

## Variational Methods Applied to the Particle in a Box ©

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**Prerequisites:** This Mathcad document is designed to support the quantum mechanics portion of a Junior-Senior level physical chemistry course. Students should have had at least one year of calculus and physics, as well as an introductory knowledge of quantum mechanics. While not necessary, it will also be helpful if students are familiar with the concept of a particle-in-a-box and the equations corresponding to the wavefunctions and energy levels of a particle-in-a-box [1,2]. Some basic Mathcad skills are assumed (how to enter and solve equations, both numerically and symbolically, as well as the ability to graph functions). This document requires Mathcad 2000 or higher.

**Goal:** The primary goal of this document is for the user to gain a familiarity with the variational method, a mathematical method that is commonly used to approximate the energy levels of non-trivial quantum mechanical systems. The variational method is applied here to a well known system, a particle in a one dimensional box. This idealize model represents one of the simplest quantum mechanical problems; the exact analytical solutions for the wavefunctions and energy levels of a particle-in-a-box are normally presented during the introductory quantum mechanics portion of a physical chemistry course [1,2]. Since the exact energies are known, we can apply the variational method to this model to obtain estimates for the energies, and then assess the accuracy of the variational technique by comparing the estimated and known energy levels.

**Introduction:** There are relatively few quantum mechanical problems for which the Schrodinger equation can be solved exactly; the particle-in-a-box, harmonic oscillator, rigid rotor, and H-atom nearly completes the list of exactly solvable problems that are normally presented in a quantum chemistry course. When a system contains more than two interacting particles, one must resort to the use of approximate methods for estimating the energy levels. The application of quantum mechanics to chemical systems containing possibly hundreds or even thousands of interacting particles is exclusively dependent on approximate computational methods. Such methods have evolved steadily since the advent of the computer and commercial software packages are now commonly used to model any number of complex chemical systems.

Since chemists are becoming increasingly dependent on the use of approximate quantum computational methods, it is important to assess the accuracy of these methods by applying them to simple known systems. This Mathcad document will introduce one of the more popular approximate methods called the variational method [3,4]. The use of this method involves supplying an initial guess about the form of the wavefunction for a particular system, and then calculating the energy based upon this trial wavefunction. The Variation Theorem states that the energy calculated for the system from the trial wavefunction is never less than the actual energy.

In practice, one finds that the variational method provides an excellent estimate of the system's energy, provided the trial wavefunction is chosen appropriately. The best estimates for energy are obtained by representing the trial wavefunction as a linear combination of trial functions, where the different terms in the linear combination are weighted by unknown variational coefficients. This Mathcad document is organized as follows: (1) the particle in a one dimensional box model is briefly summarized, (2) the variational method is presented and then applied to the ground state energy level of the particle-in-a-box, (3) the variational method is applied to the first excited state of the particle-in-a-box, and (4) the accuracy of the variational method is improved by writing the trial functions as linear combinations of the single trial functions used in parts (2) and (3).

### **Performance Objectives:**

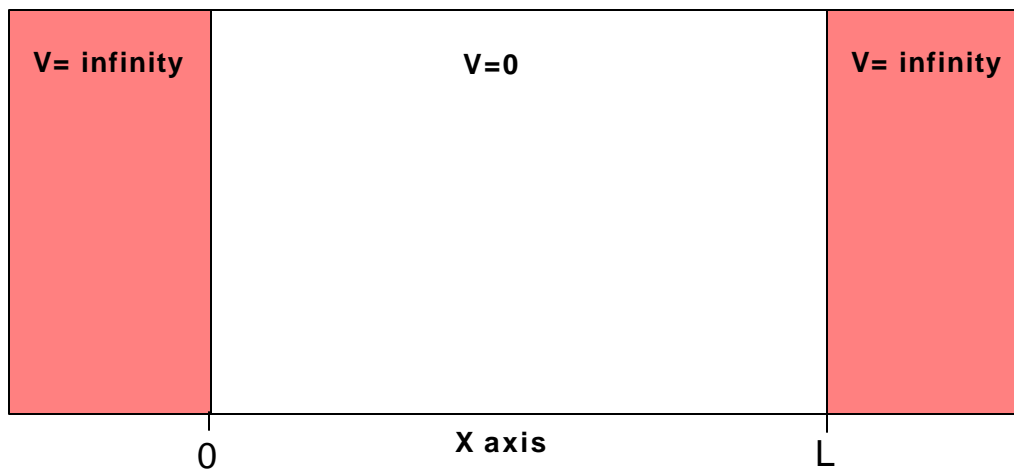
After completing this document, you should be able to

1. explain the principles of the variation theorem and the variational method;
2. select an appropriate trial wavefunction (one that satisfies the symmetry and boundary conditions of the problem at hand).
3. use any appropriate trial function and estimate an energy for the problem at hand using the variational method.
4. estimate the accuracy of a trial solution by calculating percent errors for the energy and plotting the exact wavefunction along with the trial function.
5. extend the accuracy of the variational method by using a trial function that is written as a linear combination of appropriate trial functions.

