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# ESTIMATION OF GROUND-STATE ENERGY OF PARTICLE IN 1-D POTENTIAL WELL-VARIATION METHOD

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## Abstract:

Quantum mechanics provides approximate methods like perturbation and Variation methods to solve the one electron or many electron systems. The variation method is employed to solve the problem of particle in one dimensional potential well. The exact value of ground state energy (GSE) of particle in –D potential well and form of normalized wave function was calculated. The suitable trial wavefunctions are decided after some cumbersome calculations. Starting with these trail wavefunctions the expressions for expectation values of Hamiltonian (<H>) are obtained. The computer programs are designed to solve the tedious integrals in the expressions for Hamiltonian. The GSE of each trail wavefunction and values of variational parameter ($\alpha$) are obtained. The values of GSE with exact value are then discussed how one can approaches towards the exact wavefunction and GSE.

**Key Words:** H ψ = Eψ, Variation method, trial Wavefunction, Variational parameter ($\alpha$) BASIC, GSE.

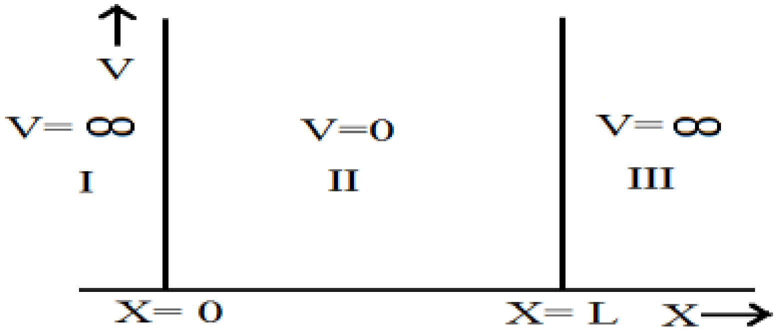
## Introduction:

There are quite few problems in quantum mechanics which cannot be solved exactly i.e. Schrödinger's equation Hψ = Eψ cannot solve exactly for such problems. Estimation of ground state energy (GSE) of the bound state system is one of such problem. There are some approximate methods available to solve such problem, viz perturbation method, variation method, W.K.B. method. The perturbation method is used in case where the problem consists small dimensionless parameter and system is exactly solvable when small parameter sent to zero. In variation method there is no requirement of small parameter and even system is not exactly solvable. Therefore it has been useful in studying Quantum Hall Effect etc.

The variational principles are very useful analytical tool for the study of the ground state energy of any dynamical system. The variational method is useful to study the ground state, but not very useful for the study of excited states. The Variation Theorem states that the energy calculated for the system from the trial wavefunction is never less than the actual energy. 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 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 Wave function is supposed to gave the “complete knowledge” about the system. The more flexible the trial function, the better the agreement between the estimated energy and the actual energy of the system. In this work, we have evaluated the method and techniques of variational principle to derive the ground state energy for the particle in one dimensional potential well. The exact solution of system was discuss with solution obtain by variation method. We are fully aware of fact that the method can be applied to estimate Helium, Lithium, and Beryllium etc. We offer computer programming in BASIC Language required for calculation of integrals. Even though the trial wavefunction seems to be simple, but expression for <H> becomes complicated to determine Variational parameter (α).The Graph of exact wave function versus trial wave function are plotted. The table gives how we are close to exact wave function using trial wave function. The GSE of 1-D Potential well are discussed and calculated for various trail wavefunctions.

## 2. Particle in one dimensional potential well:

### 2.1. Exact solution:



(**Fig. 1** shows region where particle is free to move and impenetrable walls on either side)

Consider a particle that is confined to motion along a segment of the x-axis (a one dimensional well). For simplicity, imagine the boundaries of the well to lie at x=0 and x=L. The system is described by potential-

$$V(x) = 0 \quad \text{for} \quad 0 \leq x \geq L$$

$$= \infty \quad \text{for} \quad \text{Otherwise}$$

The potential does not depends upon time therefore steady state Schrödinger equation is relevant

$$-\frac{h^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = E\Psi$$

$$\frac{d^2\Psi}{dx^2}\frac{2m}{\hbar^2}\,[E-V]\,\mathbf{\Psi}=0$$

Appling the boundary conditions on I,II,III regions and further solving we get-sinKL=0

$$KL = n\pi \quad (n=1,2,\ldots\ldots)$$

Put $K=\sqrt{\frac{2mE}{\hbar}}$, $\therefore \sqrt{\frac{2mE}{\hbar}}\,L = n\pi$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad (n = 1,2,\ldots.)$$

The allowed states are thus seen to be discreet and depending on integral values of n.

