

Solving Particle in a Box Problem Using Computation Method

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Abstract: In quantum mechanics, the variation method is one way of finding approximations to the lowest energy Eigen state or ground state, and some excited states. The method consists in choosing a "trial wave function" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wave function obtained by fixing the parameters to such values is then an approximation to the ground state wave function, and the expectation value of the energy in that state is an upper bound to the ground state energy. In the present work, Particle in a box problem is solved by applying variation method & by using MATLAB & MATHCAD software. The wave functions are solved for the ground state & the first excited state. The results obtained are compared with the chosen trial functions of various orders and their combinations. By this one can able to apply the theoretical knowledge and clearly understand the concept of Particle in a box problem.

Keywords: Computation Method, Ground State Energy, Trial Functions, Variation Energy, Variation Method

I. Introduction

1.1 Variation Method

In quantum mechanics, the variation method ^[1, 3] is one way of finding approximations to the lowest energy Eigen state or ground state, and some excited states. The method consists in choosing a "trial wave function" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wave function obtained by fixing the parameters to such values is then an approximation to the ground state wave function, and the expectation value of the energy in that state is an upper bound to the ground state energy.

Derivation is not always possible to find an analytic solution to the Schrodinger Equation. One can always solve the equation numerically, but this is not necessarily the best way to go; one may not be interested in the detailed Eigen functions, but rather only in the energy levels and the qualitative features of the Eigen functions. And numerical solutions are usually less intuitively understandable.

Fortunately, one can show that the values of the energy levels are only mildly sensitive to the deviation of the wave function from its true form, and so the expectation value of the energy for an approximate wave function can be a very good estimate of the corresponding energy Eigen value. By using an approximate wave function that depends on some small set of parameters and minimizing its energy with respect to the parameters, one makes such energy estimates. The technique is called the variation method because of this minimization process.

This technique is most effective when trying to determine ground state energies, so it serves as a nice complement to the WKB approximation, which works best when one is interested in relatively highly excited states, ones whose deBroglie wavelength is short compared to the distance scale on which the wavelength changes.

1.2 Particle In A Box

The particle in a box problem ^[1, 9] is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of E and ψ that the particle can possess. E represents allowed energy values and $\psi(x)$ is a wave function, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

II. Wave Functions

2.1 Particle In A 1-D 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 ^[1].

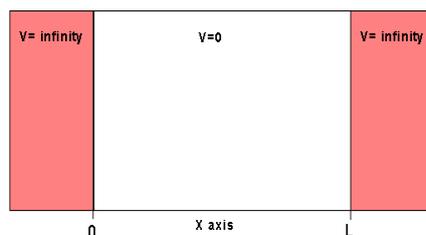


Figure-1: Diagram of a particle in a one dimensional box, illustrating the region where the particle is free to translate and the impenetrable walls to either side.

The expressions for the wave functions are,

$$\psi_n = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi x}{L}\right) \rightarrow (1)$$

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

2.2 Energy Calculation

The expressions for the corresponding energy levels are,

$$E_n = \frac{n^2 \cdot \hbar^2 \cdot \pi^2}{2 \cdot m \cdot L^2} \rightarrow (2)$$

m , \hbar and L are expressed in atomic

Mass (m) is equal to 1

Plank's constant (\hbar) is equal to 1.

The length of the box (L) to equal a unit less length of 1.

units.

For Ground State

$$n=1$$

$$E(1)=4.935$$

$$E_n = \frac{n^2 \cdot \hbar^2 \cdot \pi^2}{2 \cdot m \cdot L^2}$$

For First Excited State

$$n=2$$

$$E_n = \frac{n^2 \cdot \hbar^2 \cdot \pi^2}{2 \cdot m \cdot L^2}$$

$$E(2)=19.739$$

2.3 Expectation Value Of The Energy^[8]

Consider a normalized function ψ expanded in energy Eigen function

$$\psi = \sum_E A_E U_E \rightarrow (3)$$

Where $H U_E = E U_E$

U_E form a complete orthonormal set, the expectation value of H for the function ψ is given by,

