

Chemistry 125: Instructions for *Erwin Meets Goldilocks*

[Note the 5 problems for Monday's problem set are found at the end of this document. Many of the details on operating the program relate to an earlier version that would run only on a Mac. The new JAVA version is much improved and instructions for operating it are found by clicking "Instructions for getting started with Java version Erwin Meets Goldilocks" on the course homepage.]

To become comfortable with quantum mechanics you must reconstruct an intuition that was formed by activities like throwing balls and stretching springs that have been your daily activities since early childhood, as well as by Newtonian theory from previous science courses, such as "kinetic energy = $1/2 mv^2$ ".

Unfortunately quantized systems are too small for us to experience in any very direct, physical way, and the arcane nature of differential equations keeps most people from gaining experience with quantum theory. The first goal for Chemistry 125 quantum mechanics is to develop a quantum intuition by observing and thinking about some problems and their solutions (without having to do math explicitly). Then we'll go on to treat atoms and bonds.

Erwin meets Goldilocks is a homebuilt tool for Chem 125 that allows you to dabble with the ideas of quantum mechanics without worrying about its mathematical complexities. It treats a very simple problem (**one particle in one dimension**) and draws wave functions that satisfy the Schrödinger equation. Using *Erwin* to see what happens as you change mass, total energy, and potential energy functions can build a valuable intuition about many of the most important and surprising phenomena of quantum mechanics, such as:

Why energies are quantized under some conditions, not under others

Why atoms don't collapse

What makes a bond

Why there is "zero-point energy"

How atoms or electrons can "tunnel"

Erwin provides a sort of quantum mechanical laboratory where you can learn by observing.

The time-independent Schrödinger equation can be rearranged into the following form, which is a formula for the *curvature* of the wave function Ψ :

$$d^2\Psi/dx^2 = \text{mass} * \Psi * (\text{potential energy} - \text{total energy}) * (\text{a known positive constant})$$

For present purposes being given this formula is practically as good as being given Ψ itself, because as long as you know the amplitude and slope of Ψ at any one

point,¹ you can start drawing Ψ there and use the curvature given by the equation to guide your pen along the proper path as potential energy and Ψ change. This is exactly what the program does. It starts at the left of the screen with small positive amplitude and zero slope,² calculates the curvature, moves to the next point to the right, calculates the new slope and the new curvature, and so on. *As long as the slope isn't changing too rapidly*, this point-by-point extrapolation will work fine.

Wherever the total energy is greater than the potential energy, the curvature (positive when Ψ is negative, negative when Ψ is positive) is such as to lead the function back toward the $\Psi = 0$ baseline. But in the "classically forbidden" regions (where potential energy is greater than total energy) Ψ can run into trouble, shooting off to + or - infinity. Only by choosing just the right values of total energy can you avoid this and have Ψ approach the baseline asymptotically. In bound situations (where potential energy exceeds total energy in the far regions at both ends), the energy of systems is quantized in order to give well-behaved, non-infinite wave functions, which, as far as we can tell from Nature, are the only type that can represent reality in these situations.

To run the program you must first **define the problem** by choosing a *mass* for the particle and a form for the *potential energy* as a function of position. To get started you might choose 1 for the mass (the mass of a proton) and specify one of the potential energies from the following list (depending on the choice there may be more parameters to specify):³

Constant (zero) potential energy. This is like a particle in free space.

Decaying Exponential potential energy that starts very high on the left and falls to become essentially constant at zero on the right. This is like a particle in free space which can run into a softish wall on the left.

Harmonic Oscillator. This parabolic potential is often used as a crude approximation of a bond holding the particle (atom) whose mass you have specified. Such a potential is unrealistic, since the force pulling the atom back to the center always keeps increasing, and the bond can never break, but has been much studied because of mathematical tractability. If you choose the harmonic oscillator you must specify the *strength* of the bond

¹ The initial amplitude can be set arbitrarily, since multiplying Ψ by a constant makes no difference in its ability to solve the Schrödinger Equation. In the following applications, it is safe assume that at the far left of the region of interest the slope is zero, or close enough to zero to make no difference. Soon you'll be able to figure out why this is so.

² The mass can be subsequently altered with the *Define Problem / Mass*.

³ Initial parameters for a given type of potential can be altered with *Plot / Edit*. The type of potential may be changed by returning to *Define Problem / Potential*.

that holds your particle by typing 1 for a single bond, 2 for a double, etc. Fractional values are OK.

