

# **APPLICATION OF THE VARIATIONAL PRINCIPLE IN QUANTUM MECHANICS**

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**Abstract:** This study project deals with the application of the Variational Principle in Quantum Mechanics. In this study project, the Variational Principle has been applied to several scenarios, with the aim being to obtain an upper bound on the ground state energies of several quantum systems, for some of which, the Schrodinger equation cannot be easily solved. (Refer Section 3 - Applications of the Variational Principle). For those systems where the Schrodinger equation could be solved without much difficulty, the exact ground state energies were calculated to compare with the results obtained via the application of the Variational Principle. (Refer Section 1 of Preface).

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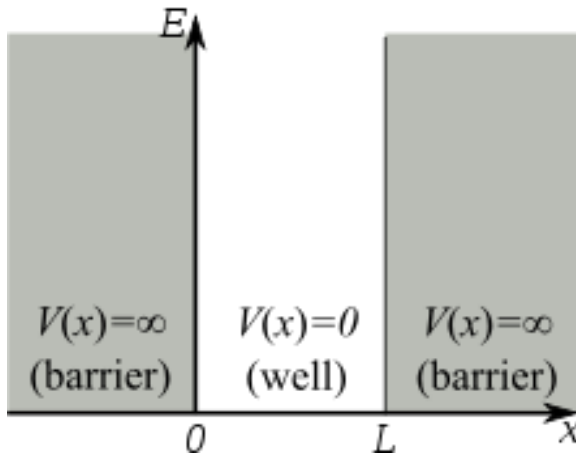
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# 1) PREFACE

## Section I): The Infinite Square Well



We shall be dealing with a system which consists of a single particle constrained to move in one dimension only (here, the x axis).

Along the axis, there exists a time-independent potential field,  $V(x)$ , whose magnitude depends only on the position from the origin along the axis. The Infinite Square Well is a scenario where we have a potential field defined as follows:

$$V(x) = \begin{cases} 0, & 0 \leq x \leq L \\ \infty, & \text{otherwise} \end{cases}$$

Thus, the particle is trapped inside the 'potential well'  $\rightarrow$  a space spanning a width 'L', with two barriers of infinite force preventing it from escaping.

Thus we can say with certainty that the wavefunction,  $\Psi(x)$ , has to be zero outside the well.

So, we solve the time-independent Schrodinger equation for  $0 \leq x \leq L$ , where  $V(x) = 0$ :

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + 0 = E\Psi$$

This can be written as,

$$\frac{\partial^2 \Psi}{\partial x^2} + k^2 \Psi = 0, \quad \text{where } k = \frac{\sqrt{2mE}}{\hbar}$$

This is the differential equation for the classical Simple Harmonic Oscillator and has the general solution:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

Applying the boundary conditions for  $\psi(x)$  :

1)  $\psi(x)$  is always continuous.

2) First derivative of  $\psi(x)$  is continuous except at the points where the potential is infinite.

Since the second condition is obviously not applicable to the Infinite Square Well, we apply the first condition only:

$$\psi(0) = \psi(L) = 0$$

Which gives us, respectively,

$$B = 0, \text{ hence } \psi(x) = A\sin(kx)$$

And,

$$A\sin(kL) = 0$$

Therefore  $kL = n\pi$  (since  $A = 0$  is an absurd solution)

And inputting the value of  $k \rightarrow k = \frac{\sqrt{2mE}}{\hbar}$ , we get,

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

These are the stationary state energies of the particle in the infinite square well. The ground state energy of the system corresponds to  $n = 1$ .

$$E_g = \frac{\pi^2 \hbar^2}{2mL^2}$$

We can find the arbitrary constant 'A' by normalizing  $\psi(x)$  over the x axis:

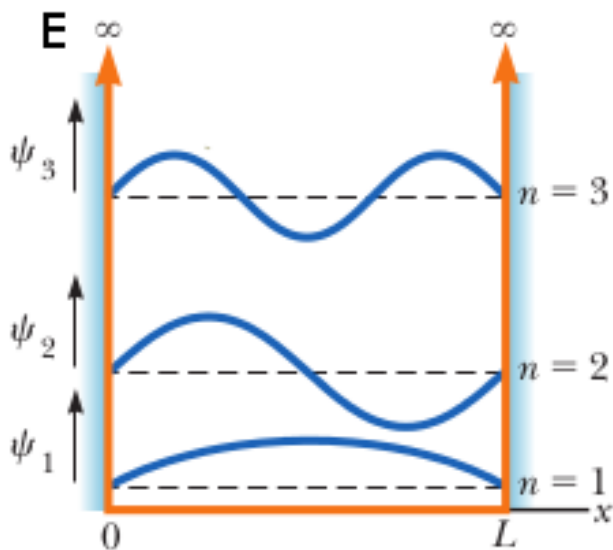
$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = |A|^2 \int_0^L \sin^2(kx) dx = 1$$

Solving, we get,

$$A = \sqrt{\frac{2}{L}} \quad (\text{We choose the positive real root because the phase of A has no physical significance})$$

Therefore, overall, we have,

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



Therefore, the solution(s) to the time-dependent Schrodinger equation i.e. the stationary states, are:

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) e^{-i(n^2 \pi^2 \hbar / 2mL^2)t}$$

And the general solution to the time-dependent Schrodinger equation is a linear combination of the stationary states:

$$\Psi(x,t) = \sum_{n=1}^{\infty} C_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) e^{-i(n^2\pi^2\hbar/2mL^2)t}$$

The arbitrary constants,  $C_n$ , can be calculated by the following method, which takes advantage of the orthonormality of the wavefunction :

$$\Psi(x,0) = \sum_{n=1}^{\infty} C_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) = \sum_{n=1}^{\infty} C_n \psi_n(x)$$