# 1. Particle in a One Dimensional Box

Consider a particle that is confined to motion along a segment of the x-axis (a one dimensional box). For simplicity, imagine the boundaries of the box to lie at  $x=0$  and  $x=L$ . We will further define the potential energy of the particle to be zero inside the box ( $V=0$  when  $0 < x < L$ ) and infinity outside the box. In other words, the walls of the box are infinitely high to prevent the particle from escaping, regardless of its kinetic energy.

Figure 1.1: Diagram of a particle in a one dimensional box, illustrating the region where the particle is free to translate and the impenetrable walls to either side.



The solution of the Schrodinger equation for this system is available in nearly any introductory textbook on quantum mechanics (for example, see references [1-2]). The expressions for the wavefunctions and corresponding energy levels are given here.

$$\Psi_n = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n \cdot \pi \cdot x}{L}\right)$$

Wavefunctions, where  $n = 1, 2, 3, \dots, \infty$  and  $(2/L)^{1/2}$  is the normalization constant.

$$E_n = \frac{n^2 \cdot h^2}{8 \cdot m \cdot L^2}$$

Energy levels, where  $m$  is the mass of the particle.

To simplify our work in this document, we will utilize atomic units where mass ( $m$ ) is equal to 1 and Plank's constant ( $h$ ) is equal to  $2\pi$ . A brief review of atomic units is available in reference [5] if you desire more details. We will also define the length of the box ( $L$ ) to equal a unitless length of 1.

$$m := 1$$

$$\hbar := 1$$

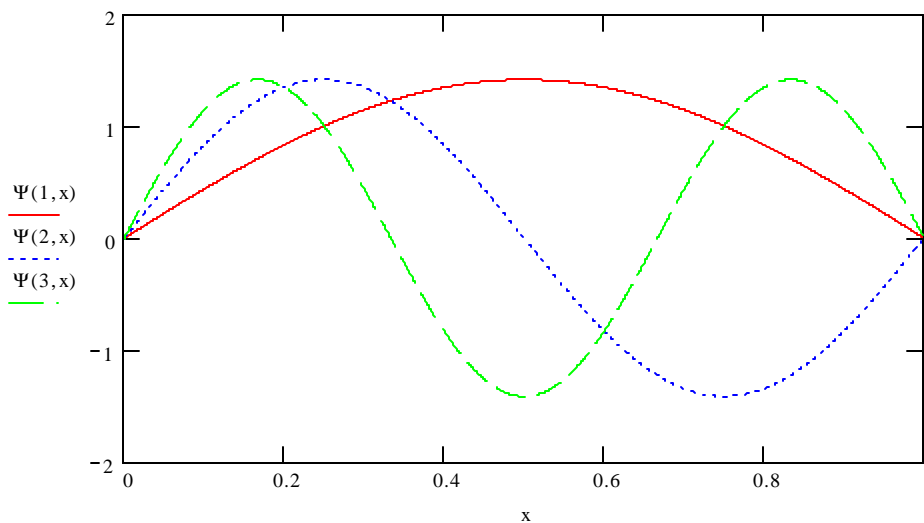
$$L := 1$$

Here we choose atomic units for  $m$ ,  $\hbar$  and  $L$ .

$$\Psi(n, x) := \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n \cdot \pi \cdot x}{L}\right) \quad \text{Equation (1)}$$

$$E(n) := \frac{n^2 \cdot \pi^2}{2 \cdot m \cdot L^2} \quad \text{Equation (2)}$$

Graph 1.1: Plot of the wavefunctions for the first three energy levels



$$E(1) = 4.935$$

$$E(2) = 19.739$$

$$E(3) = 44.413$$

Unitless energies associated with the first three particle-in-a-box states.

**Exercise 1.1:** What is the relationship between the value of  $n$  and the number of nodes in the wavefunction (values of  $x$  between 0 and  $L$  where  $\Psi$  equals zero)? We will see below that the symmetry of a wavefunction is an important consideration when selecting trial functions. Indicate whether each of the  $n$  equal 1 to 5 wavefunctions is symmetric or antisymmetric with respect to inversion through the middle of the box.

**Exercise 1.2:** Practice your Mathcad skills. Consider the function  $G(n, x) = (2/L)^{1/2} \cos(np\pi x/L)$  within the  $x$ -axis limits  $-L/2$  and  $+L/2$ . Define this function in a separate Mathcad worksheet and construct a single graph (like Graph 1.1 above) that shows how the function behaves when  $n$  equals 1, 2, and 3. Is this a valid wavefunction for a particle trapped in a 1-D box between the  $x$ -axis limits  $-L/2$  and  $+L/2$  ?

## 2. The Variational Method and the Variation Theorem

The expectation value for energy associated with any wavefunction of a system is given by the following expression where H is the Hamiltonian operator for the system and the integration is over all available space.

$$\text{Energy} = \frac{\int \Psi \cdot H \cdot \Psi \, d\tau}{\int \Psi \cdot \Psi \, d\tau}$$

**Equation (3)**

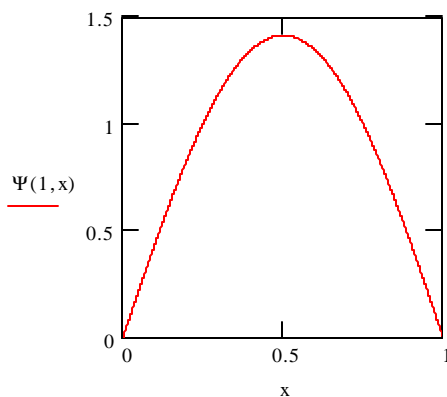
The integral in the denominator guarantees that the expression works even for wavefunctions that are not normalized.