$$\langle H \rangle = \int \psi^* H \psi d\tau \rightarrow (4)$$

We get the equation

$$\begin{aligned} \langle H \rangle &= \sum_E A_E^* \cdot U_E^* \cdot H \cdot A_E \cdot U_E d\tau \\ \langle H \rangle &= \sum_E |A_E|^2 \int U_E^* E U_E d\tau \\ \langle H \rangle &= \sum_E H |A_E|^2 \quad \rightarrow (5) \end{aligned}$$

The energy Eigen values are discrete in nature. A useful inequality can be obtained by replacing each Eigen value E in the summation on the right side by the lowest Eigen value E_0 .

$$\langle H \rangle = E_0 \sum_E A_E^2 \quad \rightarrow (6)$$

For a normalized function

$$\psi \sum_E A_E^2 = 1 \quad \rightarrow (7)$$

$$E_0 \leq \int \psi^* H \psi d\tau \quad \rightarrow (8)$$

If ψ is not normalized then,

$$E_0 \leq \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} \quad \rightarrow (9)$$

The variation method consists in evaluating the integrals on the right side of equation (6) & (7) with a trial function ψ that depends on a number of parameters & varying these parameters until the expectation value of the energy is minimum. The result is an upper limit for the ground state energy of the system.

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

$$H = -\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2} \quad \rightarrow (10)$$

The exact energy (actual energy) for the ground state can be obtained by substituting the actual wave function $\psi(n,x)$ (equation (1)) in equation (11),

$$\mathbf{actualenergy} = \frac{\int_0^L \psi(n,x) \cdot \left(-\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2} \psi(n,x)\right) dx}{\int_0^L \psi(n,x) \cdot \psi(n,x) dx} \quad \rightarrow (11)$$

The estimated energy (variation energy) is obtained by substituting the chosen trial functions $\varphi(x)$ in equations (12)

$$\mathbf{varenergy} = \frac{\int_0^L \varphi(x) \cdot \left(-\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2} \varphi(x)\right) dx}{\int_0^L \varphi(x) \cdot \varphi(x) dx} \quad \rightarrow (12)$$

The percent error between actual energy and variation energy is calculated for comparison.

$$\mathbf{percenterror} = \frac{\mathbf{actualenergy} - \mathbf{varenergy}}{\mathbf{actualenergy}} \times 100 \quad \rightarrow (13)$$

III. Trial Functions – Matlab ^{[2],[5]}

3.1 The Ground State^[1]

The trial function should approximate the shape of the true wave function, shown in the plot 5.1.1, 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

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

Where N is 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 wave function for comparison.

$$\int_0^L N^2 [x \cdot (L - x)]^2 dx = 1 \quad \rightarrow (14)$$

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

Evaluation of normalization constant, N

$$N = \sqrt{\frac{1}{\int_0^L [x \cdot (L-x)]^2 dx}} \quad \rightarrow (15)$$

The Different Trial Functions

$$1. \quad \varphi(x) = N \cdot (x \cdot (L - x)) \quad \rightarrow (16)$$

$$2. \quad \varphi(x) = N \cdot (x^2 \cdot (L - x)^2) \quad \rightarrow (17)$$

$$3. \quad \varphi(x) = N \cdot (x^3 \cdot (L - x)^3) \quad \rightarrow (18)$$

$$4. \quad \varphi(x) = N \cdot (x^4 \cdot (L - x)^4) \quad \rightarrow (19)$$

$$5. \quad \varphi(x) = N \cdot (x^5 \cdot (L - x)^5) \quad \rightarrow (20)$$

3.2 The Excited State

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

The 1st excited state wave function 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 in equation (14),

$$\varphi(x) = N \cdot x \cdot (L - x) \cdot \left(\frac{L}{2} - x\right)$$

Where N is normalization constant.