Multiplying on both sides by  $\psi_m(x)^*$  and integrating over the x axis, we get,

$$\int \psi_m(x)^* \Psi(x,0) dx = \sum_{n=1}^{\infty} C_n \int \psi_m(x)^* \psi_n(x) dx = \sum_{n=1}^{\infty} C_n \delta_{mn} = C_m$$

where  $\delta_{mn}$  is the Kronecker delta defined in the usual way:

$$\delta_{mn} = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$$

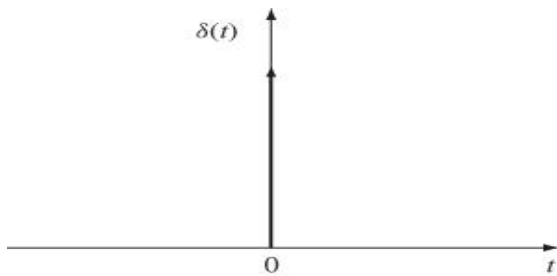
Hence, replacing the dummy index 'm' by 'n' for consistency,

$$C_n = \int \psi_n(x)^* \Psi(x,0) dx$$

Or in Dirac's bra-ket notation, this can be written as:

$$C_n = \langle \psi_n(x) | \Psi(x,0) \rangle$$

## Section II):The Dirac Delta Function Well



The Dirac Delta function is defined as:

$$\delta(t) = \begin{cases} \infty, & t = 0 \\ 0, & \text{otherwise} \end{cases}$$

Such that,

$$\int_{-\infty}^{\infty} \delta(t) dt = 1$$

The delta function has the following properties:

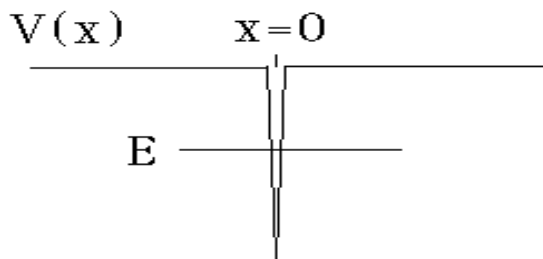
1)  $f(t)\delta(t-a) = f(a)\delta(t-a)$  .... (This follows because the delta function is zero everywhere except at  $t=a$ . Therefore at all other points, it is the same as multiplying  $f(t)$  by zero)

2) Integrating both sides of the above equation, we get,

$$\int_{-\infty}^{\infty} f(t)\delta(t-a)dt = f(a) \int_{-\infty}^{\infty} \delta(t-a)dt = f(a)$$

The Delta Potential Well is a scenario wherein (again, we consider a system consisting of a single particle constrained to move in one dimension only) there exists a time-independent potential  $V(x)$  such that

$$V(x) = -a\delta(x)$$



We will consider only the bound states i.e. where the total energy of the particle  $E < 0$ .

Thus, the particle is bound/trapped inside a potential well that is like an infinitely deep, narrow spike.

Therefore, the time-independent Schrodinger equation reads,

$$-\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} - a \delta(x) = E \psi$$

In the region  $x < 0$  we have  $V(x) = 0$ . So,

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{2mE}{\hbar^2} \psi = \kappa^2 \psi, \text{ where } \kappa = \frac{\sqrt{-2mE}}{\hbar}$$

Since  $E$  is negative,  $\kappa$  is real and positive.

Therefore the general solution is,

$$\psi(x) = Ae^{kx} + Be^{-kx}$$

Since the second term blows up to infinity as  $x \rightarrow -\infty$ , it cannot be a realizable solution. Hence, we neglect it. Thus for  $x < 0$ ,

$$\psi(x) = Ae^{kx}$$

In the region  $x > 0$  also  $V(x) = 0$ , and so the time-independent Schrodinger equation and its solution take the same form as above. So,

$$\psi(x) = Ce^{kx} + De^{-kx}$$

Here, the first term blows up to infinity and therefore is neglected. So for  $x > 0$ ,

$$\psi(x) = De^{-kx}$$

Now, we apply the boundary conditions:

1)  $\psi(x)$  is always continuous.

$$\text{i.e. } \psi(0^-) = \psi(0^+)$$

That gives us  $A = D$ . But this does not tell us anything about the stationary state energies.

2) The first derivative of  $\psi(x)$  is continuous except at the points where the potential is infinite.

The second condition does not apply here since the potential blows to negative infinity at  $x=0$ . Hence we use a different technique to derive the stationary state energies.

We take the time independent Schrodinger equation and integrate it from  $-\epsilon$  to  $\epsilon$ , (where  $\epsilon$  is a positive constant) and then set a limit for  $\epsilon$  to tend to zero.

$$-\frac{\hbar^2}{2m} \int_{-\epsilon}^{\epsilon} \frac{\partial^2 \psi(x)}{\partial x^2} dx + \int_{-\epsilon}^{\epsilon} V(x)\psi(x)dx = E \int_{-\epsilon}^{\epsilon} \psi(x)dx$$

As  $\epsilon \rightarrow 0$ ,

$$\text{The first term becomes } -\frac{\hbar^2}{2m} \int_{-\epsilon}^{\epsilon} \frac{\partial^2 \psi(x)}{\partial x^2} dx = -\frac{\hbar^2}{2m} \left( \frac{d\psi}{dx} \Big|_{0^+} - \frac{d\psi}{dx} \Big|_{0^-} \right) = \frac{\hbar^2 \kappa A}{m},$$

since  $\psi(x) = Ae^{-\kappa x}$  for  $x > 0$ , and  $\psi(x) = Ae^{\kappa x}$  for  $x < 0$ , as proved above.

$E \int_{-\epsilon}^{\epsilon} \psi(x)dx$  becomes zero, because  $\psi(x)$  is finite everywhere.