What if we do not know the exact wavefunction corresponding to an energy state of a system and consequently use an arbitrary trial function ( $\phi$ ) when evaluating equation (3)? The *Variation Theorem states that the expectation value for energy calculated from a trial function is always greater than the actual energy of the system.* The variational method involves 'guessing' a trial function and calculating the energy using the above statement. The Variation Theorem by itself does not guarantee that the estimated energy will be close to the actual energy, it only states that the estimated energy will always be too large. The true power of the variational method lies in choosing a trial function with one or more 'variational' parameters that can be varied to minimize the estimated energy. The more flexible the trial function, the better the agreement between the estimated energy and the actual energy of the system.

### Selecting Appropriate Trial Functions

How do we pick a trial function that approximates the energy of the particle-in-a-box ground state?

Graph 2.1: Ground state wavefunction for the particle-in-a-box.



The trial function should approximate the shape of the true wavefunction, shown in the plot to the left, meaning it should obey the boundary conditions of the model (the function should equal zero when  $x=0$  and  $x=L$ ).

A trial function that meets this requirement is

$$\phi(x) = N \cdot x \cdot (L - x)$$

where N is a normalization constant.

One does not need to know the value of N to calculate an energy according to equation (3); the N factors can be brought outside the integrals in both the numerator and denominator and subsequently cancel. However, we do need to know the value of N if we desire to plot the trial function with the actual wavefunction for comparison.

$$\int_0^L N^2 \cdot [x \cdot (L - x)]^2 dx = 1$$

A particle-in-a-box trial function is normalized by selecting a value of N such that the integral to the left is obeyed.

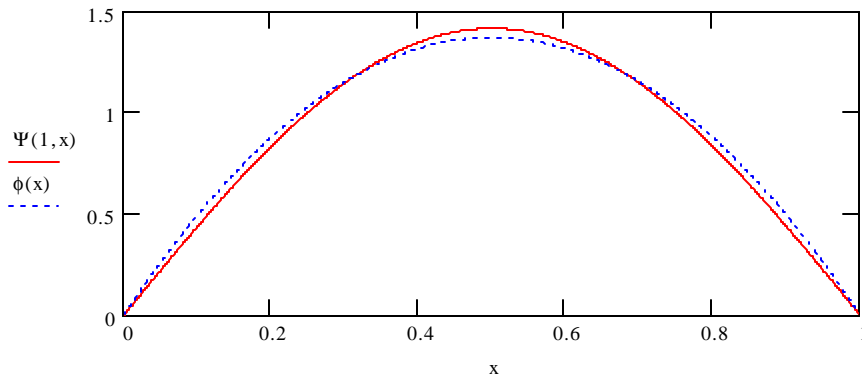
$$N = \sqrt{\frac{1}{\int_0^L [x \cdot (L - x)]^2 dx}} \rightarrow \sqrt{30}$$

Evaluation of the normalization constant, N.

$$\phi(x) := \sqrt{30} \cdot x \cdot (L - x)$$

The normalized trial function.

Graph 2.2: Plot of the normalized wavefunction with the actual ground state particle-in-a-box wavefunction.



The above plot already reveals reasonable agreement between the trial function and the actual wavefunction. Now that we have a suitable trial function, we can illustrate the Variation Theorem by using equation (3) to estimate the energy and compare the value to the actual ground state energy.

**Exercise 2.1:** Repeating the steps shown immediately above in a separate worksheet, find the value of N that normalizes the following trial function for the particle-in-a-box and plot this function with the actual ground state wavefunction.

$$\theta(x) = N \cdot [x \cdot (L - x) + x^2 \cdot (L - x)^2]$$

**Mathcad Tip:** To speed this and other exercises along, you are welcome to copy and paste any of the sample calculations shown here into a new worksheet and then edit them to achieve your particular goal.

## Variation Theorem Illustration

The Hamiltonian operator for the particle-in-a-box system contains only the kinetic energy term, since the potential energy equals zero inside the box.

$$H = \frac{-\hbar^2}{2 \cdot m} \cdot \frac{d^2}{dx^2}$$

The exact energy for the ground state can be obtained by putting the actual wavefunction into equation (3).

$$\text{actualenergy} := \frac{\int_0^L \Psi(1, x) \cdot \left( \frac{-\hbar^2}{2 \cdot m} \cdot \frac{d^2}{dx^2} \Psi(1, x) \right) dx}{\int_0^L \Psi(1, x) \cdot \Psi(1, x) dx} \quad \text{actualenergy} = 4.9348022$$

Note that this value agrees exactly with the value calculated from equation (2) when  $n=1$ .

$$E(1) = 4.9348022$$

The estimated energy is obtained by putting the trial function into equation (3).

$$\text{varenergy} := \frac{\int_0^L \phi(x) \cdot \left( \frac{-\hbar^2}{2 \cdot m} \cdot \frac{d^2}{dx^2} \phi(x) \right) dx}{\int_0^L \phi(x) \cdot \phi(x) dx} \quad \text{varenergy} = 5.000000$$

