E_1/n^2 (that's cool!) For this case, we will need to consider the three-dimensional Schrödinger equation, since the hydrogen atom is, in fact, three-dimensional. This means our wavefunction $\psi(r, \theta, \phi)$ is a function of all three spherical coordinates.

Fortunately, if we restrict our attention to states where ψ depends only on r and not on θ or ϕ, we can still obtain all the energy levels. (The solutions correspond to the s orbitals in chemistry.) For these states, the derivatives with respect to θ and ϕ drop out of the 3D Schrödinger equation, giving the somewhat simpler expression

$$-\frac{\hbar^2}{2m_e}\left[\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr}\right] - \frac{ke^2}{r}\psi(r) = E\psi(r). \tag{19.13}$$

Now we can treat this like a one-dimensional problem, where our spatial variable is r instead of x.

Re-arranging the equation to isolate the second derivative results in

$$\frac{d^2\psi}{dr^2} = -\frac{2}{r}\frac{d\psi}{dr} - \frac{2m_eE}{\hbar^2}\psi - \frac{2m_eke^2}{\hbar^2}\frac{\psi}{r} \tag{19.14}$$

We will need to plug in some values, and to keep the numbers reasonably nice, let's use eV for energy and nanometers for length. Before we plug in numbers, we can simplify things by plugging the Bohr radius into the last term,

$$a_0 = \frac{\hbar^2}{m_eke^2} = 0.052918 \text{ nm}. \tag{19.15}$$

We also bring in some factors of c to make the units nicer:

$$\psi''(r) = -\frac{2}{r}\psi' - \frac{2(m_ec^2)}{(\hbar c)^2}E\psi - \frac{2}{a_0 r}\psi. \tag{19.16}$$

Now we just need two additional constants:

$$m_ec^2 = 511\,000\,\text{eV} \qquad \hbar c = 197.33\,\text{eV}\cdot\text{nm}. \tag{19.17}$$

Procedure

(a) Download the template `hydrogen.xls` from the PHYS 212 lab folder. Enter the values for a_0, $\hbar c$ and $m_e c^2$ into the appropriate spaces. For the step size use $\Delta r = 4 \times 10^{-4}\,\text{nm}$, and put in an value of $E = -16\,\text{eV}$ to begin with.

(b) In the position column we cannot begin with $r = 0$ since the expression for $\psi''(r)$, Eq. (19.16), has $1/r$ terms in it. That is why we use $r = \Delta r$ for the first row.

For initial conditions, we can set $\psi(r = \Delta r) = 1$. The initial value for ψ' is tricky. What happens is that the two $1/r$ terms in Eq. (19.16) can't really be blowing up as $r \to 0$. Rather, they must be canceling. Therefore we can conclude that

$$\psi' \simeq -\frac{1}{a_0}\psi \qquad \text{for } r \approx 0 \tag{19.18}$$

This gives us our initial value for ψ'.

(c) Carefully enter the expression for ψ'' into the first row. This is where most mistakes will be made!

(d) Now build the second row using the update equations analogous to Eqs. 19.10 and 19.11 to obtain $\psi(r+\Delta r)$ and $\psi'(r+\Delta r)$. Copy the formula from cell `D18` into cell `D19`. Once you have the second row programmed into Excel, you can copy all formulae downwards by highlighting cells `B19`, `C19`, `D19`, moving the cursor to the right bottom corner of cell `D19` until the cursor shows the black + and then double-clicking.

(e) Verify that you obtain for the first three lines the following values:

x (nm)	$\psi(x)$	$\psi'(x)$	$\psi''(x)$
0.004	1	-18.8972	419.937
0.008	9.92E-01	-18.7292	353.928
0.012	9.85E-01	-18.5876	371.727

(f) Once you have entered these initial values, you should see a plot of of ψ vs. r in the graph to the right of your equation cells. Now, increase the value of E successively from $-16\,\text{eV}$ to $-15\,\text{eV}$ then to $-14\,\text{eV}$ etc. and see how the wave function responds. Try to obtain the ground state energy to three digits of accuracy using the same method as you did for the harmonic oscillator. Compare your answer to the accepted value $E_1 = -13.606\,\text{eV}$. How does this compare to the ground state energy you found in the emission spectra lab? Print your graph and put it into your notebook, fill in the dots in $\ldots < E < \ldots$, and draw the **ideal** solution.

(g) Next, use your numerical method to obtain the first excited state energy, E_2. You should change the step size to $\Delta r = 8 \times 10^{-4}\,\text{nm}$. To also change the range of the horizontal axis: double click on the x-axis, that opens the "Format Axis" menu, and set the maximum to a fixed value of 2. Then vary E initially by increasing E in steps of $3\,\text{eV}$. Once you narrowed down E_2 to two values, successively change E until you have three significant figures of accuracy. Compare your value to the accepted value $E_n = E_1/n^2$. Print your graph, specify E and sketch the corresponding ideal solution and put it into your lab notebook.

(h) Change the step size to $\Delta r = 16 \times 10^{-4}\,\text{nm}$ and calculate E_3. Change the x-axis range again to have a maximum value of 3. Compare your result to the accepted value. Print your graph, specify E and sketch the corresponding ideal solution and put it into your lab notebook.

(i) Look at your ideal wave functions for E_1, E_2, and E_3. Which pattern do you find?

STOP Discuss your results with your instructor or a TA.