

Visualizing Particle-in-a-Box Wavefunctions using Mathcad

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Abstract

Using the built-in differential equation solvers and graphical capabilities of Mathcad, students can visualize the wavefunctions of the particle-in-a-box potential. By applying the mathematical requirements of the wavefunction, the particle-in-a-box is seen to have quantized energies. By plotting possible solutions, students are able to visualize the consequences of requiring the wavefunction to be continuous. Also, the step potential and barrier potential can be examined thus allowing students to see how requiring the wavefunction to be finite results in the quantum mechanical phenomenon of tunneling. The instructor notes, also available at JCE Online, include graphics from Mathcad that illustrate some of the peculiar features of the simple particle-in-a-box, the step potential and the double well barrier potential.

Keywords: Computational Chemistry, Physical Chemistry, Quantum Chemistry, Theoretical Chemistry

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Instructor's Notes

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Introduction

The application of the one-dimensional particle-in-a-box potential to the Schrödinger equation is one of the first quantum mechanical models introduced to beginning physical chemistry students (1-4).

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

where \hbar is the reduced Planck's constant, $\hbar = h/2\pi$, m is the particle mass, $V(x)$ is the potential energy, $\Psi(x)$ is the wavefunction and E is the energy eigenvalue. The mathematics software program, Mathcad, has been used as an aid to teach students a variety of concepts in quantum chemistry (5,6). One application of the program has been to visualize quantum mechanical wavefunctions (7,8). In addition, Mathcad worksheets have been constructed to find solutions to the Schrödinger equation numerically (9,10). Other applications of the Mathcad program for the particle-in-a-box problem have been presented in this Journal (11,12). Additionally, other mathematical software packages (13) such as Mathematica (14,15) and Maple (16) have been used to illustrate solutions to the Schrödinger equation and specifically, the particle-in-a-box wavefunctions.

The solutions of the Schrödinger equation, aptly known as wavefunctions, have severe restrictions if they are to contain physically meaningful information.

- i. The wavefunction must be finite everywhere.
- ii. The wavefunction must be continuous everywhere.
- iii. The first derivative of the wavefunction must be finite.
- iv. The first derivative of the wavefunction must be continuous.
- v. The wavefunction must be normalizable.

The rationales behind some of these restrictions are illustrated by examining possible solutions to the particle-in-a-box model.

The potential energy for the particle-in-a-box can be expressed as

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & x < 0, x > L \end{cases}, \quad (2)$$

where L is the length of the box. Finding the analytic solution for the particle-in-a-box potential is a relatively easy endeavor. The Schrödinger equation is a simple second-order differential equation. The general solution of the equation is the same solution for the model of a particle-in-free-space. The particle-in-free-space solution, i.e. the wavefunction, can be expressed in two different ways.

$$\Psi(x) = A \sin\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} x + B \cos\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} x. \quad (3)$$

$$\Psi(x) = A'e^{i\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} x} + B'e^{-i\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} x}. \quad (4)$$

Solution (3) contains only real arguments and easily illustrates the static properties of the model such as the probability density. Furthermore, solution (3) makes the application of the boundary conditions easier. Solution (4) contains complex arguments and illustrates the quantum dynamics of a particle trapped inside a box (17,18). In this exercise, using solution (3) is most convenient.

Since the wavefunction must be continuous, the wavefunction is subject to the following boundary conditions

$$\Psi(0) = 0, \quad (5)$$

$$\Psi(L) = 0. \quad (6)$$

Application of the boundary condition (5) on solution (3) yields $B = 0$. Application of boundary condition (6) on solution (3) yields

$$\Psi(L) = A \sin\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} L = 0. \quad (7)$$

However, $\Psi(L) = 0$ if and only if

$$\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} L = n\pi \Rightarrow E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}. \quad (8)$$

Thus forcing the wavefunction to be finite, i.e., applying boundary condition (6), yields the quantization of the energies in the particle-in-a-box model as well as the quantization of the wavefunctions. This quantization is characteristic of any quantum mechanical particle within a potential well.

The quantization of the wavefunction and the quantization of the energy are also related to each other via the curvature of the wavefunction. The Hamiltonian operator for the particle-in-a-box is the kinetic energy operator. The kinetic energy operator is proportional to the second derivative of the wavefunction whereas the second derivative of a function is a measure of its curvature. Thus, quantization implies that our wavefunction must have the correct curvature to satisfy the boundary conditions. This condition creates a visual cue that permits the student to picture whether a chosen energy eigenvalue is too low or too high.