The estimated energy is slightly higher than the actual energy, in accordance with the variation theorem. The percent error is calculated for comparison.

$$\text{percenterror} := \frac{\text{actualenergy} - \text{varenergy}}{\text{actualenergy}} \cdot 100 \quad \text{percenterror} = -1.321$$

## Selecting a Different Trial Function

Let us try an alternate trial function and see how the percent error in our estimated energy is affected. Another trial function that satisfies the boundary conditions is the square of our previously considered trial function.

$$\Theta(x) = N \cdot x^2 \cdot (L - x)^2$$

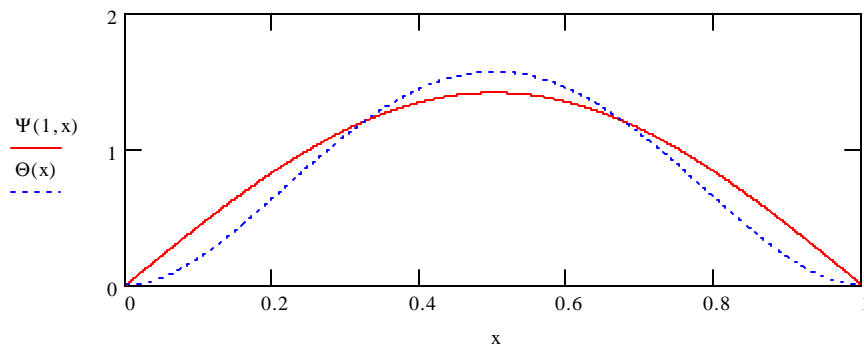
In this case, the normalization constant is

$$\sqrt{\frac{1}{\int_0^L [x^2 \cdot (L - x)^2]^2 dx}} \rightarrow 3 \cdot \sqrt{70}$$

$$\Theta(x) := 3 \cdot \sqrt{70} \cdot x^2 \cdot (L - x)^2$$

A new trial function.

Graph 2.3: Plot of new trial function with the ground state particle-in-a-box wavefunction



The trial function is similar to the actual ground state wavefunction, although the agreement between the two is not as close as in the previous case. The estimated energy is considerably less accurate in this case.

$$\text{varenergy2} := \frac{\int_0^L \Theta(x) \cdot \left( \frac{-\hbar^2}{2 \cdot m} \cdot \frac{d^2}{dx^2} \Theta(x) \right) dx}{\int_0^L \Theta(x) \cdot \Theta(x) dx} \quad \text{varenergy2} = 6.000000$$

$$\text{percenterror2} := \frac{\text{actualenergy} - \text{varenergy2}}{\text{actualenergy}} \cdot 100 \quad \text{percenterror2} = -21.585$$

**Exercise 2.2:** Use the following trial function in a separate worksheet to estimate the energy of the ground state particle-in-a-box (estimate the energy, the percent error in energy, find the normalization constant, and plot the trial function with the actual ground state wavefunction).

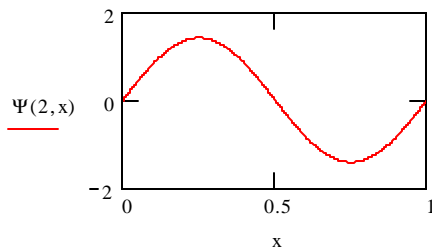
$$\beta(x) = N \cdot \left( \sin\left(\frac{\pi \cdot x}{L}\right) \right)^2$$

Note: this trial function is essentially the square of the actual ground state wavefunction.

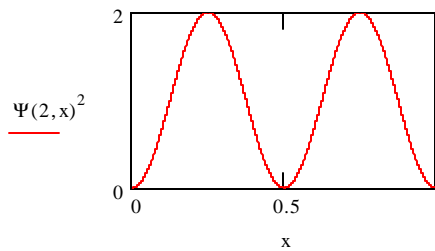
### 3. Applying the Variational Method to the First Excited State of the Particle-in-a-box

The variational method can be applied to excited states as long as the trial function possesses the same nodal properties as the exact wavefunction. Consider the wavefunction for the 1st excited state ( $n=2$ ) of the particle in a box.

Graph 3.1: 1st Excited State Wavefunction



Graph 3.2: Probability amplitude of 1st Excited State



The 1st excited state wavefunction is antisymmetric with respect to inversion through the middle of the box, meaning it contains a node at  $L/2$ . Any selected trial functions must also possess this symmetry and node. The trial solutions used for estimating the ground state energy can be altered to obey the symmetry and nodal properties of the 1st excited state by adding a  $(L/2-x)$  term.

$$\Omega(x) = A \cdot x \cdot (L - x) \cdot \left( \frac{L}{2} - x \right)$$

Trial function #1 (A is the normalization constant).

$$\Pi(x) = B \cdot x^2 \cdot (L - x)^2 \cdot \left( \frac{L}{2} - x \right)$$

Trial function #2 (B is the normalization constant).