$\int_{-\epsilon}^{\epsilon} V(x)\psi(x)dx$  would also have been zero, if  $V(x)$  had been finite, but since that is not so,

$$\text{we get } \int_{-\epsilon}^{\epsilon} V(x)\psi(x)dx = -a \int_{-\epsilon}^{\epsilon} \delta(x)\psi(x)dx = -a\psi(0) \int_{-\epsilon}^{\epsilon} \delta(x) = -aA$$

Thus the equation becomes,

$$\frac{\hbar^2 \kappa A}{m} - aA = 0$$

$$\text{So we get, } \kappa = \frac{ma}{\hbar^2}$$

$$\text{Inputting the value, } \kappa = \frac{\sqrt{-2mE}}{\hbar}, \text{ we end up with, } E = \frac{-ma^2}{2\hbar^2}$$

Hence we see that the particle can only exist in a single stationary state inside the Dirac Delta Potential Well.



We can find the constant 'A' by normalizing  $\psi(x)$  :

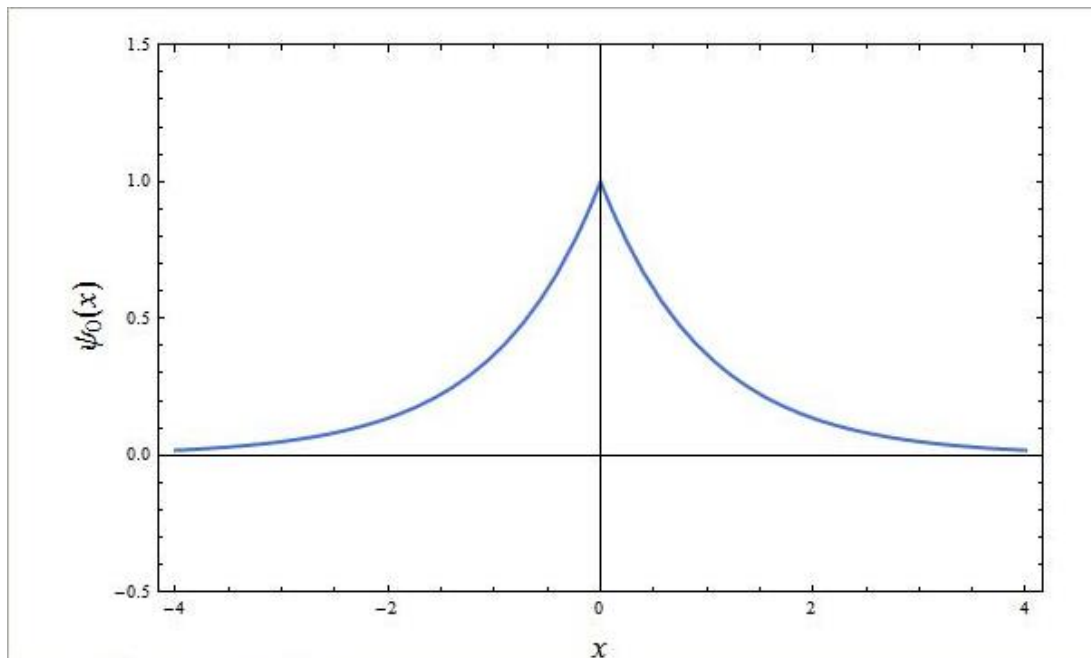
$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = |A|^2 \int_{-\infty}^0 e^{2kx} dx + |A|^2 \int_0^{\infty} e^{-2kx} dx = \frac{|A|^2}{\kappa} = 1$$

Thus,

$$A = \sqrt{\kappa} = \frac{\sqrt{ma}}{\hbar}$$

So, the one and only stationary bound state of the delta function well is:

$$\psi(x) = \frac{\sqrt{ma}}{\hbar} e^{-\frac{ma|x|}{\hbar^2}}, E = -\frac{ma^2}{2\hbar^2}$$



And the wavefunction for this single stationary state is:

$$\Psi(x, t) = \frac{\sqrt{ma}}{\hbar} e^{-\frac{ma}{\hbar^2}|x|} \cdot e^{\frac{ima^2}{2\hbar^3}t}$$

### SectionIII): A Very Brief Introduction to Quantum Mechanics in Three Dimensions

The time dependent Schrodinger equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

The Hamiltonian operator is obtained from the classical energy by replacing the positions and momenta in the three mutually independent directions by their corresponding operators.

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V$$

$$p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad p_y \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial y}, \quad p_z \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial z} \quad \text{or} \quad p \rightarrow \frac{\hbar}{i} \nabla$$

Therefore ,

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V = -\frac{\hbar^2}{2m} \nabla^2 + V$$

Where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

is the Laplacian in Cartesian coordinates.

Now, the potential  $V$  and the wavefunction  $\Psi$  are functions of  $r = (x, y, z)$  and time 't'

The probability of finding a particle in a volume  $d^3r = dx dy dz$  is  $|\Psi(r, t)|^2 d^3r$

**Note:** In spherical coordinates we can write  $d^3r = dx dy dz = r^2 dr \cdot \sin \theta d\theta \cdot d\phi = r^2 dr \cdot d(\cos \theta) \cdot d\phi$

. The change of variables is carried out using the Jacobian  $|J| \rightarrow d^3r = dx dy dz = |J| dr d\theta d\phi$ .

The transformation from spherical coordinates  $(r, \theta, \phi)$  to Cartesian coordinates  $(x, y, z)$ , is given by:

$$x = r \sin \theta \cos \phi;$$

$$y = r \sin \theta \sin \phi;$$

$$z = r \cos \theta.$$

The Jacobian matrix for this coordinate change is

$$\mathbf{J}_{\mathbf{F}}(r, \theta, \varphi) = \begin{bmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \varphi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \varphi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \varphi} \end{bmatrix} = \begin{bmatrix} \sin \theta \cos \varphi & r \cos \theta \cos \varphi & -r \sin \theta \sin \varphi \\ \sin \theta \sin \varphi & r \cos \theta \sin \varphi & r \sin \theta \cos \varphi \\ \cos \theta & -r \sin \theta & 0 \end{bmatrix}.$$

The determinant is  $r^2 \sin \vartheta$ . Thus, as  $dV = dx dy dz$  this determinant implies that the differential volume element  $dV = r^2 \sin \vartheta dr d\vartheta d\varphi$ . Nevertheless this determinant varies with coordinates.