Method: Details of the Mathcad Worksheet

An exercise for the quantum chemistry portion of an undergraduate physical chemistry course has been created using the mathematics program, Mathcad. The program allows for the numerical solution of the Schrödinger equation using the Runge-Kutta method or Bulirsch-Stoer method. In the exercise described below, both methods can be used; however, the Runge-Kutta method is most general; thus, it will be used in examples that follow.

Construction of the potential function

Mathcad's programming features allow for the construction of a piecewise continuous potential function such as the square box potential. These features are available in Mathcad 8.0 and higher. To create a piecewise function, the feature *add line* is used on Mathcad's programming toolbox. Potential regions can be specified using the *if* and *otherwise* features. Figure 1 is an example of a simple square box potential.

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq 4 \\ \infty & \text{otherwise} \end{cases}$$

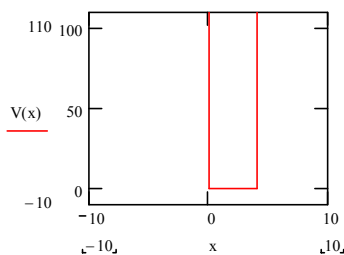


Figure 1: Square box potential using piecewise continuous functions in Mathcad.

To create similar potentials such as step potentials and barrier potentials, the student needs to use the *add line* and *if* programming features. See Figures 2 and 3 for examples.

$$V(x) := \begin{cases} 0 & \text{if } 0 < x < 2 \\ 20 & \text{if } 2 \leq x < 4 \\ \infty & \text{otherwise} \end{cases}$$

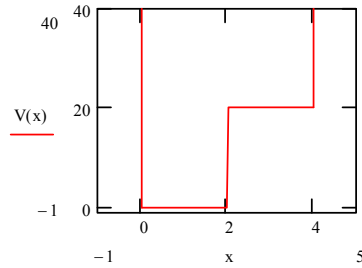


Figure 2: Step potential using piecewise continuous functions in Mathcad.

$$V(x) := \begin{cases} 0 & \text{if } 0 < x < 1.5 \\ 10 & \text{if } 1.5 \leq x < 2.5 \\ 0 & \text{if } 2.5 \leq x < 4.0 \\ \infty & \text{otherwise} \end{cases}$$

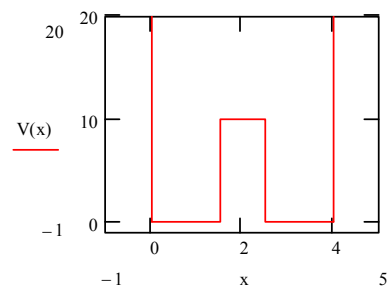


Figure 3: Barrier potential using piecewise continuous functions in Mathcad.

The infinity value used for the walls of the box is acceptable to plot the potential energy function. However, the value of the wall needs to be finite when the potential function is used in the numerical differential equation solvers. Choosing a wall height such that the wall height/box width ratio of approximately 100 yields consistent energy values for the first dozen or so energies.

Defining the differential equation

Once the potential is defined, the differential equation is constructed by creating a derivative vector that defines the derivatives of the solution and their relationships.

$$D(x, y) := \begin{bmatrix} y_1 \\ 2(V(x) - E) \cdot y_0 \end{bmatrix}$$

The top element of the above vector contains the first derivative and the bottom element contains the second derivative. Note that setting the second derivative equal to the bottom element yields the Schrödinger equation for

the particle-in-a-box in atomic units where the reduced Planck's constant, \hbar , and the mass of the particle (electron) are both unity. The correct energy eigenvalues for the simple particle-in-a-box will have the following form,

$$E_n = n^2 \pi^2 / L^2 .$$

Constructing a numerical solution of the differential equation

The solution, labeled ψ in the example below, is found using either one of Mathcad's built-in numerical differential equation solvers. The *rkfixed* function uses the Runge-Kutta method, whereas the *bulstoer* function uses the Bulirsch-Stoer method. Either method will calculate satisfactory results. The Runge-Kutta method will be used for the illustrations in this paper.