The normalization constants A and B are respectively:

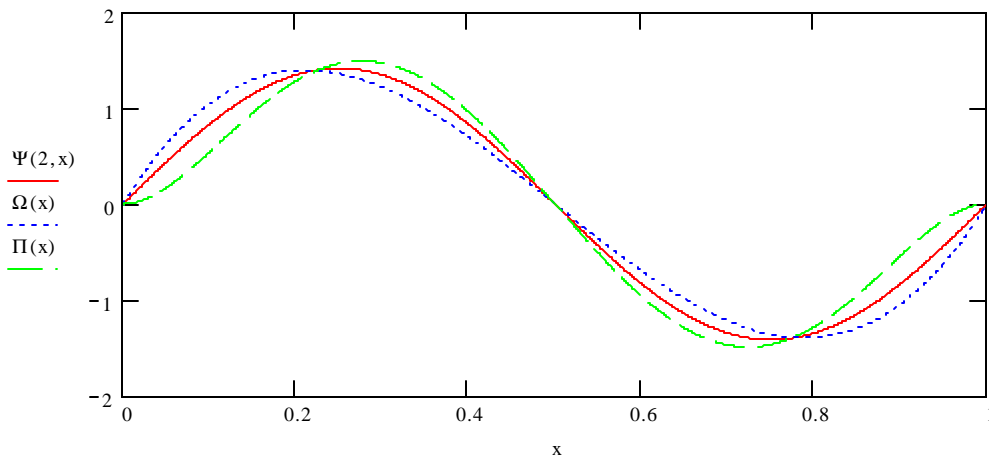
$$\sqrt{\int_0^L \frac{1}{\left[ x \cdot (L-x) \cdot \left( \frac{L}{2} - x \right) \right]^2} dx} \rightarrow 2 \cdot \sqrt{210}$$

$$\sqrt{\int_0^L \frac{1}{\left[ x^2 \cdot (L-x)^2 \cdot \left( \frac{L}{2} - x \right) \right]^2} dx} \rightarrow 6 \cdot \sqrt{770}$$

$$\Omega(x) := 2 \cdot \sqrt{210} \cdot x \cdot (L-x) \cdot \left( \frac{L}{2} - x \right) \quad \text{Trial function \#1}$$

$$\Pi(x) := 6 \cdot \sqrt{770} \cdot x^2 \cdot (L-x)^2 \cdot \left( \frac{L}{2} - x \right) \quad \text{Trial function \#2}$$

Graph 3.3: Plot of Above Trial Functions with 1st excited state wavefunction.



The above plots show that both trial functions are reasonable estimates for the 1st excited state. Using equation (3) to estimate the corresponding energies yields

$$\text{varenergy3} := \frac{\int_0^L \Omega(x) \cdot \left( \frac{-\hbar^2}{2 \cdot m} \cdot \frac{d^2}{dx^2} \Omega(x) \right) dx}{\int_0^L \Omega(x) \cdot \Omega(x) dx}$$

Estimated energy based on Trial function #1

$$\text{varenergy3} = 21.000000$$

$$\text{varenergy4} := \frac{\int_0^L \Pi(x) \cdot \left( \frac{-\hbar^2}{2 \cdot m} \cdot \frac{d^2}{dx^2} \Pi(x) \right) dx}{\int_0^L \Pi(x) \cdot \Pi(x) dx}$$

Estimated energy based on  
Trial function #2

$$\text{varenergy4} = 22.000000$$

Actual Energy of 1st Excited  
State

$$E(2) = 19.739$$

$$\text{percenterror3} := \frac{E(2) - \text{varenergy3}}{E(2)} \cdot 100$$

Percent error in Trial #1  
estimate

$$\text{percenterror3} = -6.387$$

$$\text{percenterror4} := \frac{E(2) - \text{varenergy4}}{E(2)} \cdot 100$$

Percent error in Trial #2  
estimate

$$\text{percenterror4} = -11.453$$

Again, we have obtained energy estimates for the 1st excited state that are consistent with the variation theorem, although the accuracy of the estimates is poor. To improve the accuracy in the next section, we will consider trial functions that possess a variational parameter.

**Exercise 3.1:** Use the following trial function in a separate worksheet to estimate the energy of the 1st excited state of the particle-in-a-box (estimate the energy, the percent error in energy, find the normalization constant, and plot the trial function with the actual 1st excited state wavefunction).

$$\chi(x) = N \cdot \left( x^3 - \frac{3}{2} \cdot L \cdot x^2 + \frac{1}{2} \cdot L^2 \cdot x \right)$$

## 4. Variational Methods Involving a Linear Combination of Trial functions

One is fortunate if an accurate energy is obtained from a single term trial function; the percent error in the estimated energy for the cases considered above are greater than 5% for all but the first case. The accuracy of the variational method can be greatly enhanced by using a trial function that is more flexible. Flexibility can be attained by adding additional terms to our trial function and weighting the various terms against each other by including one or more variational parameters.

### Two Term Trial Function for the Ground State Particle-in-a-Box

We can generate a two term trial function for the ground state of the particle-in-a-box by using the two, single trial functions from section 2.

$$\Gamma(C, x) := x \cdot (L - x) + C \cdot x^2 \cdot (L - x)^2$$

Two term trial function. Note how the normalization constants have been dropped (since we really do not need them to calculate the expectation value for energy). The weight of the second term, relative to the first term, is adjustable because we have included a variational parameter (C).

