Visualizing Particle-in-a-Box Wavefunctions©

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Prerequisites

This document was constructed for use in a physical chemistry computational modeling laboratory using Mathcad 8.0. To use the Mathcad worksheet, students need a minimal amount of experience with the program. Instructions have been written as to allow the student to construct the worksheet keystroke by keystroke. Students should have a rudimentary understanding of the particle-in-a-box problem as covered in texts such as:

Physical Chemistry, 3rd ed., Keith J. Laidler and John H. Meiser, Houghton Mifflin Co., (1999).
Physical Chemistry, 6th ed., Peter W. Atkins, W. H. Freeman and Co., (1998).
Physical Chemistry, 3rd ed., Robert J. Silbey and Robert A. Alberty, John Wiley and Sons, (2001).
Physical Chemistry, 5th ed., Ira N. Levine, McGraw-Hill, (2002).

Learning Goals

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.

Learning Objectives

At the end of this exercise you should be able to:

1) Compare and contrast the wavefunctions for a particle in a box when V=0 throughout the box to the situations where there is a step potential in the box or a barrier potential in the box.
2) Explain how the boundary conditions forces the energy levels of the particle-in-a-box to be quantized.
3) Verify the relationship between quantum number and energy for a simple-particle-in-a-box.
4) Verify the relationship between the length of the box and energy for a simple particle-in-a-box.
5) Describe tunneling with respect to the barrier and step potential in a box. Explain how the wavefunctions behave under these conditions.
6) Correlate curvature of a wavefunction with the energy associated with the wavefunction and the potential and kinetic energy components of the total energy.

INSTRUCTOR NOTE: The laboratory procedure follows below. Instructors notes are given in green text. Students should be given a student version to use during a laboratory session. Instructors annotations are removed in the student version.

Introduction

The particle-in-a-box is usually the first or second potential energy function considered when quantum chemistry students begin solving the Schroedinger equation. The potential function consists of putting a particle with no potential energy between two walls that have infinite potential energy. A general solution or wavefunction for the particle inside the box is

$$\psi(x) := A\cdot\sin\left[\left(\frac{8\cdot\pi^2\cdot m\cdot E}{h^2}\right)^{\frac{1}{2}} x\right] + B\cdot\cos\left[\left(\frac{8\cdot\pi^2\cdot m\cdot E}{h^2}\right)^{\frac{1}{2}} x\right].$$

where n is the quantum number, m is the particle mass and h is Planck's constant.

This general wavefunction is the same wavefunction as for a particle-in-free-space, that is, a particle no potential energy anywhere. However, the particle-in-a-box wavefunction becomes different than the particle-in-free-space wavefunction when the boundary requirements of the wavefunction are forced upon it.

The wavefunction must thus meet the following requirements if the wavefunction is to contain meaningful information.

1. The wavefunction must be finite everywhere.

3. The wavefunction must be continuous everywhere.
4. The first derivative of the wavefunction must be continuous everywhere.
5. The wavefunction must be normalizable. (The integral of the square of the wavefunction over all space must be finite.)

The most relevant requirements for our purposes are that the wavefunction must be finite everywhere and that the wavefunction must be continuous everywhere. These requirements, sometimes referred to as boundary conditions, force the value of the wavefunction at the walls of the box to be zero, that is.

$$\psi(0) := 0 \qquad \psi(L) := 0.$$

where L is the length of the box.

When these conditions are applied, the wavefunction becomes

$$\psi(x) := A\cdot\sin\left[\left(\frac{8\cdot\pi^2\cdot m\cdot E}{h^2}\right)^{\frac{1}{2}} x\right]. \quad \text{where} \quad E := \frac{n^2\cdot h^2}{8\cdot m\cdot L^2}.$$

Thus the energy, E, becomes quantized. Only specific values of E will yield a wavefunction that satisfies the boundary conditions.

Let us consider the energy for a particle-in-a-box.
The Hamiltonian for the particle inside the box is the kinetic energy operator.

$$H := \frac{-h^2}{8\pi^2\cdot m}\cdot\frac{d^2}{dx^2}$$

Applying the Hamiltonian within the Schroedinger equation implies that we find the energy for the particle-in-a-box by taking the second derivative of the wavefunction and multiplying by some constants.

Recall from calculus that the second derivative is a measure of the curvature of a function. When the wavefunction has the correct energy, i.e., the correct curvature, the boundary conditions are met. Thus looking at the curvature of a particle-in-a-box wavefunction can help in finding correct energy eigenvalues.