$$\psi := \text{rkfixed}(y, 0, 4, 800, D)$$

The arguments, which are the same for both the *rkfixed* and the *bulstoer* function, are as follows. The first argument, y , supplies the function with initial values for the solution and its first derivative. y is a 2×1 vector that needs to be defined before ψ is defined. For the particle-in-a-box, the solution is zero when the coordinate is zero. The first derivative at zero coordinate is set to one arbitrarily. The initial value of the first derivative will not change the energy eigenvalues but will affect the scaling of the solution's plot. The second and third arguments define the endpoints of the solution. The fourth argument defines the number of evaluation points and the fifth argument is the derivative vector discussed above. The number of evaluation points affects the accuracy of the wavefunction. An adequate number of points is especially important for evaluating the function when tunneling is involved. The examples in this paper use 800 evaluation points. For slow computers, at least 300 points should be used to find a reasonably accurate wavefunction.

Supplying initial guess for energy eigenvalue

The final input needed is the energy eigenvalue. The student supplies an initial guess for the eigenvalue. Since Mathcad evaluates worksheets left to right and top to bottom, the definition for the energy eigenvalue must be above the definition of the derivative vector. Once the eigenvalue guess has been supplied, the worksheet can be evaluated to find the solution.

Plotting the numerical solution on x-y graph

The numerical solution of the wavefunction is returned as an array where the rows are the evaluation points and the columns are the coordinate, solution and solution first derivative respectively. The solution can be plotted in the standard Mathcad fashion using the first column of the solution array for the abscissa and second column of the solution array for the ordinate. The columns of the array can be inputted into the placeholders of an x-y graph by using the *matrix column* button on the *matrix* toolbox or by typing the name of the solution and accessing the matrix column template by the keystroke *Ctrl 6*.

Adjusting the energy eigenvalue so boundary condition is met

Once the solution is plotted, the student can see whether an appropriate energy eigenvalue has been chosen. The boundary condition fixes the value of the wavefunction at the left-hand side of the box at zero. For an arbitrary guess of the energy, the value at the right-hand side could have any value. One of the goals of the exercise is to find the appropriate energy eigenvalues that lead to a wavefunction with a value of near zero at the right-hand side of the box.

Visualizations of Particle-in-a-Box Wavefunctions

One-dimensional particle-in-a-box potential

As stated above, the curvature of the wavefunction is related to the kinetic energy of the particle-in-the-box. In the exercise, the student adjusts the curvature of the wavefunction by adjusting the energy eigenvalue. If the curvature of the wavefunction is too high, the energy eigenvalue must be lowered. If the curvature is too small, the energy eigenvalue must be raised. Using these visual cues, the student should be able to begin to find an accurate value for the energy. Once inspection of the graph is not able to discern between the results of energy guesses, the x-y trace feature can be used to find the value of the wavefunction at the right-hand side of the box. This relationship between the curvature of the wavefunction and the energy guess is illustrated in Figure 4.

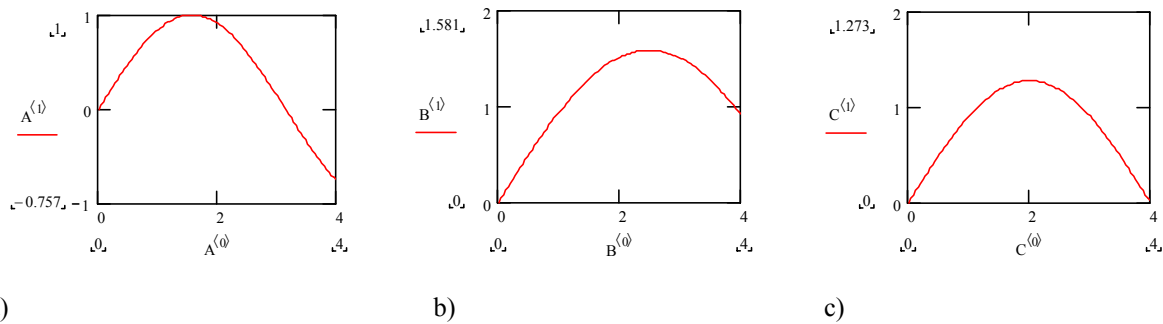


Figure 4: Plots of trial solutions to square box potential.

- a) Energy guess is too high; curvature is too high
- b) Energy guess is too low; curvature is too low
- c) Energy guess is correct; curvature is correct. Boundary conditions have been met.