This trial function is now inserted into equation 3 and solved symbolically, yielding an expression for energy in terms of our variational parameter C. Contrary to parts 2 and 3 of this document, our trial function now contains an undefined parameter (C), which means we must use the symbolic evaluation capabilities of Mathcad to obtain an analytical expression for energy (as opposed to an actual numerical value for energy). This is accomplished by entering the expression shown to the right of the arrow shown immediately below, highlighting the entire expression, and then clicking on the 'Evaluate Symbolically' button in the *Evaluation Toolbar*. Users of Mathcad 6.0 etc. should consult their user manual for the evaluation procedure.

$$\frac{\left[ \int_0^L \Gamma(C, x) \cdot \left( \frac{-\hbar^2}{2 \cdot m} \cdot \frac{d^2}{dx^2} \Gamma(C, x) \right) dx \right]}{\left( \int_0^L \Gamma(C, x) \cdot \Gamma(C, x) dx \right)} \rightarrow \frac{\left( \frac{1}{105} \cdot C^2 + \frac{1}{15} \cdot C + \frac{1}{6} \right)}{\left( \frac{1}{630} \cdot C^2 + \frac{1}{70} \cdot C + \frac{1}{30} \right)}$$

$$\text{varenergy2term}(C) := \frac{\left( \frac{1}{105} \cdot C^2 + \frac{1}{15} \cdot C + \frac{1}{6} \right)}{\left( \frac{1}{630} \cdot C^2 + \frac{1}{70} \cdot C + \frac{1}{30} \right)}$$

The variation theorem states that the right-hand-side of the above expression can never yield an energy that is less than the actual energy of the state under consideration, regardless of the value of C. Therefore, we are free to find the value of C that minimizes this equation for energy. This is done by symbolically taking the derivative of *varenergy2term(C)* with respect to C, setting the resultant expression equal to zero, and solving for C.

$$\frac{d}{dC} \text{varenergy2term}(C) \rightarrow \frac{\left(\frac{2}{105} \cdot C + \frac{1}{15}\right)}{\left(\frac{1}{630} \cdot C^2 + \frac{1}{70} \cdot C + \frac{1}{30}\right)} - \frac{\left(\frac{1}{105} \cdot C^2 + \frac{1}{15} \cdot C + \frac{1}{6}\right)}{\left(\frac{1}{630} \cdot C^2 + \frac{1}{70} \cdot C + \frac{1}{30}\right)^2} \cdot \left(\frac{1}{315} \cdot C + \frac{1}{70}\right)$$

$$\frac{\left(\frac{2}{105} \cdot C + \frac{1}{15}\right)}{\left(\frac{1}{630} \cdot C^2 + \frac{1}{70} \cdot C + \frac{1}{30}\right)} - \frac{\left(\frac{1}{105} \cdot C^2 + \frac{1}{15} \cdot C + \frac{1}{6}\right)}{\left(\frac{1}{630} \cdot C^2 + \frac{1}{70} \cdot C + \frac{1}{30}\right)^2} \cdot \left(\frac{1}{315} \cdot C + \frac{1}{70}\right)$$

$$3 \cdot \frac{(4 \cdot C^2 + 14 \cdot C - 21)}{(C^2 + 9 \cdot C + 21)^2}$$

This simplified expression for the derivative was obtained by highlighting the entire expression for the derivative (shown directly above) and clicking on the *Simplify* option in the *Symbolics* menu.

The roots of this simplified expression will yield the value of C that corresponds to the best estimate for energy. The roots are most easily found by highlighting one of the C variables in the equation directly above and clicking on the *Variable-Solve* option in the *Symbolics* menu.

$$\begin{pmatrix} \frac{-7}{4} + \frac{1}{4} \cdot \sqrt{133} \\ \frac{-7}{4} - \frac{1}{4} \cdot \sqrt{133} \end{pmatrix}$$

2 roots are obtained for our variational parameter C. We will only need one of them; the one corresponding to the lowest energy.

$$E1 := \text{varenergy2term}\left(\frac{-7}{4} + \frac{1}{4} \cdot \sqrt{133}\right)$$

$$E1 = 4.9348748$$

Lowest Energy

$$E2 := \text{varenergy2term}\left(\frac{-7}{4} - \frac{1}{4} \cdot \sqrt{133}\right)$$

$$E2 = 51.0651252$$

Discard this Energy

$$\text{percenterror} := \frac{E(1) - E1}{E(1)} \cdot 100$$

$$\text{percenterror} = -1.471 \times 10^{-3}$$

The agreement between the estimated energy and the actual energy for the ground state particle-in-a box is impressive (only -0.001471%), illustrating the power of the variational method.

