Construction of A Trial Function In The Variational Procedure of Quantum Mechanics

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Abstract

A form of variational method for calculating the ground state energy of a quantum mechanical system is considered. The method is based on a systematic construction of a trial variational function at each step of the calculation of the ground state energy. The construction involves introducing more variational parameters to the trial wave function such that; the more variational parameters retained, the more accurate the calculated ground state energy. The method is tested using two different quantum mechanical systems. Good agreement between the calculated ground state energy and the corresponding exact value is found. The forms of the wave function in the transition from one step of the calculation to the next are also obtained.

1.0   Introduction

Variational method is one of the approximation methods, which is popularly used in estimating the ground state energy of quantum mechanical systems. The accuracy of the method is absolutely dependent on the optimum choice of the trial variational function. Once a right choice of the trial variational function is made, more accurate ground state energy is obtained.   Hence, one may conclude that, making an optimum choice of the trial function is the major problem of the variational approximation. To solve that problem, this paper target at constructing a simple procedure that involves steps for successive "improvement'' of a trial function ; with the aim of obtaining best trial function and hence most accurate approximation to the ground state energy of the system under consideration.

The construction starts with the Eigen value form of Schrödinger differential equation given as:

$$H\Psi = E\Psi$$

(1.1)

Where H is the Hamiltonian of the system, Ψ and E are the wave function and energy Eigen value respectively.

Following the approach of [1], equation (1.1) can be expressed in matrix form. We therefore represent the function Ψ in the form of series as:

$$\Psi = \sum_m C_m |m\rangle$$

(1.2)

Where C_m are the expansion coefficients and the functions $|m\rangle$ form an arbitrary complete orthonormal set. Using equations (1.1) and (1.2) we obtain:

$$H \sum_m C_m |m\rangle = E \sum_m C_m |m\rangle$$
(1.3)

Simplification gives

$$H\left(C_n|n\rangle + \sum_{m\neq n} C_m |m\rangle \right) = E\left(C_n|n\rangle + \sum_{m\neq n} C_m |m\rangle \right)$$

$$C_n H|n\rangle + \sum_{m\neq n} C_m H|m\rangle = C_n E|n\rangle + \sum_{m\neq n} E C_m |m\rangle$$
(1.4)

Further simplification and manipulation of equation (1.4) gives

$$C_n (E - H_{nn}) = \sum_{m\neq n} C_m H_{nm}$$
(1.5)

Subsequently from (1.2) and (1.5) using the simplified form of C_n, we obtain:

$$E = H_{nn} + \sum_{m\neq n} \frac{H_{nm}H_{mn}}{E - H_{mm}} + \sum_{\substack{m\neq n \\ p(\neq nm)}} \frac{H_{nm}H_{mp}H_{pn}}{(E - H_{mm})(E - H_{pp})} + \cdots$$
(1.6)

$$\Psi = C_n\left(|n\rangle + \sum_{m\neq n} \frac{H_{mn}}{E - H_{mm}}|m\rangle + \sum_{\substack{m\neq n \\ p(\neq nm)}} \frac{H_{mp}H_{pn}}{(E - H_{mm})(E - H_{pp})}|m\rangle + \cdots \right)$$
(1.7)

Equations (1.6) and (1.7) give the matrix form of E and Ψ.

H_{mn} Is the matrix element of the operator H on the states $|m\rangle$ and $|n\rangle$ of some arbitrary complete orthonormal basis; and C_n is a normalisation constant. If we take $H = H_0 + V$, where H_0 is the unperturbed Hamiltonian, V is the perturbation; and as basis functions choose the Eigen functions of H_0, it is then shown in [2] that (1.6) and (1.7) can reduce to:

$$E = H_{nn} + \frac{1}{E}\sum_{m(\neq n)} H_{nm}H_{mn} + \frac{1}{E^2}\sum_{mp(\neq n)} H_{nm}H_{mp}H_{pn} + \cdots$$
(1.8)

$$\Psi = C_n\left(|n\rangle + \frac{1}{E}\sum_{m(\neq n)} H_{mn}|m\rangle + \frac{1}{E^2}\sum_{mp(\neq n)} H_{mp}H_{pn}|m\rangle + \cdots \right)$$
(1.9)

It is further shown in [2] that, using the property of completeness of the basis function, all terms of the series (1.8) can be expressed as the expectation values of the operators $H, H^2, H^3, \ldots$ corresponding to a particular state $|n\rangle$.