The number of acceptable energy eigenvalues that permits the wavefunction to meet the boundary conditions is infinite. Thus, many eigenvalues can be found. The student can be assisted in finding an inclusive set of eigenvalues between any two quantum numbers (e.g., between 1 and 10) by the number of nodes seen in the wavefunction. The number of nodes of the wavefunction is equal to the quantum number plus one when the sides of the box are included as nodes. See Figure 5. Once a set of eigenvalues has been found, the students are asked to find a relationship between the energies and the quantum number. The correct energy eigenvalues yield the analytic relationship that the energies are proportional to the square of the quantum number.

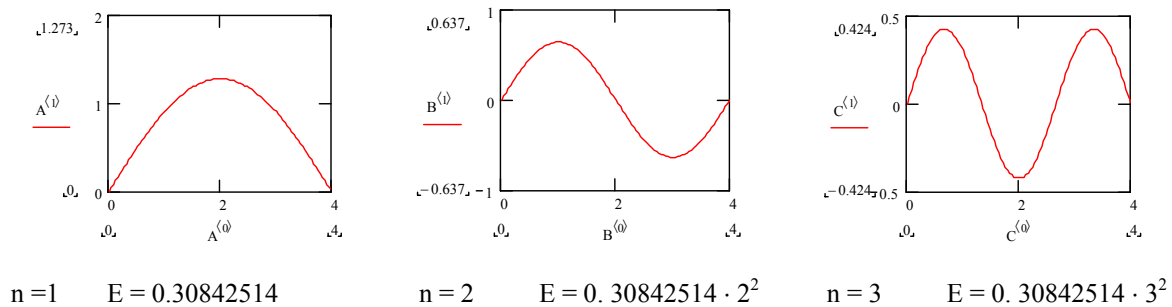


Figure 5: Plots of the first three particle-in-a-box wavefunctions with their energies. The plots illustrate the relationship between nodes of the wavefunction and quantum number.

The energy eigenvalues change as the width of the potential changes. Students are asked to vary the length of the box to find the relationship between the energies and box length. Finding the first five energy levels of square

box potentials with half the original length and double the original length allows the student to find the relationship between the energy eigenvalues and the length of the box. One of the goals of the lab is to have the students recognize the dependence of the energy on the length of the box, $E \propto 1/L^2$

Step potential

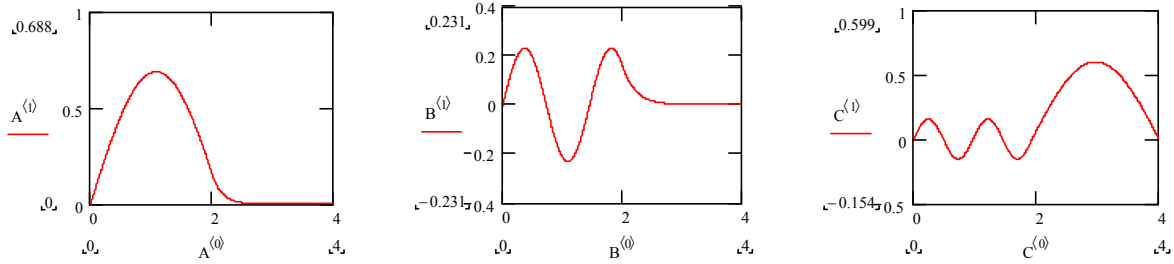
The quantitative investigations finish with the pure particle-in-a-box; however, qualitative investigations continue by examining the step potential and the barrier potential. The same procedure is used to find the energy eigenvalues; only the potential energy function changes.

The students begin the investigation by being given a step potential where the length of the step is half of the box length. Students are asked to find the first five energies and qualitatively compare them to the energies found from the potential of the same width with no step. Comparing energies with the same quantum number, the energies for the step potential are higher than the energies for the simple square box potential. The students should find this result sensible since the particle in a step potential is influenced by a greater amount of potential energy.

Hopefully, the students will make two qualitative observations about the wavefunctions for a step potential.

- 1) The wavefunctions for energies less than the step height demonstrate the phenomenon of tunneling. As the energy of the wavefunction approaches the step height, the tunneling is more prominent.
- 2) The wavefunctions for energies greater than the step height demonstrate a decrease in the curvature of the wavefunction above the step. The decrease in curvature of the wavefunction shows a decrease in kinetic energy of the particle.