We will need to add a normalization constant to plot our two term trial function along with the actual ground state wavefunction. Now that we know the value of  $C$ , we can find the normalization constant as before.

$$C := \frac{-7}{4} + \frac{1}{4} \cdot \sqrt{133} \quad \text{Set the value of } C \text{ to the root found above.}$$

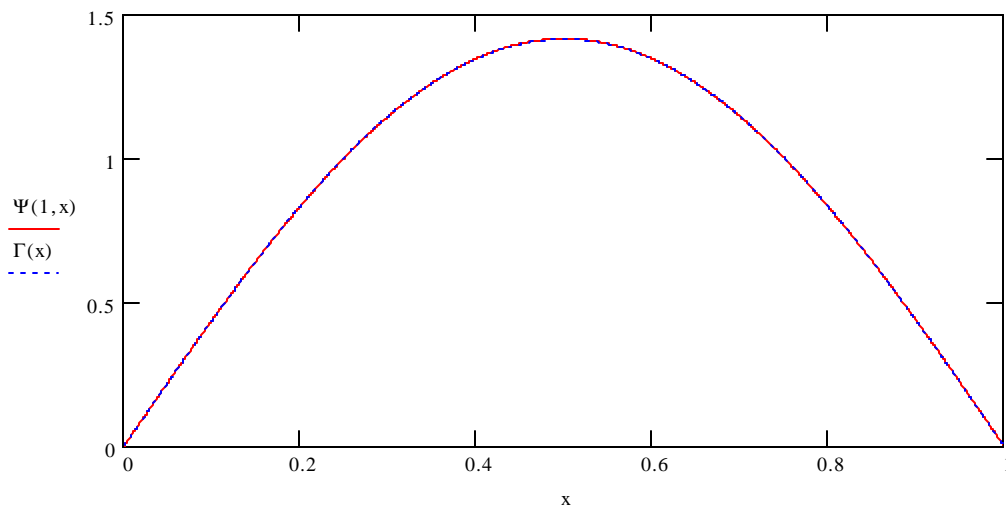
The normalization constant is found by symbolically evaluating the expression shown below.

$$\sqrt{\int_0^L \Gamma(C, x)^2 dx} \rightarrow \frac{1}{\left(\frac{19}{720} + \frac{11}{5040} \cdot \sqrt{133}\right)^{\left(\frac{1}{2}\right)}}$$

Therefore the final form of our two term trial function is defined as ...

$$\Gamma(x) := \frac{1}{\left(\frac{19}{720} + \frac{11}{5040} \cdot \sqrt{133}\right)^{\left(\frac{1}{2}\right)}} \cdot [(x) \cdot (L - x) + C \cdot x^2 \cdot (L - x)^2]$$

Graph 4.1: Plot of two term trial function with the actual ground state wavefunction, revealing excellent agreement.



**Exercise 4.1:** Repeat the entire variational method illustrated above for the ground state particle-in-a-box in a separate worksheet using the following two term trial function, where N is the normalization constant and M is the variational parameter.

$$\alpha(x) = N \cdot [x^2 \cdot (L - x)^2 + M \cdot x^3 \cdot (L - x)^3]$$

### Two Term Trial Function for the 1st Excited State of a Particle-in-a-Box

We can generate a two term trial function for the 1st excited state of the particle-in-a-box by using the two, single trial functions from section 3.

$$\Lambda(D, x) := x \cdot (L - x) \cdot \left(\frac{L}{2} - x\right) + D \cdot x^2 \cdot (L - x)^2 \cdot \left(\frac{L}{2} - x\right)$$

Two term trial function. Again, the normalization constants have been dropped and the weight of the second term relative to the first term is adjustable because we have included a variational parameter ( $D$ ).

This trial function is now inserted into equation 3 and solved symbolically, yielding an expression for energy in terms of our variational parameter  $D$ .

$$\frac{\left[ \int_0^L \Lambda(D, x) \cdot \left( \frac{-\hbar^2}{2 \cdot m} \cdot \frac{d^2}{dx^2} \Lambda(D, x) \right) dx \right]}{\left( \int_0^L \Lambda(D, x) \cdot \Lambda(D, x) dx \right)} \rightarrow \frac{\left( \frac{1}{1260} \cdot D^2 + \frac{1}{40} + \frac{1}{140} \cdot D \right)}{\left( \frac{1}{27720} \cdot D^2 + \frac{1}{840} + \frac{1}{2520} \cdot D \right)}$$

$$\text{varenergy2termexcited}(D) := \frac{\left( \frac{1}{1260} \cdot D^2 + \frac{1}{40} + \frac{1}{140} \cdot D \right)}{\left( \frac{1}{27720} \cdot D^2 + \frac{1}{840} + \frac{1}{2520} \cdot D \right)}$$

Symbolically taking the derivative of  $\text{varenergy3term}(D)$  with respect to  $D$ , setting the resultant expression equal to zero, and solving for  $D$  yields the root value of  $D$  corresponding to the best estimate for energy.

$$\frac{\left(\frac{1}{1260} \cdot D^2 + \frac{1}{40} + \frac{1}{140} \cdot D\right)}{\left(\frac{1}{27720} \cdot D^2 + \frac{1}{840} + \frac{1}{2520} \cdot D\right)}$$

An alternate method for finding the expression for the derivative involves clicking on any  $D$  variable in the expression to the left and then selecting *Variable - Differentiate* from the *Symbolics* menu. This should generate the expression given directly below.

$$\frac{\left(\frac{1}{630} \cdot D + \frac{1}{140}\right)}{\left(\frac{1}{27720} \cdot D^2 + \frac{1}{840} + \frac{1}{2520} \cdot D\right)} - \frac{\left(\frac{1}{1260} \cdot D^2 + \frac{1}{40} + \frac{1}{140} \cdot D\right)}{\left(\frac{1}{27720} \cdot D^2 + \frac{1}{840} + \frac{1}{2520} \cdot D\right)^2} \cdot \left(\frac{1}{13860} \cdot D + \frac{1}{2520}\right)$$

$$11. \frac{(6 \cdot D + 4 \cdot D^2 - 99)}{(D^2 + 33 + 11 \cdot D)^2}$$

The simplified expression for the derivative, obtained by highlighting the entire expression for the derivative (shown directly above) and clicking on the *Simplify* option in the *Symbolics* menu.

