Variational method.

Principles of the method:

The expectation value of the Hamiltonian H of a system in any state $|\psi\rangle$ is given by

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad \cdots\cdots \quad (1)$$

If the state $|\psi\rangle$ is normalized, we can write

$$\langle H \rangle = \langle \psi | H | \psi \rangle \equiv (\psi, H\psi) . \quad \cdots\cdots \quad (2)$$

We shall now prove that $\langle H \rangle$ is an upperbound to the ground state energy E_0 of the system, i.e.,

$$\langle H \rangle \geqslant E_0 \quad \cdots\cdots \quad (3)$$

Proof:

We expand $|\psi\rangle$ as a linear combination of the complete set of states $\{|\phi_i\rangle, i = 0, 1, 2, \cdots\}$ where the $|\phi_i\rangle$'s are the orthonormal eigenstates of H belonging to the eigenvalues $E_0, E_1, E_2 \cdots$, respectively. Thus

$$|\psi\rangle = \sum_{i=0}^{\infty} a_i |\phi_i\rangle . \quad \cdots\cdots \quad (4)$$

Since $|\psi\rangle$ is normalized, i.e., $\langle \psi|\psi\rangle = 1$, it follows that

$$\sum_{i=0}^{\infty} |a_i|^2 = 1 . \quad (5)$$

The expectation value of H in the state $|\psi\rangle$ can now be written as

$$\langle H\rangle = \langle\psi|H|\psi\rangle = \sum_{i,j} a_i^* a_j \langle\phi_i|H|\phi_j\rangle$$

$$= \sum_{i,j} a_i^* a_j E_j \langle\phi_i|\phi_j\rangle$$

Since the eigenstates $|\phi_i\rangle$, $i=0,1,2,\cdots$ are orthonormal, we have

$$\langle\phi_i|\phi_j\rangle = \delta_{ij} .$$

Hence

$$\langle H\rangle = \sum_{i,j} a_i^* a_j E_j \delta_{ij} = \sum_i |a_i|^2 E_i$$

$$\geq E_0 \sum_i |a_i|^2 \quad (\text{since } E_i > E_0 \text{ for } i>0$$

$$= E_0 . \quad (\text{since } \textstyle\sum_i |a_i|^2 = 1 \text{ (Eq. 5)})$$

Thus,

$$\langle H\rangle \geq E_0 ,$$

The equality sign holds if $|\psi\rangle$ is exactly equal to the ground state vector $|\phi_0\rangle$, in which case $a_0 = 1$ and all other a_i's are zero. Thus we have shown that the expectation value of H in any state $|\psi\rangle$ gives an upper bound to the ground state energy. This result is the basis of the variational method for finding the ground state energy and the wavefunction.

The inequality $E_0 \le \langle H \rangle$ shows that if we choose a number of trial wavefunctions $\psi_1, \psi_2 \dots$ and calculate the corresponding expectation values $\langle H \rangle_i$, then each of the expectation values is greater than E_0. Therefore, the lowest expectation value is closest to E_0. In this variation method we thus proceed as follows:

1. Choose an appropriate trial wave function $\psi_{\alpha\beta\dots}$ depending on the parameters $\alpha, \beta, \dots$.
2. Calculate the expectation value $\langle H \rangle_{\alpha\beta\dots}$ using the wavefunction $\psi_{\alpha\beta\dots}$.
3. Vary the trial wavefunction by varying the parameters $\alpha, \beta \dots$ such that $\langle H \rangle_{\alpha\beta\dots}$ attain its minimum value. To find the values of the parameters for which the expectation value is minimum, we set

$$\frac{\partial \langle H \rangle_{\alpha\beta\dots}}{\partial \alpha} = 0$$

$$\frac{\partial \langle H \rangle_{\alpha\beta\dots}}{\partial \beta} = 0$$

and so on. Solving these equations we obtain $\alpha_0, \beta_0, \dots$. Thus $\langle H \rangle_{\alpha_0\beta_0\dots}$ is a minimum and so is the best approximation to the ground state energy. The wavefunction $\psi_{\alpha_0\beta_0\dots}$ is the variational approximation to the ground state wavefunction. Usually, the approximation to the wavefunction is poorer than the approximation to the ground state energy.

Variational method for excited states

The variational method can also be adapted to obtain approximate values for the energy of an excited state provided that the wavefunctions of states of lower energy are accurately known. The trial wave function of the n^{th} state is taken to be orthogonal to the known states of lower energy. Thus, the trial wavefunction for the n^{th} state is of the form

$$|\psi\rangle = |\chi\rangle - \sum_{i=0}^{n-1} |\phi_i\rangle\langle\phi_i|\chi\rangle$$

where $|\chi\rangle$ is an arbitrary ket conforming to the general features of Quantum Mechanics. It is obvious that

$$\langle\phi_0|\psi\rangle = \langle\phi_1|\psi\rangle = \cdots = \langle\phi_{n-1}|\psi\rangle = 0 .$$

Therefore, in the expansion of $|\psi\rangle$ in terms of the basis states $|\phi_i\rangle$, we will have $a_i = 0$ for $i = 0, 1, 2, \cdots n-1$,

i.e.,

$$|\psi\rangle = \sum_{i=n}^{\infty} a_i |\phi_i\rangle .$$

Normalizing $|\psi\rangle$, i.e., $\langle\psi|\psi\rangle = 1$, we have $\sum_{i=n}^{\infty} |a_i|^2 = 1$.