The actual GSE after putting ħ=m=L=1

$$E_0 = \frac{\pi^2}{2} = 4.93480 \text{ units.}$$

This is the exact value of GSE of particle in 1-D potential well.

### 2.2 Exact wavefunction:

$K_n = \frac{n\pi}{L}$ , Which on substituting on equation $\Psi_{II}$ = sinkx. Now using normalization condition $\Psi_n(x)$ =F sin$\frac{n\pi}{L}$

$$\int_0^L \Psi_n^* \Psi_n \, dx = 1$$

$$\therefore |F|^2 \int_0^L \sin^2\frac{n\pi x}{L}\,dx = 1 \qquad (|F|^2 = F^*F)$$

$$|F|^2 \int_0^L \frac{(1-\cos\frac{2n\pi x}{L})}{2}\,dx = 1$$

$$\frac{|F|^2}{2}\left[x - \frac{L}{2n\pi}\sin\frac{2n\pi x}{L}\right]_0^L = 1$$

$$\therefore \frac{|F|^2}{2}L = 1, \quad F = \sqrt{\frac{2}{L}}$$

Thus normalized **exact function** is $\Psi_n(x) = \sqrt{\frac{2}{L}}$ sin$\frac{n\pi}{L}$ .

### 3. Choice of trail wavefunction:-

The choice of trail wavefunction has great importance in this method. The following points are considered while choosing trial wavefunction .

1. Any suitable trail wavefunction which should be square integrable.
2. The wave function should satisfy boundary conditions of problem under consideration.

3. The wavefunction should have very few parameters. No doubt, as numbers of parameters are increased better would be the results obtained. But for the method to be more practice, it is better to involve few parameters depending upon the accuracy.
4. The trail wave function should be simple in its form so that the algebra involve become simple.

## 4. Determination of ground state energy (GSE):

### 4.1. Trial wave function- $\Psi_{trial}$ = A $(x^2 + \alpha x^3 - xL - x^2\alpha L)$

The $\alpha =$ $Variational\ parameter$ and A= Normalization constant.

$$\Psi_{trial} = \text{A}\ (x^2 + \alpha x^3 - xL - x^2\alpha L)$$

$$\frac{d^2\Psi}{dx^2} = \text{A}\ (2+6\alpha x + 2\alpha L)$$

The Hamiltonian operator for particle in 1-d potential well is- H=-$\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\therefore \text{H}\Psi = -\ \frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}$$

$$\therefore \text{H}\Psi = -\ \frac{\hbar^2}{2m}\ \text{A}\ (2+6\alpha x + 2\alpha L)$$

$$\langle \text{H} \rangle = \frac{\int_0^L \Psi^* H\Psi\, dx}{\int_0^L \Psi^*\Psi\, dx}$$

$$= \frac{-\frac{\hbar^2}{2m}\int_0^L x^2+\alpha x^3-xL-x^2\alpha L(\,2+6\alpha x-2\alpha L)dx}{\int_0^L x^2+\alpha x^3-xL-x^2\alpha L}$$

$$= \frac{(\frac{-L^2}{3}-\frac{\alpha L^4}{3})-\frac{2}{15}\alpha^2 L^5}{\frac{-L^5}{30}+\frac{\alpha L^6}{30}+\frac{\alpha^2 L^7}{105}}$$

$$= (\ \frac{[2\alpha^2 5\alpha+5]}{3.5+3.5\alpha+\alpha^2}\ )\ \frac{7}{5}$$

$$= 7\text{-}\ \frac{(2\alpha+2)}{(1+\alpha\frac{2\alpha^2}{7})}$$

Now for ⟨H⟩ is to be minimum $\frac{\partial\langle H\rangle}{\partial\alpha} = 0$

$$\frac{\partial\langle H\rangle}{\partial\alpha} = \frac{\partial}{\partial\alpha}\ (\ \frac{2\alpha+2}{1+\alpha+\frac{2}{7\alpha^2}})$$

$$\frac{\frac{4}{7}(\alpha^2+2\alpha)}{(1+\alpha+\frac{2}{7\alpha^2)})} = 0$$

$$(\alpha^2 + 2\alpha) = 0$$

$$\alpha = 0 \text{ or } \alpha = -2$$

$$\langle H \rangle_{min} = 7 - \frac{(2\alpha+2)}{(1+\alpha+\frac{2}{7\alpha^2})} \quad = 7 - \frac{2}{1}$$

$$\langle H \rangle_{min} = 5$$

Hamiltonian operator solved exactly so it need not require computer programme for solution of the wave function.