The roots of the simplified expression are most easily found by highlighting one of the  $D$  variables in the equation directly above and clicking on the *Variable-Solve* option in the *Symbolics* menu.

$$\begin{pmatrix} \frac{-3}{4} + \frac{9}{4} \cdot \sqrt{5} \\ \frac{-3}{4} - \frac{9}{4} \cdot \sqrt{5} \end{pmatrix}$$

Again, 2 roots are obtained for our variational parameter  $D$ . We will only need one of them; the one corresponding to the lowest energy.

$$E3 := \text{varenergy2termexcited}\left(\frac{-3}{4} + \frac{9}{4} \cdot \sqrt{5}\right)$$

$$E3 = 19.7507764$$

Lowest Energy

$$E4 := \text{varenergy2termexcited}\left(\frac{-3}{4} - \frac{9}{4} \cdot \sqrt{5}\right)$$

$$E4 = 100.2492236$$

Discard this Energy

$$\text{percenterror} := \frac{E(2) - E3}{E(2)} \cdot 100$$

$$\text{percenterror} = -0.059$$

The agreement between the estimated energy and the actual energy for the 1st excited state is again impressive (only -0.059%).

Now that we know the value of  $D$ , we can find the normalization constant as before.

$$D := \frac{-3}{4} + \frac{9}{4} \cdot \sqrt{5}$$

Set the value of  $D$  to the root found above.

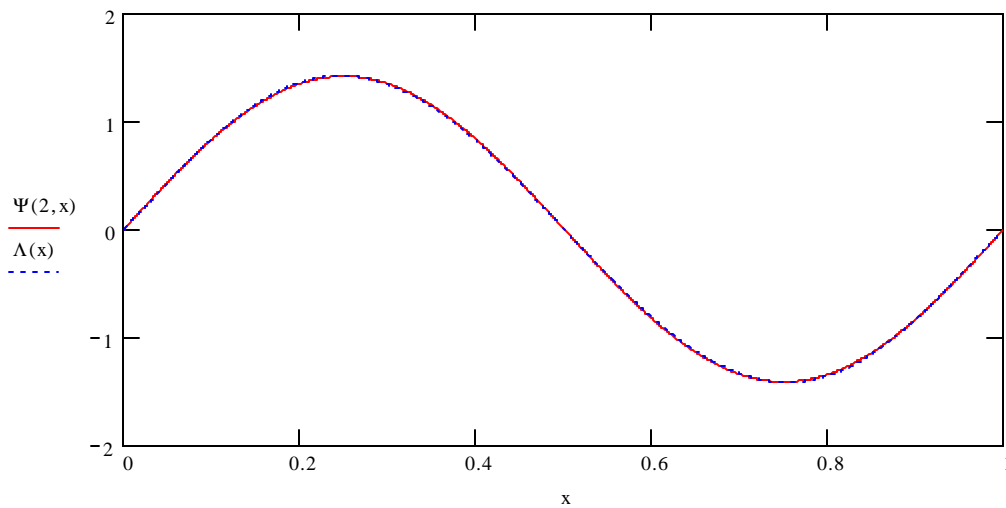
The normalization constant is found by symbolically evaluating the expression shown to the left below.

$$\sqrt{\int_0^L \Lambda(D, x)^2 dx} \rightarrow \frac{1}{\left( \frac{19}{24640} \cdot \sqrt{5} + \frac{9}{4928} \right)^{\left(\frac{1}{2}\right)}}$$

Therefore, the final form of our two term trial function is defined as ...

$$\Lambda(x) := \frac{1}{\left( \frac{9}{4928} + \frac{19}{24640} \cdot \sqrt{5} \right)^{\left(\frac{1}{2}\right)}} \left[ (x) \cdot (L - x) \cdot \left( \frac{L}{2} - x \right) + D \cdot x^2 \cdot (L - x)^2 \cdot \left( \frac{L}{2} - x \right) \right]$$

Graph 4.2: Plot of two term trial function with the actual 1st excited state wavefunction, again revealing excellent agreement.



**Exercise 4.1:** Propose another two term trial function for the 1st excited state of the particle-in-a-box and make sure you include a variational parameter. Use the variational method to estimate the energy, calculate the percent error, and then plot the trial function with the actual 1st excited state wavefunction.

## **5. Conclusions**

The variational methods practiced in this document are still rather trivial in comparison to the techniques used to calculate the energy levels of real chemical systems. Even so, the methods employed in current computational software packages are based upon the same principles. For example, it is possible to obtain reasonable estimates for the electronic energies of molecules containing on the order of 100 atoms. In these cases, the trial function for a particular state can be described as a linear combination of the hydrogen-like atomic orbitals for each atom in the structure. The coefficients in front of each atomic orbital term are treated as the variational parameters. In general, the more terms and variational parameters included in the linear combination, the better the estimate for energy. Of course, there is always a trade-off between the complexity of the trial function and the computational efficiency of the variational calculations.

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