Also, since the kinetic energy operator is proportional to the second derivative, the curvature of a particle's wavefunction is a measure of the particle's kinetic energy.

In this laboratory, we will be examining the effects of the potential energy function on the energies and wavefunctions of a particle trapped in a box. For each investigation, four steps will be followed.

1. We will learn how to construct the potential function.
2. We will construct a simple algorithm that will allow us to use Mathcad's differential equation solvers to solve the Schroedinger equation.
3. We will learn how to plot the solution of the Schroedinger equation so that we can see the results.
4. We will vary the energy of the particle so that solution meets the correct boundary conditions.

Use the procedure that follows during the laboratory session.

Laboratory Procedure

Construction of the potential function

1. Type V(x), followed by a colon(:)

   $V(x) :=$ ∎

2. Now from the Programming toolbar, click on *Add Line*.

   $V(x) := \left|\begin{array}{l} ∎ \\ ∎ \end{array}\right.$

3. Type 0, click on *if*
   $0 \le x \le 4$ using the operations on the Evaluation toolbar. This the zero potential portion of the box.

   $V(x) := \left|\begin{array}{l} 0 \quad \text{if } 0 \le x \le 4 \\ ∎ \end{array}\right.$

4. In the bottom placeholder, type the height of the potential well (choose 400 initially). Then click *otherwise* from the Programming toolbox. (Ideally, the value should be infinity, but an infinite potential energy causes the numerical solution of the differential equation to diverge.)

   $V(x) := \left|\begin{array}{l} 0 \quad \text{if } 0 \le x \le 4 \\ 400 \quad \text{otherwise} \end{array}\right.$

5. You can view the graph of the potential function by first setting the domain of x.
   a. Type x:-10 to set the starting value of x.

   $x := -10$

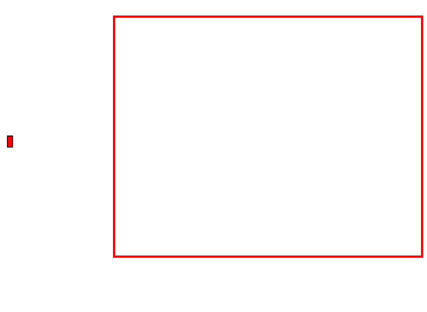
   b. Type ,-9.99 to set the next value of x and also the interval of subsequent x values. In this case, the x interval is 0.01.

   $x := -10, -9.99$

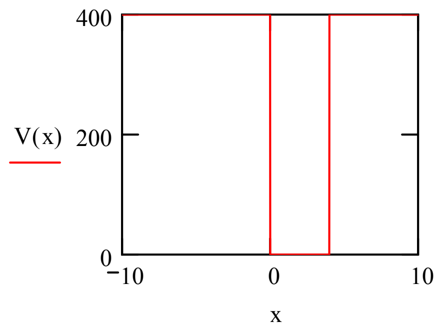
   c. Last, type ;10 to set the end value of x.

   $x := -10, -9.99 .. 10$

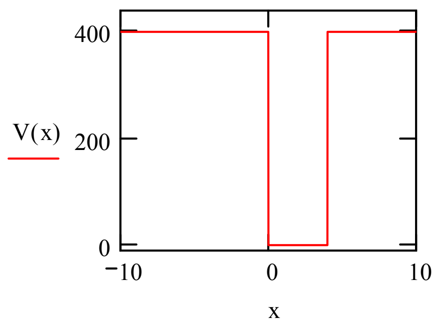
6. From the Graph toolbox or from the Insert --> Graph menu, choose X-Y Plot



7. In the placeholder on the left, type V(x) and in the placeholder on the bottom, type x.



8. To get a better view of the potential, click on the graph and change the top value of y to 440 and the bottom value of y to -10.



INSTRUCTOR NOTE: **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.**

Construction of Schroedinger equation solution algorithm

To solve the Schroedinger equation for a particle-in-a-box, we will use a built-in numerical differential equation solver function, which in Mathcad is called rkfixed.

rkfixed(y, 0, 4, 800, D) has five arguments.

y is a vector (2x1 matrix) with the boundary conditions of the solution and its first derivative at the initial value. We will be using 0 as our initial value as that is the initial x value in the potential box.

0 and 4 represent the initial and final values of x where the differential equation is to be solved.

800 is the number of points between the initial and final value where the differential equation is to be solved.

D is a vector that contains a first and second derivative of the solution.

INSTRUCTOR NOTE: The bulstoer differential equation solver works as well. For the particle-in-a-box Schroedinger equation, the two methods appear to be equivalent.