The normalization constant for the first excited state is calculated as done for the ground state,

$$\int_0^L N^2 [x \cdot (L - x) \cdot \left(\frac{L}{2} - x\right)]^2 dx = 1 \quad \rightarrow (22)$$

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

Evaluation of normalization constant, N

$$N = \sqrt{\frac{1}{\int_0^L [x \cdot (L-x) \cdot \left(\frac{L}{2}-x\right)]^2 dx}} \quad \rightarrow (23)$$

The Different Trial Functions

$$1. \quad \varphi(x) = N \cdot (x \cdot (L - x) \cdot \left(\frac{L}{2} - x\right)) \quad \rightarrow (24)$$

$$2. \quad \varphi(x) = N \cdot (x^2 \cdot (L - x)^2 \cdot \left(\frac{L}{2} - x\right)^2) \quad \rightarrow (25)$$

$$3. \quad \varphi(x) = N \cdot (x^3 \cdot (L - x)^3 \cdot \left(\frac{L}{2} - x\right)^3) \quad \rightarrow (26)$$

$$4. \quad \varphi(x) = N \cdot (x^4 \cdot (L - x)^4 \cdot \left(\frac{L}{2} - x\right)^4) \quad \rightarrow (27)$$

$$5. \quad \varphi(x) = N \cdot (x^5 \cdot (L-x)^5 \cdot (\frac{L}{2} - x)^5) \quad \rightarrow (28)$$

IV. Combination Of Trial Functions - Mathcad

4.1 The Ground State

One is fortunate if an accurate energy is obtained from a single term trial function^[6, 7]. The accuracy of the variation 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 variation parameters.

We can generate a two & three term trial function for the ground state of the particle-in-a-box by using the three, single trial functions,

Two & Three term trial function. The weight of the second & third term, relative to the first term, is adjustable because we have included a variation parameter (C).

Combination of 1st & 2nd trial functions (equations 16 & 17)

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) + C1 \cdot \left(x^2 \cdot (L-x)^2 \right) \right) \rightarrow (30)$$

Combination of 1st & 2nd & 3rd trial functions (equations 16, 18)

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) + C1 \cdot \left(x^3 \cdot (L-x)^3 \right) \right) \rightarrow (31)$$

Combination of 1st & 2nd & 3rd trial functions (equations 16, 17, 18)

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) + C1 \cdot \left(x^2 \cdot (L-x)^2 \right) + C1 \cdot \left(x^3 \cdot (L-x)^3 \right) \right) \rightarrow (32)$$

4.2 The Excited State

We can generate a two term & three term trial functions for the first excited state of the particle-in-a-box by means of linear combination of trial functions,

Combination of 1st & 3rd trial functions (equations 24, 26)

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) \cdot \left(\frac{L}{2} - x \right) + C1 \cdot \left(x^3 \cdot (L-x)^3 \cdot \left(\frac{L}{2} - x \right)^3 \right) \right) \rightarrow (33)$$

Combination of 1st & 5rd trial functions (equations 24, 28)

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) \cdot \left(\frac{L}{2} - x \right) + C1 \cdot \left(x^5 \cdot (L-x)^5 \cdot \left(\frac{L}{2} - x \right)^5 \right) \right) \rightarrow (34)$$

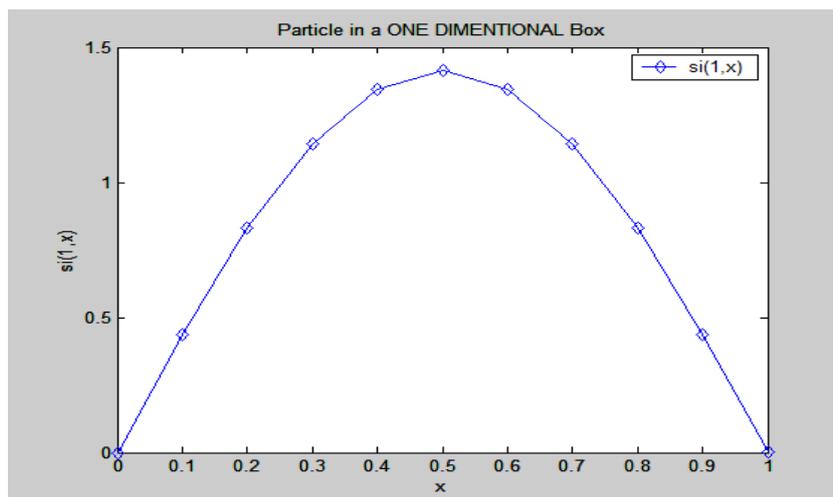
Combination of 1st & 3rd & 5rd trial functions (equations 24, 26, 28)