Thus, the student can see that when a particle of a given energy increases its potential energy, the kinetic energy of the particle must decrease correspondingly. The change in the curvature of the wavefunction demonstrates this conservation of energy. This effect is dramatic when the particle energy is close to the step height. The decrease in the kinetic energy also increases the probability density of the particle over the step since the particle slows as its kinetic energy decreases. See Figure 6.



$n = 1 \quad E = 1.05732840$

$n = 3 \quad E = 9.38822998$

$n = 5 \quad E = 21.14894371$

Figure 6: Plots of the first three odd step-potential wavefunctions with their energies for the potential $V(x) = 0$ when $0 < x < 2$ and $V(x) = 20$ when $2 < x < 4$. The first two plots illustrate how the degree of tunneling increases as the particle energy becomes closer to the step height and the third plot illustrates how the potential energy of the step affects the curvature of the wavefunction.

To illustrate the necessity of tunneling to keep the wavefunction finite, the students are instructed to attempt to find the energy value where the wavefunction is zero at the edge of the step. In other words, the students attempt to keep the wavefunction in the classically allowed region. The energy value cannot be found; however, in the attempt, the students see that the wavefunction at the right-hand side of the graph goes to infinity. Thus, the students confirm visually that the correct wavefunction cannot end in the classically allowed region. The wavefunction must intrude into the classically forbidden region, i. e. tunnel, if the wavefunction is to be finite. See Figure 7.

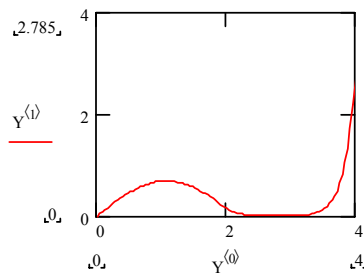


Figure 7: An illustration of how the step potential wavefunction diverges as one attempts to force it to be contained in the classically allowed region, $0 < x < 2$.

Barrier potential

The tunneling phenomenon is illustrated also with the solutions to the barrier potential. The students examine the solutions to a barrier potential where the barrier is centered in the box. Students are asked to find the first five energies and qualitatively compare them to the potential of the same width with no barrier. Increasing the height or

the width of the barrier increases the energy eigenvalues when compared to energy eigenvalues of the simple box.

As in the case of the step potential, the students should find this result sensible since increasing the potential energy of the particle will increase the total energy of the particle.

The observations about the wavefunction that the students make for the step potential are valid for the barrier potential: the penetration of the tunneling particle increases as the particle energy approaches the barrier height and the curvature of wavefunction decreases over the barrier. See Figures 8, 9, 10.

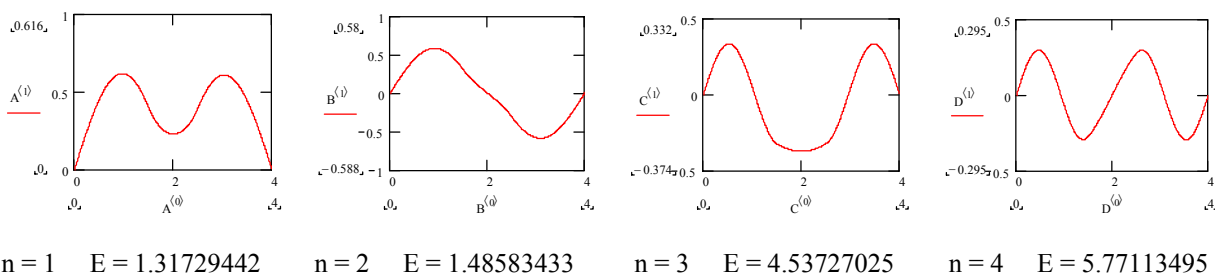


Figure 8: Plots of the first three barrier potential wavefunctions with their energies for the potential, $V(x) = 0$, when $0 < x < 1.5$, $2.5 < x < 4.0$ and $V(x) = 4$ when $1.5 < x < 2.5$. The plots illustrate how the potential energy of the barrier affects the curvature of the wavefunction.