INSTRUCTOR NOTE: The range of the solution must correlate to the size of the box. Students may forget

1. Type E:0.5

   $E := 0.5$

   This value of E (energy of the particle) is our first guess. Later we will be changing this value to find a valid wavefunction of the particle.

2. Type y: then create a 2x1 matrix with 0 in the top placeholder to set the initial value of the solution and 1 in the bottom placeholder to set the initial value of the derivative of the solution. You can create the matrix using the Vector and Matrix Toolbar within the Math Toolbar.

   $$y := \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

INSTRUCTOR NOTE: The initial value of the first derivative can be set to any nonzero positive number. The value changes the amplitude of the wavefunction when plotted but does not change the energy.

3. Create the derivative vector by typing D(x,y): then create a 2x1 matrix and type y[1 in the top placeholder and type 2*(V(x) - E))*y[0 in the bottom placeholder.

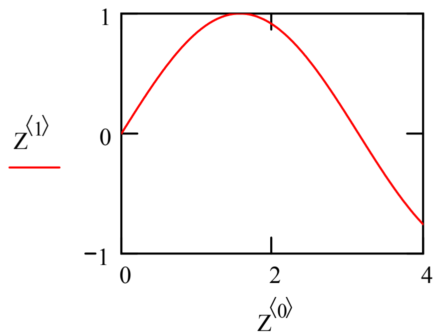
   $$D(x,y) := \begin{bmatrix} y_1 \\ 2(V(x) - E) \cdot y_0 \end{bmatrix}$$

4. Now create a vector that contains the solution (i.e., wavefunction) by typing Z:rkfixed(y,0,4,800,D)

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

INSTRUCTOR NOTE: The number of evaluation points affects the accuracy of the numerical wavefunction. An adequate number of points is especially important for evaluating the function when tunneling is involved. The examples in this exercise use 800 evaluation points. For slower computers, at least 300 points should be used to find a reasonably accurate wavefunction.

5. To see a plot of the wavefunction for the energy = 0.5, using the Graph Toolbar on the Math *Ctrl* 6 1 and type Z *Ctrl* 6 0 in the x-axis placeholder.



Note that the wavefunction does not equal zero at x = 4. We have chosen an energy that is not allowed. (See step 1 above.) The precise value of the wavefunction at x = 4 can be found by using the trace option on the Graph Toolbar.

Since the boundary condition at x = 4 is not met, we will need to adjust the energy eigenvalue, E. From the plot we see that the curvature of the wavefunction is too high. Thus we need to decrease the value of E.

If the value of the wavefunction is less than zero at the edge of the box, then the curvature of the wavefunction is too high and the energy is too high. If the value of the wavefunction is greater than zero at the edge of the box, the curvature of the wavefunction is too low and the energy value is too low.

INSTRUCTOR NOTE: Visual cues should be sufficient to find the first two or three decimal places of 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.

Part A: Single well potentials

Assignments

Your first assignment is to find the ground state energy of the above potential well to eight decimal places. Then find the energies of next nine states to five decimal places by choosing correct values for the energy. You should also plot the first ten wavefunctions. Describe the relationship between quantum number of the state and the shape of the wavefunction.

Next, find the first five energies of a well that is half as wide and the first five energies of a well that is twice as wide. Try to find the numerical relationship between the three sets of energies.

Other questions to consider:

1. How does the curvature of the wavefunction change as the energy of the particle in increased?

2. What is the relationship between the number of nodes of the wavefunction and the quantum number?

INSTRUCTOR NOTE: 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. 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. Students should be able to find the inverse square relationship between the energy eigenvalues and the length of the box.

Part B: Step barrier well potentials

In this portion the lab, you will examine the effects of putting a step barrier into the box. Below is the algorithm to construct the step barrier well potential.

Construct a step potential

1. Type V(x), followed by :

   $V(x) :=$ ▪

2. Now from the Programming toolbar, click on *Add Line*.

   $V(x) := \left| \begin{array}{l} ▪ \\ ▪ \end{array} \right.$

3. Type 0 in the top placeholder, click on *if* from the Programming toolbar, and in the placeholder on the right type $0 \le x \le 2$
portion of the box.

$$V(x) := \begin{cases} 0 & \text{if } 0 \le x \le 2 \\ \blacksquare & \end{cases}$$

4. Click on the second placeholder and click on *Add Line* from the Programming toolbar. In the second placeholder, type the height of the step well (choose 20 initially). Then click *if* from the Programming toolbox. In the right placeholder type $2 < x < 4$.