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) \cdot \left(\frac{L}{2} - x \right) + C1 \cdot \left(x^3 \cdot (L-x)^3 \cdot \left(\frac{L}{2} - x \right)^3 \right) + C1 \cdot \left(x^5 \cdot (L-x)^5 \cdot \left(\frac{L}{2} - x \right)^5 \right) \right) \rightarrow (35)$$

V. Result & Discussion

5.1 The Ground State

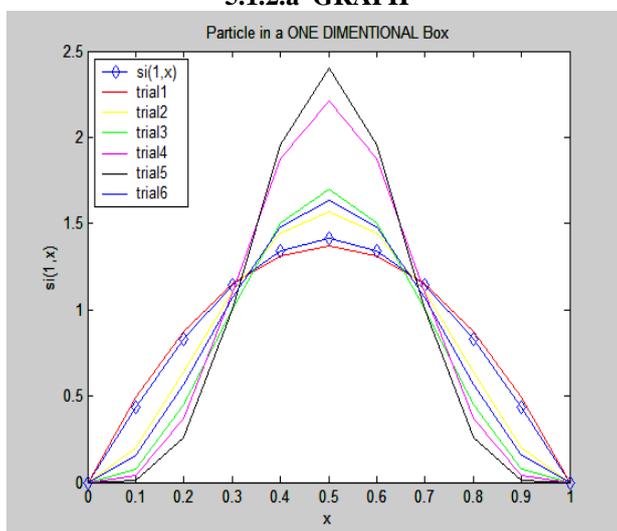
5.1.1 Wave Function



Graph 1.1: Plot of the wave functions for the ground state wave function.

5.1.2 Trial Functions - Matlab

5.1.2.a GRAPH



Graph 1.2: Plot of the wave functions for the ground state trial functions & wave function .

5.1.2. b The Trial Functions

TRIAL FUNCTIONS	ACTUAL ENERGY	VARIATION ENERGY	PERCENT ERROR
1	4.9348	5	1.3212
2		6	21.5854
3		7.8000	58.0610
4		9.7143	96.8526
5		11.6667	136.4161

- ❖ As the order of the trial function increases
- The variation energy increases than that of the actual energy.
- The percent error also increases.

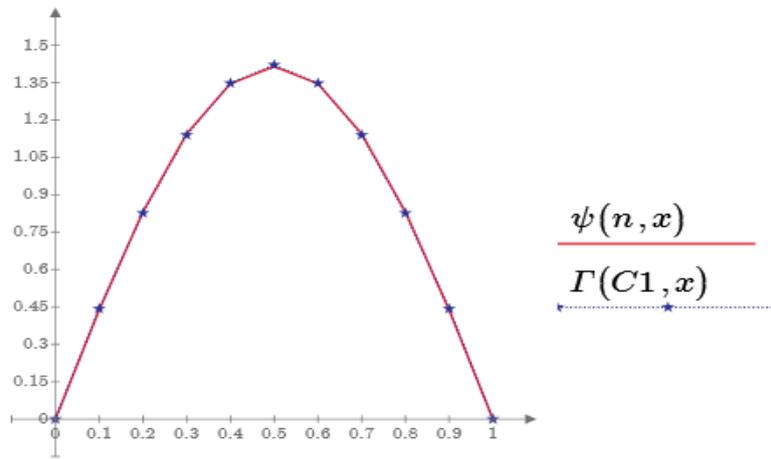
Inference:

So compared to all the trial function, the 1st trial function suits the best.