### 4.2. Trail wavefunction- $\boldsymbol{\Psi_{trial}} = \textbf{A sin}\boldsymbol{\alpha x(x - L)}$

$$\Psi = \text{A sin}\,(\alpha x^2 - \alpha x L)$$

$$\frac{d^2\Psi}{dx^2} = \text{A}[(\,2\alpha x - \alpha L^2\,(-sin(\alpha x^2 - \alpha x L)] \;\; + 2\alpha \cos\,(\alpha x - \alpha x L)$$

The Hamiltonian operator for particle in 1-d potential well is- H= $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \text{V}(x)$

$$\therefore \text{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}$$

$$\text{H}\psi = \frac{A\,\hbar^2}{2m}\,\{-2\alpha\cos\,(\alpha x^2 - \alpha x L) + (2\alpha x - \alpha L)^2 \sin\,(\alpha x^2 - \alpha x L)\}$$

$$\langle H \rangle = \frac{\int_0^L \Psi^* H \Psi\, dx}{\int_0^L \Psi^* \Psi\, dx}$$

$$\langle H \rangle = \frac{\frac{\hbar^2}{2m}\int_0^L (2\alpha x - \alpha L)^2\,(sin)^2\left(\alpha x^2 - \alpha x L\right) - \alpha sin[2(\alpha x^2 - \alpha x L)]\,dx}{\int_0^L (sin)^2\,(\alpha x^2 - \alpha x L)\,dx}$$

The value of $\langle H \rangle$can be calculated for different values of $\alpha$ using a computer programming.

### 4.3. Trial wavefunction – $\boldsymbol{\Psi_{trial} = \frac{A\,(x^2 - xL)}{(1+\alpha x^2)}}$

$$\frac{d^2\psi}{dx^2} = \text{A}\left\{\frac{(1+\alpha x^2)^2[\,2\alpha\, xL + 2] - [\alpha x^2 L - 2L - L]4\alpha x(1+\alpha x^2)}{(1+\alpha x^2)^4}\right\}$$

$$\text{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \text{V}(x)$$

$$\therefore \text{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}$$

$$\langle H \rangle = \frac{\int_0^L \Psi^* H \Psi\, dx}{\int_0^L \Psi^* \Psi\, dx}$$

$$\langle H \rangle = \frac{\frac{\hbar^2}{2m}\int_0^L [(x^2 - xL)(\alpha^2 Lx^3 + 3x^2 - 3\alpha x L - 1)]\,dx}{\int_0^L \left[\frac{x^2 - xL}{1+(\alpha x^2)}\right]^2 dx}$$

Now the integration solved by computer programming.

### 4.4. Trial wavefunction $\boldsymbol{\Psi_{trial} = \frac{A(x^2 - xL)}{(1+x^2)^\alpha}}$:-

$$\Psi_{trial} = \frac{A(x^2 - xL)}{(1+x^2)^\alpha}$$

$$\frac{d^2\Psi}{dx^2} = \text{A}\left\{\frac{2}{(1+x^2)^\alpha} + \frac{6xL\alpha - 10\alpha x^2}{(1+x^2)^{\alpha+1}} + \frac{4\alpha(\alpha+1)(x^4 - x^3 L)}{(1+x^2)^{\alpha+2}}\right\}$$

The Hamiltonian is - $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ , $H\Psi = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}$

$$H\Psi = -\frac{\hbar^2 A}{2m}\{\frac{1}{(1+x^2)^{\alpha}} + \frac{3\alpha Lx-5+\alpha x^2}{(1+x^2)^{\alpha+1}} + \frac{2\alpha(\alpha+1)(x^4-x^3L)}{(1+x^2)^{\alpha+2}}$$