Integrals are to be performed one by one with respect to each variable, with  $\phi$  going from 0 to  $2\pi$ ,  $\theta$  going from 0 to  $\pi$  and  $r$  going from 0 to  $\infty$ .

The condition for normalization then becomes,

$$\int |\Psi(\mathbf{r}, t)|^2 d^3r = 1$$

With the integral taken over all space.

If the potential is independent of time, we can use the variables-separable method to solve the time dependent Schrodinger equation where we get a complete set of stationary states. Thus, we have,

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-\frac{iE_n t}{\hbar}}$$

Where the spatial wave function  $\psi_n(\mathbf{r})$  satisfies the time-independent Schrodinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

And the general solution to the time-dependent Schrodinger equation is a linear combination of the particular solutions i.e. the stationary states

$$\Psi_n(\mathbf{r}, t) = \sum_{n=1}^{\infty} C_n \psi_n(\mathbf{r}) e^{-\frac{iE_n t}{\hbar}}$$

Where the constants  $C_n$  are determined in the same way there were in Chapter 1 - The Infinite Square Well:

$$C_n = \langle \psi_n(\mathbf{r}) | \Psi(\mathbf{r}, 0) \rangle = \int \psi_n(\mathbf{r})^* \Psi(\mathbf{r}, 0) d^3 r$$

If the potential admits continuum states, then the sum in the summation in the general solution of the Schrodinger equation becomes an integral and in that case, the constants  $C_n$  can be determined using the Fourier transform of  $\Psi(\mathbf{r}, 0)$

**Note:** Typically, the potential is a function only of the distance from the origin and hence is centrosymmetric. In that case it is better to adopt spherical coordinates  $(r, \theta, \varphi)$ . The Laplacian in terms of the spherical coordinates can be obtained using transformation of variables (explained above):

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2}{\partial \varphi^2} \right)$$

The Hamiltonian becomes,

$$\hat{H} = \frac{-\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2}{\partial \varphi^2} \right) \right] + V$$

And the time-independent Schrodinger equation reads:

$$\frac{-\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2 \psi}{\partial \varphi^2} \right) \right] + V\psi = E\psi$$

This, along with the Jacobian for coordinate change, will be required later for calculating the Hamiltonian for the Hydrogen Atom and its expectation value,  $\langle H \rangle$ , using a trial wavefunction  $\psi(\mathbf{r})$ , which depends only on the distance from the origin.

#### Section IV):Multiple-Particle Systems

Consider a two-particle system where the subscript '1' corresponds to the first particle and '2' corresponds to the second particle.

The wavefunction for this system will depend, (apart from the time, 't') on the coordinates of *both* the particles -  $r_1$  and  $r_2$  :

$$\Psi(r_1, r_2, t)$$

The time dependent Schrodinger Equation will then read:

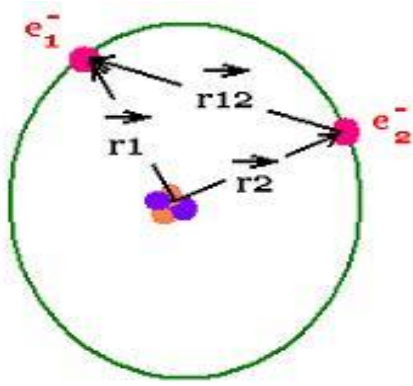
$$i\hbar \frac{\partial \Psi(r_1, r_2, t)}{\partial t} = \hat{H} \Psi(r_1, r_2, t)$$

Where the Hamiltonian for the whole system is given by:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + V(r_1, r_2, t)$$

It is obtained, as usual, by replacing the positions and momenta by their corresponding operators in the classical energy expression of the system. The classical energy of the system is of course, the sum of the kinetic energies of all the particles plus the potential energy of the whole system. The subscript in the Laplacian indicates the particle with respect to whose coordinates the differentiation is being done.

As an example, consider the Helium atom as shown in the diagram. Two electrons (particle 1 and particle 2) are shown revolving the nucleus consisting of two protons and two neutrons.  $r_1$  stands for the coordinates of electron no. 1 and  $r_2$ , for electron no. 2.  $r_{12}$  represents the position of electron 1 with respect to electron two. I.e.  $r_{12} = |r_1 - r_2|$  is the separation between the two electrons.



Helium atom

The classical energy of this system comprises of the kinetic energies of the two electrons, and the potential energies due to the electron-proton attractions and the electron-electron repulsions. Therefore the Hamiltonian for this system reads,

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi \epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{r_{12}} \right)$$

Moving on, the statistical interpretation for a two particle system is:

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3 r_1 d^3 r_2$$

is the probability of finding particle 1 in volume  $d^3 r_1$  and particle 2 in  $d^3 r_2$ .

And the normalization process reads:

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3 r_1 d^3 r_2 = 1$$

If the potential is independent of time, we can use separation of variables to achieve

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2) e^{-\frac{iE_n t}{\hbar}}$$

Where the spatial wave function  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  satisfies the time independent Schrodinger equation:

$$-\frac{\hbar^2}{2m} \nabla_1^2 \psi - \frac{\hbar^2}{2m} \nabla_2^2 \psi + V\psi = E\psi$$

Where  $-\frac{\hbar^2}{2m} \nabla_1^2$  represents the kinetic energy of the first particle,  $-\frac{\hbar^2}{2m} \nabla_2^2$  represents the

kinetic energy of the second particle and  $V$  represents the potential energy due to the interaction between them. This is how the Hamiltonians of complicated systems like molecules, are obtained.