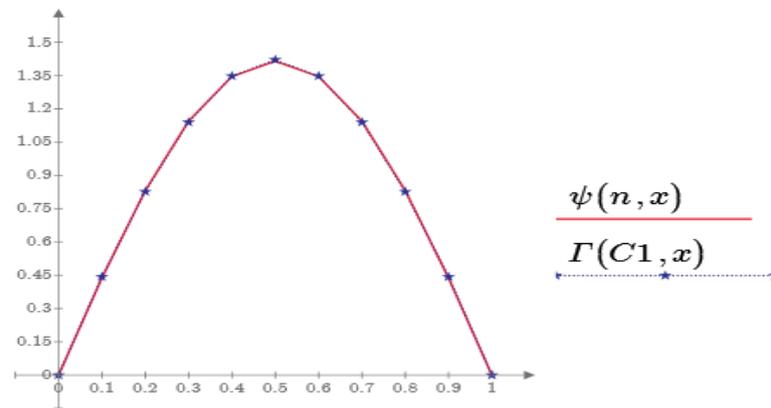
5.1.3 Combination Of Trial Functions - Mathcad

5.1.3.A Graph

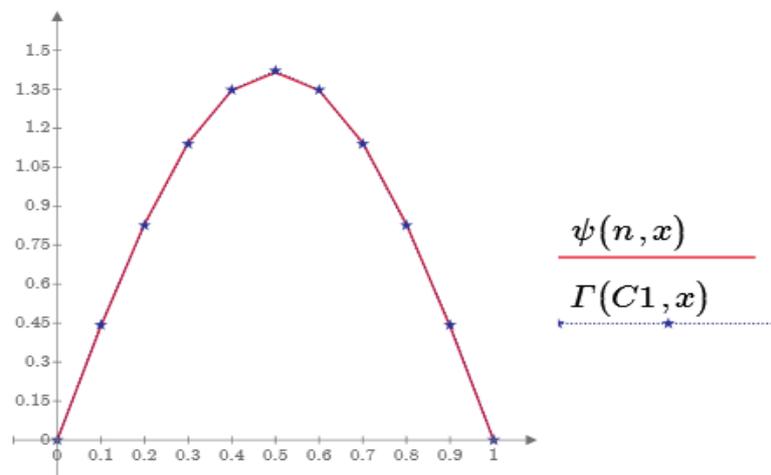
$$\Gamma(C1, x) := N1 \cdot (x \cdot (L - x) + C1 \cdot (x^2 \cdot (L - x)^2))$$



$$\Gamma(C1, x) := N1 \cdot (x \cdot (L-x) + C1 \cdot (x^3 \cdot (L-x)^3))$$



$$\Gamma(C1, x) := N1 \cdot (x \cdot (L-x) + C1 \cdot (x^2 \cdot (L-x)^2) + C1^2 \cdot (x^3 \cdot (L-x)^3))$$



Graph 1.3: Plot of the wave functions for the ground state. (Combination of trial functions)

5.1.3.B The Combination Of Trial Functions

TRIAL FUNCTIONS	ACTUAL ENERGY	VARIATION ENERGY	PERCENT ERROR
1&2	4.9348	4.935	0.001
1&3		4.939	0.083
1,2&3		4.935	0.002

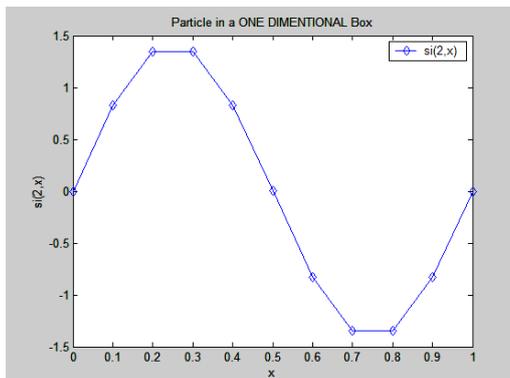
- ❖ From the table, one can infer that,
- The variation energy approximately equal to the actual energy.
- Percent error is very small compared to the individual trial functions.