I.e.

$$\epsilon_1 = H_{nn}$$
(1.10)

$$\sum_{m(\neq n)} H_{nm}H_{mn} = (H^2)_{nn} - H_{nn}\epsilon_1$$
(1.11)

$$\sum_{mp(\neq n)} H_{nm}H_{mp}H_{pn} + \cdots = (H^3)_{nn} - (H^2)_{nn}\epsilon_1 - H_{nn}\epsilon_2 \cdots$$
(1.12)

Equation (1.8) is then expressed as:

$$E = \epsilon_1 + \frac{1}{E}\epsilon_2 + \frac{1}{E^2}\epsilon_3 + \cdots$$
(1.13)

Where,

$$\epsilon_1 = H_{nn}, \epsilon_2 = (H^2)_{nn} - H_{nn}\epsilon_1, \epsilon_3 = (H^3)_{nn} - (H^2)_{nn}\epsilon_1 - H_{nn}\epsilon_2$$

This implies that generally,

$$\epsilon_p = (H^p)_{nn} - (H^{p-1})_{nn}\epsilon_1 - (H^{p-2})_{nn}\epsilon_2 \ldots H_{nn}\epsilon_{p-1}$$
(1.14)

Similar analysis using (1.9) shows that

$$\left\{ \begin{array}{c} \sum_{m(\neq n)} H_{mn}|m\rangle = (H - \epsilon_1)|n\rangle \\ \sum_{mp(\neq n)} H_{mp}H_{pn}|m\rangle = (H^2 - \epsilon_1 H - \epsilon_2)|n\rangle \end{array} \right\}$$
(1.15)

This property of the wave function (1.9) given by (1.15) is the basis used to construct a successive trial variational function.

Since the wave function (1.9) is formally the exact solution of the Schrödinger equation (1.1). Now let us modify it.

Suppose that as variational function we take the function (1.9), having replaced in it the unknown energy E by corresponding variational parameters G_p.

Then, equation (1.9) is modified to

$$\psi^{(k)} = C_n\left(|n\rangle + G_1 \sum_{m(\neq n)} H_{mn}|m\rangle + G_2 \sum_{mp(\neq n)} H_{mp}H_{pn}|m\rangle + \cdots + G_k \sum_{mpl\ldots f(\neq n)} H_{mp}H_{pl}\ldots H_{fn}|m\rangle \right) \qquad (1.16)$$

Where k Is an index that indicates the highest number of variational parameters retained in (1.16).

Now, retaining one variational parameter in (1.16) gives

$$\psi^{(1)} = C_n\left(|n\rangle + G_1 \sum_{m(\neq n)} H_{mn}|m\rangle \right) \qquad (1.17)$$

Similarly retaining two variational parameters gives

$$\psi^{(2)} = C_n\left(|n\rangle + G_1 \sum_{m(\neq n)} H_{mn}|m\rangle + G_2 \sum_{mp(\neq n)} H_{mp}H_{pn}|m\rangle \right) \qquad (1.18)$$

Using equation (1.15) , equations (1.17) and (1.18) reduce to:

$$\psi^{(1)} = C_n\{(1 - G_1\epsilon_1)|n\rangle + G_1 H|n\rangle\} \qquad (1.19)$$

$$\psi^{(2)} = C_n\{(1 - G_1\epsilon_1 - G_2\epsilon_2)|n\rangle + (G_1 - G_1\epsilon_1)H|n\rangle + G_2 H^2|n\rangle\} \qquad (1.20)$$

Equations (1.19) and (1.20) are the implicit form of the constructed trial wave functions corresponding to retaining one and two variational parameters respectively. They are the wave functions used throughout this paper. That is the work is limited to retaining the highest number of two variational parameters; though the larger the number of parameters retained the more accurate the result.