Now expectation value is $\langle H\rangle = \frac{\int_0^L \Psi^* H\Psi\, dx}{\int_0^L \Psi^*\Psi\, dx}$

$$\langle H\rangle = \frac{\int_0^L \frac{A(x^2-xL)}{(1+x^2)^{\alpha}}[\frac{-A\hbar}{m}(\frac{1}{(1+x^2)^{\alpha}}+\frac{3\alpha Lx-5\alpha x^2}{(1+x^2)^{\alpha+1}}+\frac{2\alpha(\alpha+1)(x^4-x^3L)}{(1+x^2)^{\alpha+2}}]dx}{[\int_0^L \frac{A(x^2-xL)}{(1+x^2)^{\alpha}}\ \frac{A(x^2-xL)}{(1+x^2)^{\alpha}}]dx}$$

$$\langle H\rangle = \frac{-\frac{\hbar^2}{m}[\int_0^L \frac{(x^2-xL)}{(1+x^2)^{2\alpha}}+\frac{(x^2-xL)(3\alpha Lx-5\alpha x^2)}{(1+x^2)^{2\alpha+1}}+\frac{2\alpha(\alpha+1)(x^2-xL)(x^4-x^3L)}{(1+x^2)^{2\alpha+2}}]dx}{\left[\int_0^L \frac{(x^2-xL)}{(1+x^2)^{\alpha}}\right]^2 dx}$$

The integration solved further by computer programming.

### 4.5 Trial wavefunction

**$\Psi_{trial}$ = A [sin $(\frac{\alpha x}{L})$ - $\frac{x}{L}sin\alpha$]:-**

$$\Psi_{trial} = A\,[\sin(\frac{\alpha x}{L}) - \frac{x}{L}sin\alpha]$$

$$\frac{d^2\Psi}{dx^2} = -\frac{A\alpha^2}{L^2}\sin(\frac{x\alpha}{L})$$

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\ ,\quad H\Psi = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}$$

$$\langle H\rangle = \frac{\int_0^L \Psi^* H\Psi\, dx}{\int_0^L \Psi^*\Psi\, dx}$$

$$\langle H\rangle = \frac{[\frac{\hbar^2\alpha}{2mL^2}^{2}\int_0^L sin^2\left(\frac{\alpha x}{L}\right)-sin\left(\frac{\alpha x}{L}\right)(\frac{\alpha}{L})sin\alpha]dx}{[\int_0^L sin\left(\frac{\alpha x}{L}\right)-(\frac{\alpha}{L})sin\alpha]^2dx}$$

The value of $\langle H\rangle_{min}$ can be calculated for different values of $\alpha$ using computer programming.

### 5. Sample computer programme and corresponding values of veriational parameter ($\alpha$)

### 5.1Computer programme- $\Psi_{trial}$ = A sin$\alpha x(x-L)$

The computer program is developed using BASIC language for all trial wavefunctions. The given computer program is corresponding to the trail wavefunction -A sin$\alpha x(x-L)$ .

```
20      PRINT"                          PROBLEM NO – 2
30      PRINT" PARTICALE IN ONE DIMENTIONAL POTENTIAL WELL"
40      PRINT" ESTIMATION OF GROUND STATE ENERGY BY VARIATION
        METHOD"
50      PRINT" ALPHA IS VARIATION PARAMETER"
60      A = O
```

```
70      B = 1
80       N = 200
90       R1 = -1.01
100      R2 = 1.5
110       S = 0.1
120     H = (B-A) / N
130      FOR AL = R1 TO R2 STEPS    S
140      X=0
150     Y= 0
160      SUM = 0
170     FOR I = 0 TO N
180     X = I *  H
190     V1 = ( 2*AL*X- AL) ^ 2
200     V2 = (SIN (AL*X^2 – AL* X ))^ 2
210     V3 = AL*SIN (2*AL*X^2-2*AL*X)
220     C1= 0.5*(V1*V2 –V3)
230     IF I=0 THEN SUM = SUM = SUM + C1 : GOTO 280
240     IF I=N THEN SUM = SUM = SUM + C1 : GOTO 280
250     IF M1= (I/2) – INT (I/2)
260     IF M1=0 THEN SUM = SUM + 4*C1 : GOTO 280
270     SUM = SUM + 2*C1
280     NEXT I
290     T1 = (SUM * H )/3
300     SUM = 0
310     FOR J = 0 TO N
320     Y = J * H
330     U1 = SIN ( AL * Y^2 – AL * Y )
340      U2 = U1^2
350     C2 = U2
360      IF J =0 THEN SUM = SUM = SUM + C2 : GOTO 410
370     IF J = N THEN SUM = SUM = SUM + C2 : GOTO 410
380     M2 = (J/2) – INT (J/2)
390     IF M2 = 0 THEN SUM = SUM + 4*C2 : GOTO 410
400     SUM = SUM + 2* C2
410     NEXT J
420     T2 = SUM * H/3
430     E = T1/T2
440     PRINT” ALFHA =”; AL:” < H > =”; E
450     NEXT AL
460     ENDS
```