Inference:

Comparing both the individual & combination of trial functions the combination of 1st & 2nd trial functions suits the best.

Also from the graph 5.1.2.a we came to know that all the chosen trial functions obey the nodal & symmetry properties.

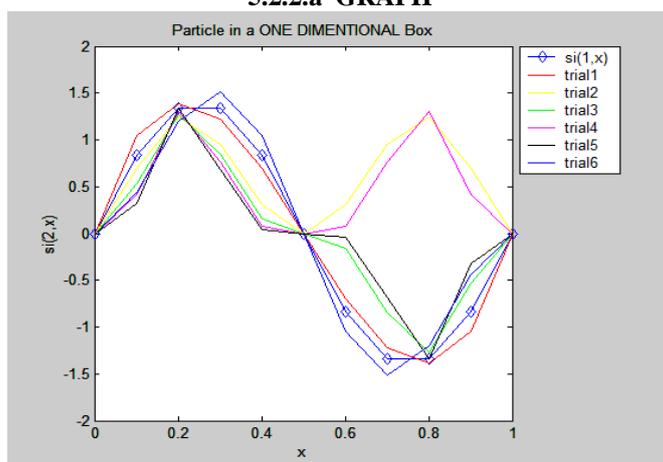
5.2 The Excited State
5.2.1 Wave Function



Graph 2.1: Plot of the wave functions for the 1st excited state wave function

5.2.2 Trial Functions - Matlab

5.2.2.a GRAPH



Graph 2.2: Plot of the wave functions for the 1st excited state wave function & trial functions

5.2.2.b The Trial Functions

TRIAL FUNCTIONS	ACTUAL ENERGY	VARIATION ENERGY	PERCENT ERROR
1		21	6.3872
2		26	31.7175
3		34.2000	73.2592

4	19.7392	42.8571	117.1168
5		51.6667	161.7464

- ❖ As the order of the trial function increases
- The variation energy increases than that of the actual energy.
- The percent error also increases.

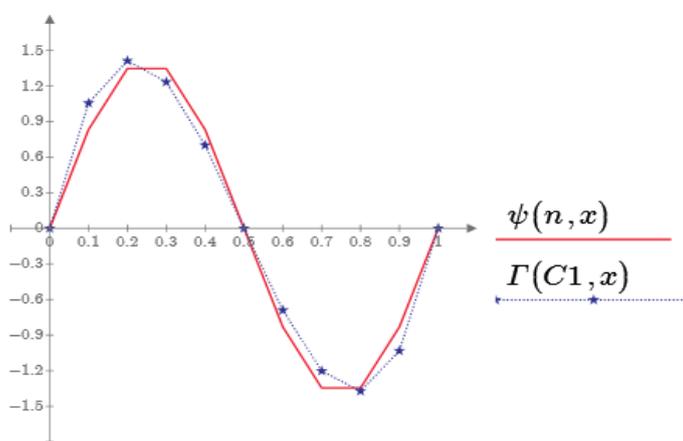
Inference:

As seen in the graph 5.2.2.a, trial function 2 & 4 behave indifferent. They didn't obey the nodal & symmetry properties. So, one can neglect those trial functions. Here also 1st trial function suits the best.