The expressions given by equations (1.19) and (1.20) are fully defined when the Hamiltonian and the respective variational parameters are known.

To determine the variational parameters G_p, it is necessary to take into account the variational theory.

From Rayleigh-Ritz variational principle in [5], the quotient

$$\langle H \rangle = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \geq E \qquad (1.21)$$

Is an upper bound to the least Eigen value of the quantum mechanical system described by the time-independent Hamiltonian H.

When ψ is the exact wave function, $\langle H \rangle = E$. The quotient of equation (1.21) is evaluated such that the variational parameters α_i contain in ψ give the values that satisfy the following minimisation condition:

$$\frac{\partial \langle H \rangle}{\partial \alpha_i} = 0, \quad i = 1,2,\ldots \qquad (1.22)$$

Applying the variational theory to the case at hand, we obtain

$$E = \frac{\langle \psi^{(k)}|H|\psi^{(k)}\rangle}{\langle \psi^{(k)}|\psi^{(k)}\rangle}, \quad \frac{\partial E}{\partial G_p} = 0, p = 1,2,\ldots,k \qquad (1.23)$$

For the case $= 1$, i.e. when allowance is made for only one variational parameter; equation (1.23) becomes:

$$E = \frac{\langle \psi^{(1)}|H|\psi^{(1)}\rangle}{\langle \psi^{(1)}|\psi^{(1)}\rangle} \qquad (1.24)$$

Subsequently, using equation (19), we obtain

$$E = \frac{\epsilon_1 + 2G_1\epsilon_2 + G_1^2\epsilon_3}{1 + G_1^2\epsilon_2} \qquad (1.25)$$

Equation (1.25) gives the expression of the energy when one variational parameter is retained. G_1 is evaluated from the minimisation condition of the variational theory.

$$\frac{\partial E}{\partial G_1} = 0 \qquad (1.26)$$

This gives:

$$\frac{2\epsilon_2 + 2G_1\epsilon_3}{1 + G_1^2\epsilon_2} - \frac{2G_1\epsilon_2(\epsilon_1 + 2G_1\epsilon_2 + G_1^2\epsilon_3)}{(1 + G_1^2\epsilon_2)^2} = 0 \qquad (1.27)$$

G_1 is then obtained as:

$$G_1 = \frac{-\epsilon_1\epsilon_2 \pm \sqrt{4\epsilon_2^3 + (\epsilon_1\epsilon_2 - \epsilon_3)^2} + \epsilon_3}{2\epsilon_2^3} \qquad (1.28)$$

Equation (1.28) gives two expressions for G_1. But it is necessary to choose the solution that when substituted
in (1.25), ensures fulfilment of the inequality

$$E < \epsilon_1 \qquad (1.29)$$

This inequality gives the simplest estimate of the energy in the variational scheme.

For the case $= 2$, i.e. when allowance is made for two variational parameters; equation (1.23) becomes:

$$E = \frac{\langle \psi^{(2)}|H|\psi^{(2)}\rangle}{\langle \psi^{(2)}|\psi^{(2)}\rangle} \qquad (1.30)$$

Subsequently, using equation (1.20), we obtain

$$E = \frac{\epsilon_1 + 2G_2\epsilon_2 + (2G_2 + G_1^2)\epsilon_3 + 2G_1G_2\epsilon_4 + G_2^2\epsilon_5}{1 + G_1^2\epsilon_2 + 2G_1G_2\epsilon_3 + G_2^2\epsilon_4} \qquad (1.31)$$

Equation (1.31) gives the expression of energy when two variational parameters are retained.
Similarly by employing the minimisation condition of the variational theory the following equations were obtained.