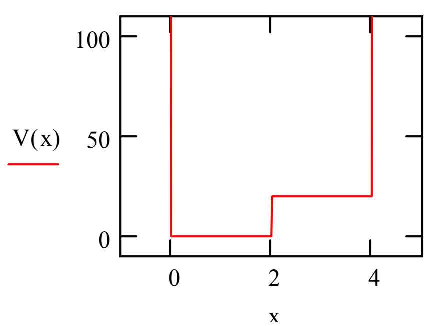
$$V(x) := \begin{cases} 0 & \text{if } 0 \le x \le 2 \\ 20 & \text{if } 2 < x < 4 \\ \blacksquare & \end{cases}$$

5. To finish constructing the step potential, click on the third placeholder and type the height of the potential well (stay with 400). Then click *otherwise* from the Programming toolbox.

$$V(x) := \begin{cases} 0 & \text{if } 0 \le x \le 2 \\ 20 & \text{if } 2 < x < 4 \\ 400 & \text{otherwise} \end{cases}$$

Plot of a step potential function

$$V(x) := \begin{cases} 0 & \text{if } 0 \le x \le 2 \\ 20 & \text{if } 2 < x < 4 \\ 400 & \text{otherwise} \end{cases}$$



Assignments

Find the first ten energies of this system and plot the wavefunctions. Make observations about any tunneling effects. Make qualitative comparisons with the single well potential. Note: Depending on the potential chosen you may need to find the energy to more than five decimal places to find a finite wavefunction.

Examine the effect of the step height and of the step width by constructing potentials of your choosing. Find the first five energies and wavefunctions of your trials and make qualitative comparisons with the step barrier potential above.

Choose a step potential and adjust the energy eigenvalue in an attempt to keep the wavefunction from tunneling into the barrier. (In the example above, you try to make the wavefunction at x = 2 equal to zero.)

Other questions to consider:

1. How does the height of the step affect the energy of a state?

2. How does the height of the step affect the curvature of the wavefunction?

3. How does the width of the step affect the energy of a state?

5. Rationalize the above observations in terms of changes in the kinetic energy of the particle.

6. What happens to the curvature as the energy of particle approaches the energy of the step? What are the implications of the change in curvature for the probability density of the particle?

7. What happens to the ground state wavefunction if you try to keep it in the classically allowed region?

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

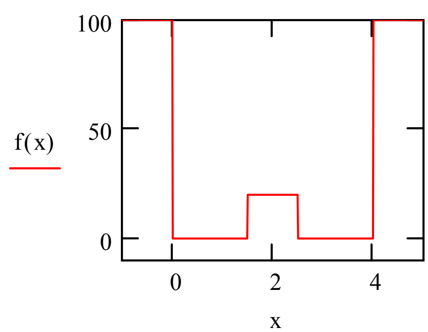
1) The wavefunctions for energies less than the step height demonstrate the phenomenon of tunneling. As the energy of the wavefunction approaches the step height, the tunneling is more prominent.
2) The wavefunctions for energies greater than the step height demonstrate a decrease in the curvature of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

INSTRUCTOR NOTE: 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.

Part C: Double well potentials

In this portion the lab, you will examine the effects of particle tunneling through a thin wall. Below is the first step barrier well potential to be examined.

$$f(x) := \begin{cases} 0 & \text{if } 0 < x < 1.5 \\ 20 & \text{if } 1.5 \le x < 2.5 \\ 0 & \text{if } 2.5 \le x < 4.0 \\ 100 & \text{otherwise} \end{cases}$$



Assignment

Find the first ten energies of this system and plot the wavefunctions. Make observations about any tunneling

Examine the effect of the wall height and of the wall width by constructing potentials of your choosing. Find the first five energies and wavefunctions of your trials and make qualitative comparisons with the double well potential above.

Other questions to consider:

1. How does the height of the barrier affect the energy of a state?
2. How does the height of the barrier affect the curvature of the wavefunction?
3. How does the width of the barrier affect the energy of a state?
4. How does the width of the barrier affect the shape of the wavefunction?
5. Rationalize the above observations in terms of changes in the kinetic energy of the particle.
6. How do the energy levels group as the barrier height increases? Extrapolate what would happen for an extremely large barrier height.
7. How is the tunneling of the particle affected with barrier height and barrier width?
8. What happens to the energies and wavefunctions if the two wells are highly asymmetrical?

INSTRUCTOR NOTE: 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.

INSTRUCTOR NOTE: 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.

INSTRUCTOR NOTE:
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 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.