5.2.3 Combination Of Trial Functions - Mathcad

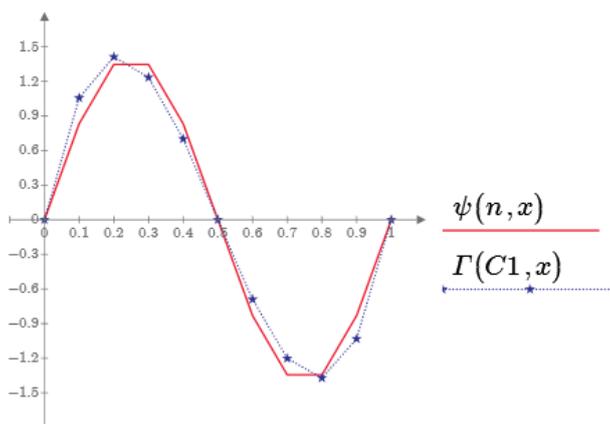
5.2.3.a GRAPH

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) \cdot \left(\frac{L}{2} - x \right) + C1 \cdot \left(x^3 \cdot (L-x)^3 \cdot \left(\frac{L}{2} - x \right)^3 \right) \right)$$



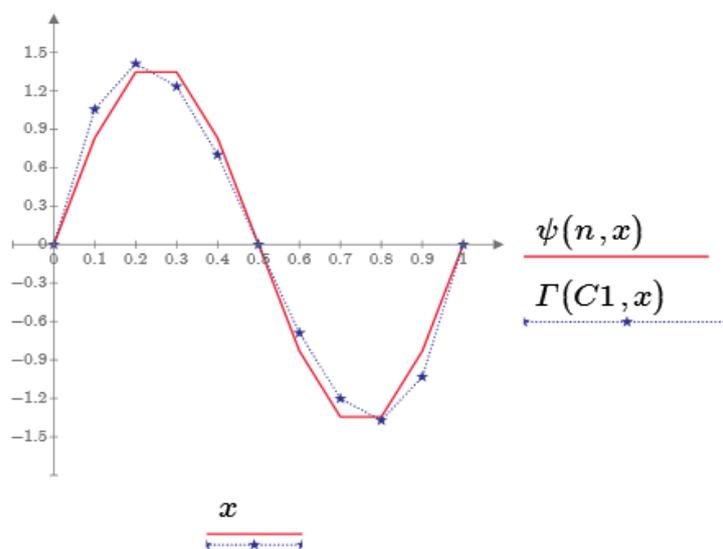
x

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) \cdot \left(\frac{L}{2} - x \right) + C1 \cdot \left(x^5 \cdot (L-x)^5 \cdot \left(\frac{L}{2} - x \right)^5 \right) \right)$$



x

$$\Gamma(C1, x) := N1 \cdot \left(x \cdot (L-x) \cdot \left(\frac{L}{2} - x \right) + C1 \cdot \left(x^3 \cdot (L-x)^3 \cdot \left(\frac{L}{2} - x \right)^3 \right) + C1 \cdot \left(x^5 \cdot (L-x)^5 \cdot \left(\frac{L}{2} - x \right)^5 \right) \right)$$



Graph 2.3: Plot of the wave functions for the 1st excited state. (Combination of trial functions)

5.2.3.b The Combination Of Trial Functions

TRIAL FUNCTIONS	ACTUAL ENERGY	VARIATION ENERGY	PERCENT ERROR
1&3	19.7392	20.872	5.74
1&5		20.906	5.909
1,3&5		20.872	5.741

- ❖ From the table, one can infer that,
 - The variation energy approximately equal to the actual energy.
 - Percent error is small compared to the individual trial functions.

Inference:

Comparing both the individual & combination of trial functions the combination of 1st & 3rd trial functions suits the best.

VI. Conclusion

This project work entitled PARTICLE IN A BOX PROBLEM is done to gain a familiarity with the variation method. By this work, one can able to apply the theoretical knowledge in quantum mechanical problems. With the help of software packages such as MATLAB & MATHCAD, the calculation part is done in an easy & interesting way. Visualizing the problem of PARTICLE IN A BOX PROBLEM graphically enhances our understanding about the variation method. This work will be helpful to the M.Sc students to understand clearly the concept of PARTICLE IN A BOX and the equations correspond to the wave functions and energy levels of a Particle in a box problem.

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