## 2) The Variational Principle

The Variational Principle is a simple but powerful method to obtain upper bounds on ground and excited state energies of quantum systems which cannot be solved exactly. In many cases this method gives us bounds which are amazingly close to the true value of the ground state energy, obtained by more involved methods or numerical solutions of Schrodinger's equation. It is a useful tool for situations where one is unable to solve the Schrodinger equation because of its mathematical complexity.

In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigenstate or ground state. This allows for calculating approximate ground state energies for complicated quantum systems such as molecules.

The method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the Hamiltonian is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an upper bound to the ground state energy.

If the trial wavefunction so chosen, exactly coincides with the true ground state wavefunction of the system, then the upper bound obtained via the Variational Principle is exactly equal to the actual ground state energy of the system. Otherwise, it is just an approximation of the ground state energy.

In simple language, the Variational Principle states that the expectation value of the Hamiltonian,  $\langle H \rangle$ , of the system, in the trial state  $\Psi$ , will always be greater than or equal to the actual ground state energy,  $E_g$ , of the system. Mathematically,

$$\boxed{E_g \leq \langle \Psi | H | \Psi \rangle \equiv \langle H \rangle}$$

**Proof:** The general solution to any differential equation is a linear combination of its particular solutions. For the Schrodinger equation, this translates to the fact that (as we have seen in the previous sections),  $\Psi$  can be expressed as a linear combination of its stationary states:

$$\Psi = \sum_{n=1}^{\infty} C_n \psi_n$$

Where each presumably normalized  $\psi_n$  satisfies the time independent Schrodinger equation,

$$H\psi_n = E_n\psi_n$$

The normalization of  $\Psi$  gives us,

$$\langle \Psi | \Psi \rangle = \left\langle \sum_m C_m \psi_m \left| \sum_n C_n \psi_n \right. \right\rangle = \sum_m \sum_n C_m^* C_n \langle \psi_m | \psi_n \rangle = \sum_m \sum_n C_m^* C_n \delta_{mn} = \sum_n |C_n|^2 = 1$$

Now,

$$\langle H \rangle \equiv \langle \Psi | H | \Psi \rangle = \left\langle \sum_m C_m \psi_m \left| H \sum_n C_n \psi_n \right. \right\rangle = \left\langle \sum_m C_m \psi_m \left| \sum_n C_n (H\psi_n) \right. \right\rangle$$

Since  $\psi_n$  satisfies the time independent Schrodinger equation,  $H\psi_n = E_n\psi_n$ . Thus,

$$\langle H \rangle = \left\langle \sum_m C_m \psi_m \left| \sum_n C_n (E_n \psi_n) \right. \right\rangle = \sum_m \sum_n E_n C_m^* C_n \langle \psi_m | \psi_n \rangle = \sum_m \sum_n E_n C_m^* C_n \delta_{mn} = \sum_n E_n |C_n|^2$$

We know that the ground state energy,  $E_g$ , corresponds to  $n=1$  in  $E_n$  and is the lowest energy state. All other higher energy excited states have a greater value of  $E$  and only provide positive contributions to the expectation value of the Hamiltonian.

Therefore,

$$E_g \leq E_n$$

Multiplying both sides by  $|C_n|^2$  and carrying out a summation, we get,

$$\sum_n E_g |C_n|^2 \equiv E_g \sum_n |C_n|^2 \leq \sum_n E_n |C_n|^2$$

And we just proved above that  $\sum_n |C_n|^2 = 1$  and  $\sum_n E_n |C_n|^2 = \langle H \rangle$ . Hence the inequation reduces to the statement of the Variational Principle:

$$\boxed{E_g \leq \langle \Psi | H | \Psi \rangle \equiv \langle H \rangle}$$

We can choose  $\psi \equiv \psi(a,b,c\dots)$ , where  $(a,b,c\dots)$  are parameters. We can now lower  $\langle H \rangle$  w.r.t these parameters and obtain an upper bound on the ground state energy. Choosing multiple parameters allows us to gain a better approximation of the ground state. This is what physical chemists do while trying to calculate the ground state energy of a complicated molecule.



### 3) Applications of the Variational Principle

#### Section I) Ground State of a Linear Potential Using a Gaussian Trial Function

Consider a one particle system constrained to move in one dimension under a potential given by

$$V(x) = a |x|$$

Now, it is possible to directly solve the Schrodinger equation for this potential. However, that is not the aim of this project. The aim is to apply the variational principle to this potential using a Gaussian trial function and get an approximate value of the ground state energy and the wavefunction.

We specifically choose a Gaussian function because of the following reasons:

- 1) It rapidly falls to zero with increasing distance and hence is a very good archetype of any bound state.
- 2) It can be easily normalized.

Hence, we assume that the ground state wave function is of the form:

$$\psi(x) = Ae^{-bx^2}$$

Where 'b' is the parameter which can be tweaked as per our requirement and 'A' is determined

by normalizing  $\psi(x)$ :  $|A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx = |A|^2 \sqrt{\frac{\pi}{2b}} = 1$

That gives us,  $A = \sqrt[4]{\frac{2b}{\pi}}$

Now,

$$\langle H \rangle = |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \left( -\frac{\hbar^2}{2m} \frac{\partial^2 e^{-bx^2}}{\partial x^2} + a|x|e^{-bx^2} \right) dx = |A|^2 \left\{ -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} (4b^2 x^2 e^{-2bx^2} - 2be^{-2bx^2}) dx + a \int_{-\infty}^{\infty} |x| e^{-2bx^2} dx \right\}$$

In the above integral, for the last term, we can write  $\int_{-\infty}^{\infty} |x| e^{-2bx^2} dx = 2 \int_0^{\infty} x e^{-2bx^2} dx$ .

Substituting the term in the exponent by a different variable, say, 'u' will simplify this integral.