$$\frac{2\epsilon_2 + 2G_1\epsilon_3 + 2G_2\epsilon_4}{1 + G_1^2\epsilon_2 + 2G_1G_2\epsilon_3 + G_2^2\epsilon_4} - \frac{(2G_1\epsilon_2 + 2G_2\epsilon_3)(\epsilon_1 + 2G_1\epsilon_2 + (G_1^2 + 2G_2)\epsilon_3 + 2G_1G_2\epsilon_4 + G_2^2\epsilon_5)}{(1 + G_1^2\epsilon_2 + 2G_1G_2\epsilon_3 + G_2^2\epsilon_4)^2}$$
$$= 0 \qquad (1.32)$$

$$\frac{2\epsilon_3 + 2G_1\epsilon_4 + 2G_2\epsilon_5}{1 + G_1^2\epsilon_2 + 2G_1G_2\epsilon_3 + G_2^2\epsilon_4} - \frac{(2G_1\epsilon_3 + 2G_2\epsilon_4)(\epsilon_1 + 2G_1\epsilon_2 + (G_1^2 + 2G_2)\epsilon_3 + 2G_1G_2\epsilon_4 + G_2^2\epsilon_5)}{(1 + G_1^2\epsilon_2 + 2G_1G_2\epsilon_3 + G_2^2\epsilon_4)^2}$$
$$= 0 \qquad (1.33)$$

G_1 and G_2 are determined by solving (1.32) and (1.33) simultaneously.
We now consider specific examples using the Hamiltonians that describe some quantum mechanical systems.

As example 1, we used a simple quantum mechanical system described by the Hamiltonian:

$$H = -\frac{d^2}{dx^2} + 4\cos^2 x \qquad (1.34)$$

As basis function, we take plane wave normalised in one dimension. I.e.

$$\psi_0 = \frac{1}{\sqrt{2l}}e^{ikx} \qquad (1.35)$$

To calculate the ground state energy when one variational parameter is retained, we recall the following equations:

$$E = \frac{\epsilon_1 + 2G_1\epsilon_2 + G_1^2\epsilon_3}{1 + G_1^2\epsilon_2}$$

$$G_1 = \frac{-\epsilon_1\epsilon_2 \pm \sqrt{4\epsilon_2^3 + (\epsilon_1\epsilon_2 - \epsilon_3)^2} + \epsilon_3}{2\epsilon_2^2}$$

We need to calculate $\epsilon_1 \dots \epsilon_3$ in order to calculate G_1 and hence E. This is done in accordance with equation (1.14),

using plane wave Ψ_0 with wave vector $k = 0$ to ensure minimum value of ϵ_1.

$$\therefore \quad \epsilon_1 = \langle H \rangle = \int_{-1}^{1} \Psi_0^* H \Psi_0 \, dx$$

This gives,

$$\epsilon_1 = 2$$

(1.36)

In a similar manner using equation (1.14) we obtained

$$\epsilon_2 = 2 \quad and \quad \epsilon_3 = 12$$

With these values, G_1 and E are calculated as:

$$G_1 = -0.224745$$

(1.37)

$$E = 1.55051$$

(1.38)

To calculate the ground state energy when two variational parameters are retained, we recall

$$E = \frac{\epsilon_1 + 2G_1\epsilon_2 + (2G_2 + G_1^2)\epsilon_3 + 2G_1G_2\epsilon_4 + G_2^2\epsilon_5}{1 + G_1^2\epsilon_2 + 2G_1G_2\epsilon_3 + G_2^2\epsilon_4}$$

ϵ_4 and ϵ_5 are obtained in the same way ϵ_2 and ϵ_3 were obtained as:

$$\epsilon_4 = 74 \qquad \epsilon_5 = 492$$

Using the values of $\epsilon_1 \dots \epsilon_5$, equations (32) and (33) reduce to

$$(4 + 24G_1 + 148G_2)(1 + 2G_1^2 + 24G_1G_2 + 74G_2^2) - (4G_1 + 24G_2)\left(2 + 4G_1 + 148G_1G_2 + 492G_2^2 + 12(G_1^2 + 2G_2)\right)$$
$$= 0$$