Double Minimum is a potential from two intersecting parabolas. This would represent a particle that is attracted to two other particles, one on the left, the other on the right by inverse force laws. Classically it would have to gather some energy to jump from one well to the other, that is, to move from being bonded from one neighbor to being bonded to the other. This potential is ideal for studying the phenomenon of tunneling, and the closely related phenomenon of chemical bonding. Here you are asked to specify five parameters: the *bond strengths* on either side of the middle (one bond could be stronger, but you might begin with them equal), the *distance* in Å between the bottoms of the two wells (how far the particle has to move to change bonds - try something fairly small at first, perhaps 0.5Å), the *difference in depth* of the two wells (you might try 0 kcal/mole at first), and the amount of "*coupling*" (this is the amount by which you decide to lower the energy at the otherwise sharp intersection of the two parabolas, it makes the potential more realistic by allowing forming the bond to the new neighbor to help offset the energy requirement of breaking the old one).

Morse is a more realistic bonding potential than the harmonic oscillator, because it describes a bond that can break. It is characterized by *depth*, the energy required to break the bond, and by the curvature at the bottom of the potential energy well, which is expressed in terms of the equivalent "*harmonic bond strength*" (1 for single bond, 2 for double, etc.). For plotting purposes you must also specify the *distance* in Å of the potential energy minimum from the left edge of the screen.¹

Coulombic (1/distance) potential. This is a sort of one-dimensional H-like atom (electron in the field of a nucleus). It needs special attention because as the distance approaches zero, the potential energy falls without limit and the curvature would become infinite. There are some bugs in this part of the program, but you should at least see what kind of solutions this potential has. Remember to choose the small mass of the electron. You are asked to specify a horizontal *plot range* (electrons are so light that they can cover much more territory than nuclei), a *maximum calculable binding energy*, *i.e.* how far below the energy of separated particles you want the graph to

¹ For the Morse potential the auto-solve feature of the program may give an erroneous solution that does not approach the baseline asymptotically. If that happens with the Morse or another confining potential, increase the horizontal plot range (Dimensions/Distance) until the approach becomes asymptotic.

extend (the true potential energy decreases without limit near the nucleus), and the *nuclear charge*.

When you have specified the potential, click the **Create** button to see a plot of the potential. You may want to rescale the potential energy by changing the upper and lower limits of the plot (**Dimensions / Energy**), or you could change the horizontal range of particle position in Å (**Dimensions / Distance**). The boundary between gray and white shows the potential energy (you can change the appearance of the potential plot with **View / Potential Fill Color** or **Potential Border Color**).

You have stated the problem by specifying the mass and the potential, you need to find the shape of the wave function for the particle in this potential. So now click **New Solution** to give a colored window to use for your **guessing game**. You are asked to guess a value for the total energy. The computer then superimposes a plot of Psi with the same horizontal axis as the potential plot. This horizontal axis is the position of the particle in Å.

So there are two graphs: **One graph** is of energy and its vertical axis goes from zero on the bottom to a value shown at the top left.¹ The energy plot includes **both** the **potential** you have chosen and a **horizontal dashed line** showing the **total energy** you have guessed.

The other graph, superimposed on the energy one, shows the **trial wave function**, which the computer draws (according to the total energy you guessed) as a **solid line** with $\Psi = 0$ being a horizontal line across the center of the plot area. Don't be confused by the superposition. It is handy because the two plots have the same horizontal axis (particle position), which makes it easy to see the influence of energy on the shape of the wave function.

If the wave function doesn't shoot off to + or - infinity anywhere, you've guessed a proper energy and found a solution (Congratulations! You're either fabulously lucky or you chose a non-quantized system). If it does shoot off, you need to change your energy guess in the attempt to keep Ψ finite. You do this by editing the **Energy** value colored solution window. Much of your sense of what it means to be quantized will be developed by the process of guessing again and again, trying to figure out what will constitute a good guess. (Don't use the *Solve* option, designed for wimps and people in a hurry who have already mastered the concept, until you've really grasped this.)

By clicking **New Solution** you can launch a new guess with a different color (chosen through **Color**).

You can spend a lot of time trying to guess an energy that will keep Ψ finite all the way to the right of the screen. For most quantized problems the program can't express numbers precisely enough to achieve this goal. It becomes a case of bracketing a proper energy between one that is too high (and shoots off one way to

infinity) and one with one fewer nodes that is too low (and shoots off the other way). This is where Goldilocks comes in. Some players get enthralled and continue guessing to bracket the solution more and more tightly, until they reach the limit of the computer's precision or their patience.