Upon solving, this term reduces to  $\frac{1}{4b}$ .

For the middle term, we have the standard Gaussian integral:

$$\int_{-\infty}^{\infty} e^{-2bx^2} dx = \sqrt{\frac{\pi}{2b}}$$

For solving the first term, we can use the following trick. It involves taking the standard Gaussian integral (the above equation) and differentiating both sides with respect to the parameter 'b'.

Applying that to the first term gives us:

$$\int_{-\infty}^{\infty} x^2 e^{-2bx^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{2}} b^{-3/2}$$

Thus, the equation reduces to:

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{a}{\sqrt{8\pi b}}$$

Now, according to the variational principle,

$$E_g \leq \langle H \rangle \equiv \frac{\hbar^2 b}{2m} + \frac{a}{\sqrt{8\pi b}}$$

So if we take the tightest upper bound by selecting 'b' such that the RHS is minimum, we can approximate this minimum upper bound to be equal to the ground state energy. Therefore, if we differentiate the RHS w.r.t 'b', and equate it to zero, we will get the value of 'b' for which the RHS is minimum. Solving and resubstituting this value of 'b' into the inequality gives us:

$$b_{\min} = \left( \frac{m^2 a^2}{8\pi \hbar^4} \right)^{1/3}$$

$$\langle H \rangle_{\min} = \frac{3}{2} \left( \frac{\hbar^2 a^2}{8\pi m} \right)^{1/3}$$

Hence,

$$E_g \approx \frac{3}{2} \left( \frac{\hbar^2 a^2}{8\pi m} \right)^{1/3}$$

We approximate this to be the ground state energy

## Section II) Ground State of Dirac's Delta Function Well Using a Gaussian Trial Function

From Preface –Section II), we know that the Hamiltonian for the Delta Function Well is,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - a\delta(x)$$

And we also know the exact ground state energy to compare the results with :  $E_g = \frac{-ma^2}{2\hbar^2}$

As in the previous chapter, we choose a Gaussian Trial Function,  $\psi(x) = Ae^{-bx^2}$ . We have

already worked out the normalization constant in the previous chapter:  $A = \sqrt[4]{\frac{2b}{\pi}}$

Thus, the expectation value of the Hamiltonian is,

$$\langle H \rangle = |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \left( -\frac{\hbar^2}{2m} \frac{\partial^2 e^{-bx^2}}{\partial x^2} - a e^{-bx^2} \delta(x) \right) dx = |A|^2 \left( \int_{-\infty}^{\infty} e^{-bx^2} \left( -\frac{\hbar^2}{2m} \frac{\partial^2 e^{-bx^2}}{\partial x^2} \right) dx - a \int_{-\infty}^{\infty} e^{-2bx^2} \delta(x) dx \right)$$

Solving, we get,

$$\langle H \rangle = \frac{\hbar^2 b}{2m} - a \sqrt{\frac{2b}{\pi}}$$

Minimizing RHS gives us,

$$\frac{d\langle H \rangle}{db} = \frac{\hbar^2}{2m} - \frac{a}{2} \sqrt{\frac{2}{\pi b}} = 0$$

Therefore,

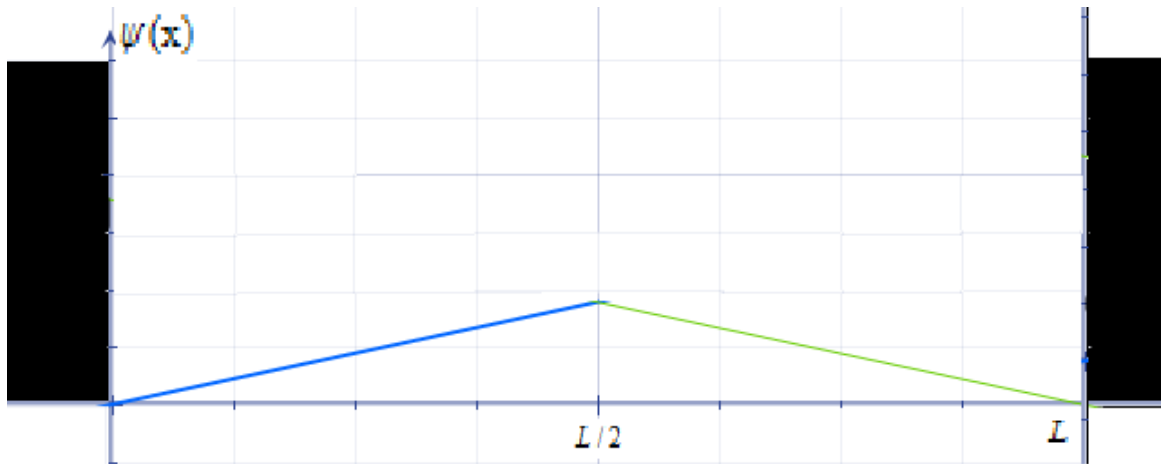
$$b_{\min} = \frac{2m^2 a^2}{\pi \hbar^4}$$

$$\langle H \rangle_{\min} = \frac{-ma^2}{\pi \hbar^2}$$

Comparing  $\langle H \rangle_{\min}$  with the actual ground state energy,  $E_g = \frac{-ma^2}{2\hbar^2}$ , we can conclude

that the variational principle holds true since  $E_g < \langle H \rangle_{\min}$

**Section III): Ground State of the Infinite Square Well Using a Triangular Trial Function**



We already know the exact value of the ground state energy of the Infinite Square Well:

$$E_g = \frac{\pi^2 \hbar^2}{2mL^2}$$

For the Infinite Square Well, we shall use a triangular wave function as a trial wave function since it vaguely resembles the sinusoidal wavefunction of the ground state of the infinite square well:

$$\psi(x) = \begin{cases} Ax, & 0 \leq x < L/2 \\ A(L-x), & L/2 \leq x < L \\ 0 & \text{otherwise} \end{cases}$$