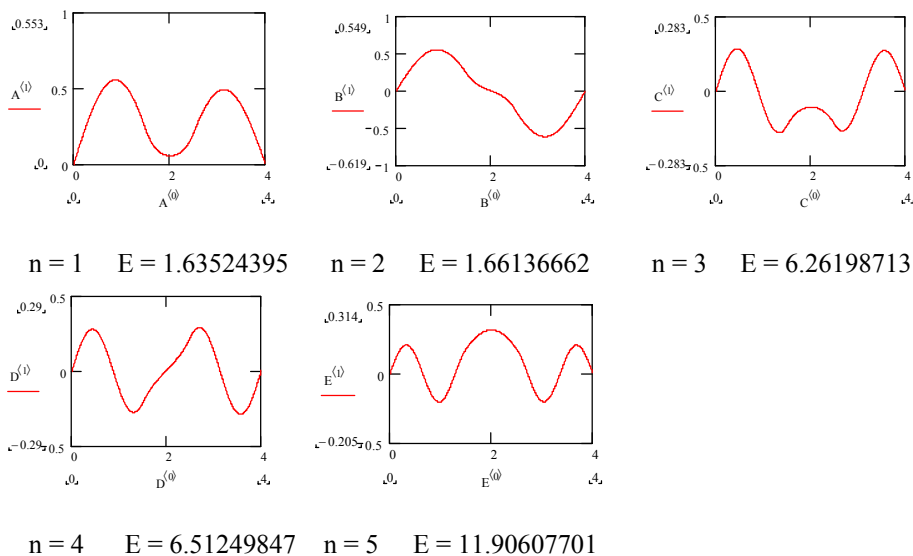
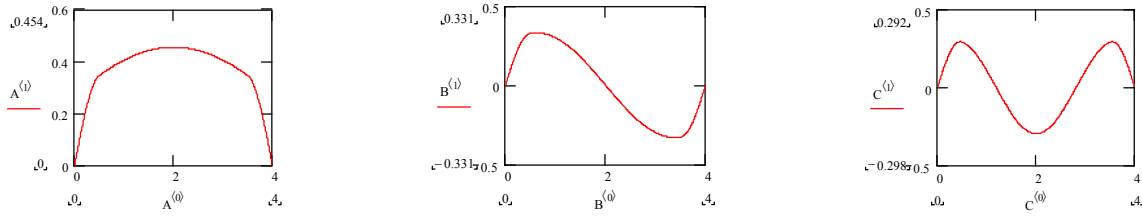


Figure 9: Plots of the first five barrier potential wavefunctions with their energies for the potential, $V(x) = 0$, when $0 < x < 1.5$, $2.5 < x < 4.0$ and $V(x) = 10$ when $1.5 < x < 2.5$. Note the increased barrier height increases the energy eigenvalues in comparison to those in Figure 8.



n = 1 E = 4.11098435

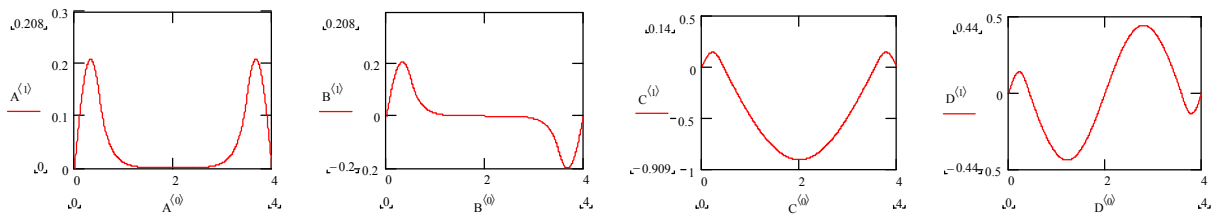
n = 2 E = 4.64390436

n = 3 E = 5.86515178

Figure 10: Plots of the first three barrier potential wavefunctions with their energies for the potential, $V(x) = 0$, when $0 < x < 0.5$, $3.5 < x < 4.0$ and $V(x) = 4$ when $0.5 < x < 3.5$. Note the increased barrier width increases the energy eigenvalues in comparison to those in Figure 8.

Increasing the barrier height causes the energy eigenvalues to group as approximately degenerate pairs. Degeneracy occurs when the barrier has infinite height. When the barrier height is finite, the lack of barrier potential energy acts as a perturbation and thus forces the “degenerate” states to split according degenerate time-independent perturbation theory. (19) The splitting becomes greater as the perturbation becomes greater, that is, the splitting of the nominally degenerate energy levels increases as the total energy of the particle approaches the energy of the barrier height.