(1.39)

$$(24 + 148G_1 + 984G_2)(1 + 2G_1^2 + 24G_1G_2 + 74G_2^2)$$
$$- (24G_1 + 148G_2)\left(2 + 4G_1 + 148G_1G_2 + 492G_2^2 + 12(G_1^2 + 2G_2)\right)$$
$$= 0$$

(1.40)

Solving (1.39) and (1.40) simultaneously gives

$$\{G_1 = -0.310541, G_2 = 0.0138294\} \qquad (1.41)$$

Subsequently G is calculated as:

$$E = 1.54487 \qquad (1.42)$$

As our second example we consider a quantum mechanical system described by the following perturbed harmonic oscillator:

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + \alpha\, x^4 \qquad (1.43)$$

Where α is some constant.

As basis function we used the wave function of harmonic oscillator

$$\epsilon_0(x) = \left(\sqrt{\beta/\alpha}\right)^{1/2} e^{-\beta x^2/2} \qquad (1.44)$$

Where β is the variational parameter.

β is determined using standard variational procedure as:

$$\beta = (6\alpha)^{1/3} \qquad\qquad (1.45)$$

This implies that,

$$\alpha = \frac{1}{6}\beta^3 \qquad\qquad (1.46)$$

Equation (1.43) becomes

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{6}\beta^3 x^4$$

(1.47)

Equation (1.47) is used in association with equation (14) to calculate the matrix elements ϵ_p that aid the calculation of ground state energy.

Since,

$$\epsilon_1 = (Ha^2 + b^2 = c^2) = \int_{-\infty}^{\infty} \psi_0 H_1 dx = \frac{3}{8}\beta \qquad\qquad (1.48)$$

Similarly we obtained

$$\langle H^2 \rangle = \frac{35}{192}\beta^2, \langle H^3 \rangle = \frac{601}{1536}\beta^3, \langle H^4 \rangle = \frac{40163}{12288}\beta^4, \langle 5^5 \rangle = \frac{4393865}{98304}\beta^5$$

With these values we can calculate the matrix elements ϵ_3.

To calculate the ground state energy when one variational parameter is retained, we need $\epsilon_1 \dots \epsilon_3$.

$$\therefore \epsilon_2 = \frac{1}{24}\beta^2 \quad , \quad \epsilon_3 = \frac{59}{192}\beta^3$$

Using equations (1.25) and (1.28) at $\alpha = \frac{1}{2}$ we obtained

$$G_1 = -0.0989675 \qquad\qquad (1.49)$$

Subsequently,

$$E = 0.532266 \qquad\qquad (1.50)$$

To calculate the ground state energy when two variational parameters are retained, we need $\epsilon_1 \dots \epsilon_5$.

$$\therefore \epsilon_4 = \frac{13819}{4608}\beta^4, \epsilon_5 = \frac{1558393}{36864}\beta^5$$

With values of $\epsilon_1 \dots \epsilon_5$, equations (1.32) and (1.33) reduce to

$$\left(\frac{\beta^2}{12} + \frac{59\beta^2 G_1}{96} + \frac{13819\beta^4 G_2}{2304}\right)\left(1 + \frac{1}{24}\beta^2 G_1^2 + \frac{59}{96}\beta^3 G_1 G_2 + \frac{13819\beta^4 G_2^2}{4608}\right) - \left(\frac{\beta^2 G_1}{12} + \frac{59\beta^2 G_2}{96}\right)\left(\frac{3\beta}{8} + \frac{\beta^2 G_1}{12} + \frac{13819\beta^4 G_1 G_2}{2304} + \frac{1558393\beta^5 G_2^2}{36864} + \frac{59}{192}\beta^3(G_1^2 + 2G_2)\right) = 0$$

(1.51)

$$\left(\frac{59\beta}{96} + \frac{13819\beta^4 G_1}{2304} + \frac{1558393\beta^5 G_2}{18432}\right)\left(1 + \frac{1}{24}\beta^2 G_1^2 + \frac{59}{96}\beta^3 G_1 G_2 + \frac{13819\beta^4 G_2^2}{4608}\right) - \left(\frac{59\beta^2 G_1}{96} + \frac{13819\beta^4 G_2}{2304}\right)\left(\frac{3\beta}{8} + \frac{\beta^2 G_1}{12} + \frac{13819\beta^4 G_1 G_2}{2304} + \frac{1558393\beta^5 G_2^2}{36864} + \frac{59}{192}\beta^3(G_1^2 + 2G_2)\right) = 0$$