When you've gotten the idea firmly and are tired of spending so much of your time guessing, you can use the **Solve** button in the New Solution window to do the guessing automatically and find the next-higher-energy (or next-lower-energy) solution from your current guess.¹

It is possible to save and recall your work under **Project**.

You can see the plot of probability distribution (Ψ^2), by checking the **prob** box in the solution window.

As you plot wavefunctions think (in term of the Schrödinger Equation) about how and why they vary with mass, total energy, potential energy. Think about where the particle spends its time in states of different energy (Ψ^2 is good for this). Think about the relation of nodes to energy. Think about what is determining the curvature of Ψ . Think why there can't be a node in a forbidden region at one end of the graph.

If you don't think carefully, your intuition won't develop as rapidly.

GROUP PROBLEMS FOR SEPTEMBER 22

Mostly I'd like you to play around with the program, making discoveries of your own, so as to build your quantum intuition. You should each learn enough to be able to answer the following questions. It is unrealistic to think that each of you will have time to make all of these discoveries for yourself and write up answers, so I suggest that you form groups of up to five students and collaborate (Experience suggests that 3 in a group gives the best learning. You can turn in one set of answers on Monday, September 24 for the group as a whole. Get together and discuss what you're finding as you go along, then assign the write-up responsibilities for different problems (or parts of problems) to different individuals. Teach each other what you've learned. Don't just copy or let your friends learn without explaining to you. Don't allow yourself to get frustrated. If in working together you don't see the answer, seek help. It's simplest to work the problems in the order given. **Start early.**

¹ Solve works by guessing and bracketing, just as you do, and it doesn't make Ψ exactly asymptotic on the right either, it just finds a very good approximation. In fact numerical approximations are used that mean the wave functions and energies are **not precisely accurate** anyway. For example, choosing a high total energy - say 400 kcal/mole - for a particle of mass 1 with constant potential energy should give a cosine wave, but the program plots a wave with increasing amplitude because of accumulating error. **This problem is especially acute when wavelengths are short.** If you want to try moderating this problem you can reduce the **step size** under Modify Details.

Troubleshooting: The most common difficulty for beginners is when the program appears to draw no Ψ at all. This results from choosing systems that involve too large a range in which the potential energy is far above the total energy, so that the computer isn't precise enough to keep Ψ manageable over the range of interest. You can narrow the range (or increase the total energy). You can get a nonsensical Ψ by guessing too high a total energy (or mass), making the wavelength too small for the program's approximations to deal with properly.

WARNING: The observations and questions in the problem set below make excellent exam fodder.

1. Use **constant** potential energy to study how mass and total energy influence Ψ . Try to discover quantitative relationships. [This relates to using an electron microscope to "see" objects with high resolution (the electron's mass is 0.00054 of the proton's; because it's so light try 50 kcal/mole and 10Å plot width for a start)].

2. Use the **exponential** potential energy to see how easy it is to find a satisfactory Ψ when the system is confined on only one side. In what ways is this Ψ similar to the Ψ for constant potential energy? *Explain* the behaviour of Ψ in regions of negative kinetic energy. How can you tell *by looking at Ψ* what region has potential energy greater than total energy (and thus negative kinetic energy) and at what point they are the same (zero kinetic energy)?

3. Use the **harmonic oscillator** to see how hard it is to find a satisfactory Ψ when the system is energetically confined ("bounded") on both sides. Find the lowest energy Ψ (no nodes) and the next lowest (one node). Then try to predict at what energies other successive Ψ s will be found, and see if you are right. What is the pattern of allowed energies, and how does it relate to the lowest possible energy? (This so-called *zero-point energy*, of the Ψ with zero nodes, is the minimum energy such a system must have even at absolute zero of temperature.) What happens to the lowest allowed energy if you double the mass, and how does it change with the strength of the bond?¹ Where does the particle with the lowest allowed energy spend most of its time? How about one in the tenth energy level? (Where does a classical pendulum spend most of its time?)

4. Use the **Morse** potential to see how a system can be quantized for some energies and not for others. How similar is its progression of allowed energies to that of the harmonic oscillator with the same bond strength?

¹ This is the source of proton/deuterium isotope effects.

5. Use the **double minimum** potential to see how a particle can "tunnel" through a region where it has negative kinetic energy. Do this by finding a pair of satisfactory Ψ s with energies that are near, but below, the top of the hill between two equivalent valleys. The lower one must have an even number of nodes, and the upper one must have one additional node. The energy difference between these functions, expressed as a frequency, is how fast the particle would tunnel through the energy barrier (multiply kcal/mole by 10^{13} to get jumps per second).