As mentioned earlier, the number of evaluation points used to calculate the wavefunction is important when finding a wavefunction that tunnels through a barrier. If too few evaluation points are used, the solutions become asymmetrical. These asymmetrical solutions are false since they do not match the symmetry of the Hamiltonian (20). Also worth noting is that when the barrier is too high, the solutions become too sensitive to the eigenvalue guess. Poor guesses yield out-of-bounds results ($> 10^{307}$). Thus finding the eigenvalue becomes difficult.



n = 1 E = 11.51595735

n = 2 E = 11.51595965

n = 3 E = 25.50444553

n = 4 E = 26.97911380

Figure 11: Plots of the first four barrier potential wavefunctions with their energies for the potential, $V(x) = 0$, when $0 < x < 1.5$, $2.5 < x < 4.0$ and $V(x) = 25$ when $1.5 < x < 2.5$. The energy values illustrate how the wavefunctions become approximately degenerate as the barrier height is increased.

Observations in the Classroom

The laboratory has been assigned during the fifth week of the semester of a junior-level quantum chemistry course after the particle-in-a-box model is introduced in lecture. The laboratory is the students' first exposure to the Mathcad program; therefore, the first hour of the lab is spent introducing the students to Mathcad's features and syntax. By providing instruction about several useful keystrokes and the toolbars available, students quickly grasp the WYSIWYG nature of the Mathcad worksheet. Continued use of the graphical capabilities and the symbolic algebra processing power of the Mathcad program occurs in the sixth week of the laboratory when the students investigate the properties of the Hermite, Legendre and Laguerre polynomials.

In constructing the lab, the following list of pedagogical goals was made.

- 1) Seeing a variety of particle-in-a-box wavefunctions with different potential functions.
- 2) Seeing how the application of boundary conditions forces the energy levels of the particle-in-a-box to be quantized.
- 3) Verifying the relationship between quantum number and energy for a simple particle-in-a-box.
- 4) Verifying the relationship between the length of the box and energy for a simple particle-in-a-box.
- 5) Seeing how the requirement for a finite wavefunction forces tunneling into a potential barrier.
- 6) Seeing how increasing the potential energy decreases the kinetic energy and thus decreases the curvature of the wavefunction.
- 7) Gaining an intuitive feel for an iterative numerical process.

Goal number 1 is easily met. Successfully accomplishing goal 2 is more difficult. Some students blur the distinction between the application of the algorithm developed to visualize the wavefunctions and the application of boundary conditions. For example, students will properly adjust the widths of the potential functions but not adjust the range of evaluation within the arguments of the differential equation solver. Goals 3 and 4 are usually met. Students that are more aware are able to recall the relationships from lecture and use the relationships to make the hunt for energy eigenvalues of the simple square box potential much easier. Other students need time outside of class to reflect upon the relationships. Goal 5 is easily met and its achievement is one of the major successes of the laboratory. Goal 6 is realized only by the best students. So far, most of my students have missed initially the relationship between the wavefunction's kinetic energy and the curvature of the wavefunction and that such a relationship is well demonstrated by the wavefunctions of the step and barrier potentials. The success of goal 7 is mixed. The students learn how to converge upon a good eigenvalue by evaluating the value of the wavefunction at

the potential wall. Thus, they do learn how to iterate. They gain experience in understanding numerical tolerance when doing calculations. An infinitely precise energy eigenvalue will yield a wavefunction value at the end of the box of zero. However, the students do not find an infinitely precise eigenvalue; thus, the students gain an intuition about judging when a numerical calculation is “good enough”. A drawback to the lab is the tedium of searching for the energy eigenvalues. The monotony can be discouraging and may reduce the pleasure of doing the lab. Perhaps a method using solve blocks could be constructed to reduce the tedium and to allow for more investigation.

Additionally, the following are common points of student confusion as they perform the laboratory:

- 1) The difference between the relational equals sign ($:$) used to create definitions and the calculation equals sign ($=$) used to evaluate expressions.
- 2) The wavefunctions are graphed by plotting two columns of an array. The column of the array looks like a simple superscript (keystroke \wedge) but must be designated with another keystroke (*Ctrl 6*).
- 3) How Mathcad evaluates worksheets. Evaluation occurs left to right then, line-by-line, top to bottom. Sometimes a student will have an equation in an incorrect spatial relationship relative to the rest of the worksheet.

All of these misunderstandings are easily corrected if the instructor is cognizant of them.

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