### **5.2. The values of veriational parameters ($\alpha$) -**

ALPHA is variation parameter.

```
ALPHA =-1.01 <H>= 5.008149 T2=3.345666E-02
ALPHA =-.9099999<H>=5.006523 T2=2.724259E-02

ALPHA =-.81<H>=5.005081 T2=2.164328E-02
```

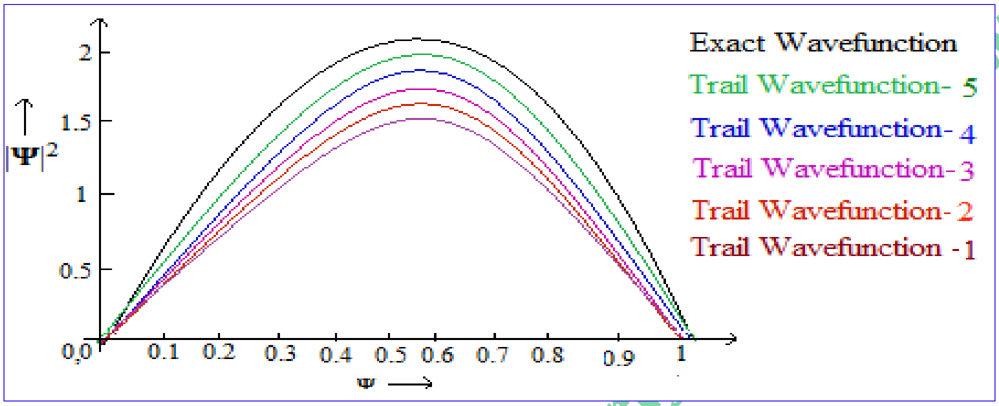
```
ALPHA =.-71<H>=5.005081 T2=2.164328E-02

ALPHA =-.81<H>=5.005081 T2=2.164328E-02

ALPHA =-.6099999<H>=5.002743 T2=1.233026E-02

ALPHA =-.5099999<H>=5.001834 T2=8.634262E-03

ALPHA =-.4099999<H>=5.001091 T2=5.588396E-03

ALPHA =-.3099999<H>=5.000513 T2=3.198449E-03

ALPHA =-.2099999<H>=5.0001 T2=1.46897E-03

ALPHA =-.1099999<H>=4.999848 T2=4.03255E-04

ALPHA =-9.999886E-03<H>=4.999753 T2=3.333251E-06

ALPHA =9.000011E-02<H>= 4.999815 T2=2.69966E-04

ALPHA =.1900001 <H>=5.000037 T2=1.202645E-03

ALPHA =.2900001<H>=5.000418T2=2.799597-03

ALPHA =.3900001<H>=5.000963T2=5.057777E-03

ALPHA=.4900001<H>=5.001672T2=7.972889E-03

ALPHA=.5900001<H>=5.00255T2=1.153938E-03

ALPHA=.6900001<H>=5.003592T2=1.575048E-02

ALPHA=.7900001<H>=5.004816T2=2.059815E-02

ALPHA=.8900002<H>=5.006222T2=.0260732
```