We can determine 'A' by normalizing  $\psi(x)$  :

$$|A|^2 \left( \int_0^{L/2} x^2 dx + \int_{L/2}^L (L-x)^2 dx \right) = |A|^2 \frac{L^3}{12} = 1$$

$$A = 2\sqrt{3}L^{-3/2}$$

Now, we will require the second derivative of  $\psi(x)$  when calculating the Hamiltonian. But  $\psi(x)$  is a piecewise defined step-function and its first derivative is discontinuous. Hence, we employ an ingenious technique to represent the second derivative:

$$\frac{d\psi(x)}{dx} = \begin{cases} A, & 0 \leq x < L/2 \\ -A, & L/2 \leq x < L \\ 0 & \text{otherwise} \end{cases}$$

We see that the slope of  $\frac{d\psi(x)}{dx}$  (which is nothing but  $\frac{d^2\psi(x)}{dx^2}$ ), becomes infinite at  $x = 0, a/2$  and  $a$ . but is zero everywhere else. It can be shown that  $\frac{d^2\psi(x)}{dx^2}$  can be written as a sum of Dirac Delta functions in the following way:

$$\frac{d^2\psi(x)}{dx^2} = A\delta(x) - 2A\delta(x - L/2) + A\delta(x - L)$$

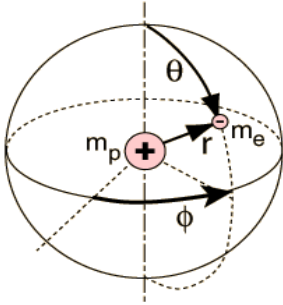
And hence,

$$\begin{aligned} \langle H \rangle &= \int_0^L \psi(x) \cdot \left( -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} \right) dx = -\frac{\hbar^2 A}{2m} \left( \int_0^L [\delta(x) - 2\delta(x - L/2) + \delta(x - L)] \cdot \psi(x) dx \right) \\ &= -\frac{\hbar^2 A}{2m} [\psi(0) - 2\psi(L/2) + \psi(L)] = \frac{\hbar^2 A^2 L}{2m} = \frac{12\hbar^2}{2mL^2} \end{aligned}$$

We can see that the expectation value of the Hamiltonian,  $\langle H \rangle = \frac{12\hbar^2}{2mL^2}$  is greater than the actual ground state energy of the Infinite Square Well,  $E_g = \frac{\pi^2\hbar^2}{2mL^2}$ .

Thus the Variational Principle holds true.

## Section IV): An Approximation of Hydrogen Atom Ground State Using a Gaussian Trial Function



We take the trial wave function  $\psi(r) = Ae^{-br^2}$

Normalization over all space gives us the constant 'A':

$$\int |\psi(r)|^2 d^3r = |A|^2 \int e^{-2br^2} r^2 dr d(\cos \theta) d\phi = 4\pi |A|^2 \int_0^\infty r^2 e^{-br^2} dr = |A|^2 \left(\frac{\pi}{2b}\right)^{3/2} = 1$$

The last integral can be calculated using the trick mentioned in [Section I\)](#) Ground State of a Linear Potential Using a Gaussian Trial Function.

$$A = \left(\frac{2b}{\pi}\right)^{3/4}$$

Now, the Hamiltonian for the Hydrogen Atom is:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi \epsilon_0} \frac{1}{r}$$

Thus,

$$\hat{H}\psi = A \left( -\frac{\hbar^2}{2m} \nabla^2 e^{-br^2} - \frac{e^2}{4\pi \epsilon_0} \frac{e^{-br^2}}{r} \right)$$

Where the Laplacian in terms of spherical coordinates is:

$$\nabla^2 e^{-br^2} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial e^{-br^2}}{\partial r} \right) = (4b^2 r^2 - 6b) e^{-br^2}$$

(The angular differential terms in the Laplacian become zero since  $\psi(r)$  is independent of  $\theta$  and  $\phi$  and hence they have been ignored.)

Hence,

$$\begin{aligned} \langle \psi | H | \psi \rangle &= |A|^2 \int \left\{ \frac{\hbar^2}{2m} (6b - 4b^2 r^2) e^{-2br^2} - \frac{e^2}{4\pi \epsilon_0} \frac{e^{-2br^2}}{r} \right\} d^3 r = |A|^2 \int \left\{ \frac{\hbar^2}{2m} (6b - 4b^2 r^2) e^{-2br^2} - \frac{e^2}{4\pi \epsilon_0} \frac{e^{-2br^2}}{r} \right\} r^2 dr d(\cos\theta) d\phi \\ &= 4\pi |A|^2 \left\{ \int \frac{\hbar^2}{2m} (6b - 4b^2 r^2) e^{-2br^2} r^2 dr - \frac{e^2}{4\pi \epsilon_0} \int \frac{e^{-2br^2}}{r} r^2 dr \right\} = 4\pi \left( \frac{2b}{\pi} \right)^{3/2} \left\{ \frac{\hbar^2}{2m} \left[ 6b \int_0^\infty r^2 e^{-2br^2} dr - 4b^2 \int_0^\infty r^4 e^{-2br^2} dr \right] - \frac{e^2}{4\pi \epsilon_0} \int_0^\infty r e^{-2br^2} dr \right\} \end{aligned}$$

The integrals can be solved using the trick mentioned in chapter i), or using integration by substitution, or integration by parts. Solving, we get,

$$\langle H \rangle = \frac{3\hbar^2 b}{2m} - \frac{e^2}{2\pi \epsilon_0} \sqrt{\frac{2b}{\pi}}$$