(1.52)

Solving equations (1.51) and (1.52) simultaneously at $\alpha = \frac{1}{2}$ we get

$$\{G_1 = -0.155624 \ , \ G_2 = 0.0039751\} \qquad\qquad (1.53)$$

E is then calculated as:

$$E = 0.53102 \qquad\qquad (1.54)$$

RESULTS AND DISCUSSION

Generally the inequality $E < \epsilon_1$ obtained from the variational theory, gives a very nice estimate of the ground state energies we calculated in this work.

In the first example we considered the Hamiltonian

$$H = -\frac{d^2}{dx^2} + 4\cos^2 x$$

We calculated the ground state energy when one variational parameter is retained as:

$$H = 1.55051$$

This value is expected, as ϵ_I was calculated in equation (1.36) to be:

$$\epsilon_j = 2$$

And by virtue of our inequality E should take value less than 2.

The value of E we obtained in equation (1.38) is in conformity with the exact value of the ground state energy Eigen value corresponding to the Hamiltonian (1.34) obtained in [4], which is:

$$E = 1.54486$$

The proximity of the value of E we calculated to the value obtained in (55) is excellently improved when second variational parameter is retained; where we obtained:

$$E = 1.54487$$

This value of E obtained in equation (1.42) clearly show the effect of retaining more variational parameters in getting the exact ground state energy.

Similarly for the second example, where we considered the Hamiltonian given by equation (1.43):

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + ax^4$$

When one variational parameter is retained, we calculated the ground state energy E as:

$$E = 0.532266$$

And from equation (1.48) we found ϵ_I to be:

$$\epsilon_j = \frac{3}{8}\beta$$

Since, $= (6a)^{1/3}$, at $\alpha = \frac{1}{2}$, $\beta = 1.44224957$, hence numerically ϵ_I is given as:

$$\epsilon_I = 0.540843588$$

(2.2)

This implies that the value E we got in equation (50) compared to the value of ϵ_I we have in equation (2.2) is expected according to the inequality $E < \epsilon_I$.

The value of E given by equation (1.50) differs slightly from the exact value obtained in [5] for the Hamiltonian (1.43) which is:

$$E = 0.530181$$

(2.3)

For further improvement of the calculated ground state energy, we retained second variational parameter and E was calculated as:

$$E = 0.53102$$

(2.4)

Equation (1.54) clearly shows the good proximity of the calculated E to the exact one and hence the positive effect of our construction.

CONCLUSION

Considering the results we obtained for the ground state energies of the two examples considered in this paper; (when retaining just one and two variational parameters). It is obvious that retaining more variational parameters produces more accurate result. However Though as more variational parameters are retained, more complex equations that are very difficult to solve are generated. It is encouraging that modern technology provides mathematical software that makes things

easier. Certainly higher version of that software are going to be developed which will surely simplify future researches. We hope future researches will retain more than two variational parameters considered in this paper to fully bring out the effect of the construction, and hence improve the efficiency of the variational approximation as compared to some other approximation methods being used presently.

REFERENCES
[1]   R.Kh. Sabirov, Teor. Mat. Fiz. 73, 79 (1987).

[2]   Zh. Eksp. Teor. Fiz. 108, 1179-1185 (October 1995)

[3]   H. Clark, A first course in Quantum Mechanics, Rev. ed. Van No strand
         Reinhold (UK) Co.Ltd. 1982.

[4]   R.C.Young, L.C.Biedenharn, and E.Feenberg.phys. Rev. 106, 1151
        (1957)

[5]   A.V.Turbiner, pis'ma zh. Eksp. Teor. Fiz. 30,379 (1979) [JETP Lett.
         30.362 (1979)].