## 5. Result and Discussion-

**Table 1:** Table showing trial wavefunctions corresponding expressions for Hamiltonian, $\alpha$ and GSE

| **Trial Wavefunction (□)** | **Expression for $< H >$** | **Value of $\alpha$** | **GSE** |
|---|---|---|---|
| A( $x^2 + \alpha x^3 - xL - x^2 \alpha L)$ | $7-\frac{(2\alpha+2)}{(1+\alpha+\frac{2\alpha^2}{7})}$ | $\alpha = 0$ or $\alpha = -$ | 5.000000 |
| A sin$\alpha x(x-L)$ | $\frac{\frac{\hbar^2}{2m}\int_0^L (2\alpha x-\alpha L)^2\,(\sin)^2\,(\alpha x^2-\alpha xL)-\alpha\sin[2(\alpha x^2-\alpha xL)]\,dx}{\int_0^L (\sin)^2\,(\alpha x^2-\alpha xL)\,dx}$ | 0.09999886 | 4.999753 |
| $\frac{A\,(x^2-xL)}{(1+\alpha x^2)}$ | $\frac{\frac{\hbar^2}{2m}\int_0^L[(x^2-xL)(\alpha^2Lx^3+3x^2-3\alpha xL-1)]\,dx}{\int_0^L [\frac{x^2-xL}{1+(\alpha x^2)}]^2dx}$ | 0.09999999 | 4.993169 |

| | | | |
|---|---|---|---|
| $\frac{A(x^2 - xL)}{(1+x^2)^\alpha}$ | $\frac{-\frac{\hbar^2}{m}[\int_0^L \frac{(x^2-xL)}{(1+x^2)^{2\alpha}} + \frac{(x^2-xL)(2\alpha Lx-2\alpha x^2)}{(1+x^2)^{2\alpha+1}} + \frac{2\alpha(\alpha+1)(x^2-xL)(x^4-x^3L)}{(1+x^2)^{2\alpha+2}}]d}{\left[\int_0^L \frac{(x^2-xL)}{(1+x^2)^\alpha}\right]^2 dx}$ | 0.1000001 | 4.980156 |
| A [sin $(\frac{\alpha x}{L})$ - $\frac{x}{L}sin\alpha$] | $\frac{[\frac{\hbar^2\alpha}{2mL^2}]^2 \int_0^L sin^2(\frac{\alpha x}{L}) - sin(\frac{\alpha x}{L})(\frac{\alpha}{L})sin\alpha]dx}{[\int_0^L sin(\frac{\alpha x}{L}) - (\frac{\alpha}{L})sin\alpha]^2 dx}$ | 3.79999 | 4.972896 |



(**Fig. 2** shows closeness of ground state exact wavefunction and Trail wavefunctions)

It is seen from above table values of GSE of various trial wavefunctions are greater than exact value of ground state energy. As trial wavefunction gets closer to exact wavefunction the energy approaches to the exact ground state energy. The value of ground state energy calculated is 4.972896. If we compare the values of GSE shown in table, it is an upper bound to the exact ground state energy. The best estimate of GSE is for 5 $^{th}$ trial wavefunction corresponding to value of variational parameter $(\alpha)$ 3.7999.The first trail wavefunction does not require computer programming as( completely solved) we got it in complete number. The estimated energy is slightly higher than actual energy.

## 7. Conclusions:

We have demonstrated the method and techniques of variational principle to derive the ground state energy for one dimensional potential well with a ground state wave function for Hamiltonian. Our result shows that the variational method is appropriate in determining the exact solutions of any physical problems. The method can be employed to estimate GSE of Simple Harmonic Oscillator (SHO), Hydrogen atom, Deuteron etc. The method can also be applied to estimation of GSE of Helium, Lithium, Beryllium were it is difficult to obtain value of expectation value of Hamiltonian. In systems were there is more than one electron the interaction of atoms are involved and therefore algebra becomes cumbersome.

Following statements can be made to summarize the results.

1. The variation method provides the excellent estimate for the system of interest provided that the trial wavefunction is chosen correctly.

2. The accuracy of variational method can be improved by writing the trial wavefunction as linear combination of single trial wavefunctions.
3. One can use newly developed computer language instead BASIC to solve complex and tedious integrals.
4. The best estimates can be obtained by representing trial wavefunction as linear combination of trial wavefunctions.
5. The terms in linear combination are weighted by variational parameter $\alpha$.
6. It is possible to obtain reasonable estimates for energy of molecule containing 100 atoms.
7. The number of Wavefunctions could be tried to get best estimate of GSE.
8. Even though trail wavefunctions are seems to be simple in its form the expression for $< H >$ becomes so complicated that the job of determination of value of variational parameter alpha becomes tedious job.

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