Minimizing the RHS gives us,

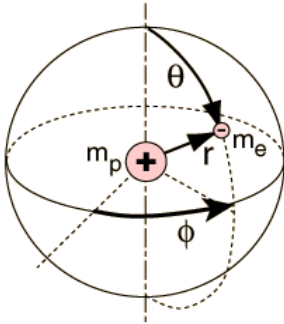
$$\frac{d\langle H \rangle}{db} = \frac{3\hbar^2}{2m} - \frac{e^2}{4\pi \epsilon_0} \sqrt{\frac{2}{\pi b}} = 0 \Rightarrow b_{\min} = \frac{m^2 e^4}{18\pi^3 \hbar^4 \epsilon_0^2}$$

Plugging 'b' back into the equation gives us:

$$E_g \square \langle H \rangle_{\min} = \frac{-me^4}{12\pi^3 \hbar^2 \epsilon_0^2} J = \frac{-me^3}{12\pi^3 \hbar^2 \epsilon_0^2} eV = -11.5eV$$

We see that the Variational Principle still holds true, since the actual ground state energy of the Hydrogen atom is known to be -13.6 eV, whereas we have overestimated it in our approximation of -11.5eV, just like the Variational Principle states. But even so, the approximation is quite good since it is close to the actual ground state energy of the hydrogen atom.

**Section V) The Exact Ground State of Hydrogen Atom Using an Exponentially Decaying Trial Function**



Instead of a Gaussian (as in the previous case), we assume the trial wavefunction to be of a linear exponential form:

$$\psi(r) = Ae^{-br}$$

This type of function, like the Gaussian, is also a good candidate for bound states because of similar reasons:

- 1) It rapidly falls to zero with increasing distance.
- 2) It can be easily normalized.

Normalization of  $\psi(r)$  over all space gives us the constant 'A':

$$\int |\psi(r)|^2 d^3r = |A|^2 \int e^{-2br} r^2 dr \cdot d(\cos \theta) \cdot d\phi = 4\pi |A|^2 \int_0^\infty r^2 e^{-2br} dr = |A|^2 \frac{\pi}{b^3} = 1$$

$$A = \sqrt{\frac{b^3}{\pi}}$$

Now, the Hamiltonian for the Hydrogen Atom is:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi \epsilon_0 r}$$

Hence,

$$\hat{H}\psi = A \left( -\frac{\hbar^2}{2m} \nabla^2 e^{-br} - \frac{e^2}{4\pi \epsilon_0} \frac{e^{-br}}{r} \right)$$

Where, the Laplacian is given by:

$$\nabla^2 e^{-br} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial e^{-br}}{\partial r} \right) = \left( b^2 - \frac{2b}{r} \right) e^{-br}$$



(The angular differential terms in the Laplacian become zero since  $\psi(r)$  is independent of  $\theta$  and  $\varphi$  and hence, they have been ignored.)

Therefore, the expectation value of the Hamiltonian is given by,

$$\begin{aligned} \langle \psi | H | \psi \rangle &= |A|^2 \int \left\{ \frac{\hbar^2}{2m} \left( \frac{2b}{r} - b^2 \right) e^{-2br} - \frac{e^2}{4\pi \epsilon_0} \frac{e^{-2br}}{r} \right\} d^3r = |A|^2 \int \left\{ \frac{\hbar^2}{2m} \left( \frac{2b}{r} - b^2 \right) e^{-2br} - \frac{e^2}{4\pi \epsilon_0} \frac{e^{-2br}}{r} \right\} r^2 dr d(\cos\theta) d\varphi \\ &= 4\pi |A|^2 \left\{ \frac{\hbar^2}{2m} \left( \frac{2b}{r} - b^2 \right) e^{-2br} - \frac{e^2}{4\pi \epsilon_0} \frac{e^{-2br}}{r} \right\} r^2 dr = 4b^3 \left\{ \frac{\hbar^2}{2m} \left[ 2b \int_0^\infty r e^{-2br} dr - b^2 \int_0^\infty r^2 e^{-2br} dr \right] - \frac{e^2}{4\pi \epsilon_0} \int_0^\infty r e^{-2br} dr \right\} \end{aligned}$$

The integrals can be solved using integration by parts. Solving, we get,

$$\langle H \rangle = \frac{\hbar^2 b^2}{2m} - \frac{e^2 b}{4\pi \epsilon_0}$$

Minimizing the RHS gives us,

$$\frac{d\langle H \rangle}{db} = \frac{\hbar^2 b}{m} - \frac{e^2}{4\pi \epsilon_0} = 0 \Rightarrow b_{\min} = \frac{me^2}{4\pi \hbar^2 \epsilon_0} = \frac{1}{a}$$

Where, 'a' is the Bohr radius,  $a = 0.529 \times 10^{-10} m$

And therefore, plugging this value of 'b' back in the equation for the Hamiltonian gives us,

$$\langle H \rangle_{\min} = \frac{-m}{2\hbar^2} \left( \frac{e^2}{4\pi \epsilon_0} \right)^2 = E_1 = -13.6 eV$$

This time, we have  $\langle H \rangle_{\min}$  exactly equal to the ground state energy of the Hydrogen atom,  $E_g$ , which is 13.6 eV. This means that our assumed trial function  $\psi(r) = Ae^{-br}$  is the exact, actual ground state wavefunction of the Hydrogen atom.

Substituting the values of 'A' and 'b' in  $\psi(r)$  gives us the exact ground state of the Hydrogen atom:

$$\boxed{\psi_g(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}}$$

#### 4) **CONCLUSION**

The Variational Principle is a powerful tool in Quantum Mechanics, and at the same time, it is very simple to use. It is especially useful for situations wherein one is unable to directly solve the Schrodinger equation due to its mathematical complexity.

The only drawback of this technique is that we never know how close we are to the actual ground state energy of the system – we only have an upper bound. Moreover, the technique only finds a good use when it is applied to a quantum system in order to gain an upper bound on its *ground* state energy.

#### **Reference:**

Introduction to Quantum Mechanics by David J Griffiths, Second Edition, Pearson, 2014