Therefore,

$$\langle H\rangle = \langle\psi|H|\psi\rangle$$

$$= \sum_{i=n}^{\infty}\sum_{j=n}^{\infty} a_i^* a_j \langle\phi_i|H|\phi_j\rangle$$

$$= \sum_{i=n}^{\infty}\sum_{j=n}^{\infty} a_i^* a_j \, E_j \, \delta_{ij}$$

i.e.,

$$\langle H \rangle = \sum_{i=n}^{\infty} |a_i|^2 E_i$$

$$\geq E_n \sum_{i=n}^{\infty} |a_i|^2$$

$$= E_n$$

Thus

$$\langle H \rangle \geq E_n$$

i.e., $\langle H \rangle$ provides an upper bound to the energy E_n.

EXAMPLES

1. One-dimensional harmonic oscillator.

We consider a one-dimensional harmonic oscillator whose Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m \omega_0^2 x^2 .$$

The potential energy $V(x) = \frac{1}{2} m \omega_0^2 x^2$ is an even function of x. Therefore, eigenstates of H must be either even or odd. The lowest state in energy, i.e., the ground state is always even. Further, the wavefunction must tend to zero as $|x| \to \infty$. These properties of the exact ground-state wavefunction suggests that we can choose the trial wavefunction to be of the form

$$\psi(x) = A e^{-\alpha x^2/2} .$$

Here ψ depends on only one parameter α. The constant A is fixed by normalization of ψ, i.e.,

$$\langle \psi | \psi \rangle = 1$$

or $$\int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = 1 .$$

or $$|A|^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = 1$$ $\left| \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \right.$

or $$|A|^2 \left(\frac{\pi}{\alpha}\right)^{1/2} = 1 .$$

Therefore, we can choose A to be real and positive having the value

$$A = \left(\frac{\alpha}{\pi}\right)^{1/4} .$$

Therefore, the normalized trial wavefunction is

$$\psi(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} .$$

In the next step, we have to calculate the expectation value of H. We have

$$\langle H \rangle_\alpha = \langle \psi | H | \psi \rangle = \int_{-\infty}^{\infty} \psi^*(x)\, H \,\psi \, dx$$

$$= \langle T \rangle_\alpha + \langle V \rangle_\alpha$$

where

$$\langle T \rangle_\alpha = \int_{-\infty}^{\infty} \psi^*(x)\, \hat{T}\, \psi(x)\, dx .$$ $\left| \hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \right.$

$$= -\frac{\hbar^2}{2m}\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} \frac{d^2}{dx^2} e^{-\alpha x^2/2} dx$$

and

$$\langle V\rangle_\alpha = \int_{-\infty}^{\infty} \psi^*(x)\, V\, \psi(x)\, dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{2} m\omega_0^2 \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$$

i.e.,

$$\langle V_\alpha\rangle = \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{2} m\omega_0^2 \frac{1}{2\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2} \quad \Bigg| \quad \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2}$$

or $\langle V\rangle_\alpha = \dfrac{m\omega_0^2}{4\alpha}$.

Next, we will calculate $\langle T\rangle_\alpha$.

$$\langle T\rangle_\alpha = -\frac{\hbar^2}{2m}\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} \frac{d^2}{dx^2} e^{-\alpha x^2/2} dx$$

Integrating by part once we have

$$\langle T_\alpha\rangle = \frac{\hbar^2}{2m}\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \left[\frac{d}{dx} e^{-\alpha x^2/2}\right]^2 dx$$

$$= \frac{\hbar^2}{2m}\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \left[-\alpha x\, e^{-\alpha x^2/2}\right]^2 dx$$

$$= \frac{\hbar^2}{2m}\left(\frac{\alpha}{\pi}\right)^{1/2} \alpha^2 \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$$

$$= \frac{\hbar^2}{2m}\left(\frac{\alpha}{\pi}\right)^{1/2} \alpha^2 \cdot \frac{1}{2\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$= \frac{\hbar^2\alpha}{4m}.$$

Therefore

$$\langle H\rangle_\alpha = \langle T\rangle_\alpha + \langle V\rangle_\alpha = \frac{\hbar^2\alpha}{4m} + \frac{m\omega_0^2}{4\alpha}$$

$$= \frac{1}{4}\left(\frac{\hbar^2\alpha}{m} + \frac{m\omega_0^2}{\alpha}\right).$$

Next, we minimize $\langle H \rangle_\alpha$ by varying the parameter α. To find the value of α for which $\langle H \rangle_\alpha$ is minimized, we write

$$\frac{\partial}{\partial \alpha} \langle H \rangle_\alpha = 0$$

or $$\frac{1}{4}\left(\frac{\hbar^2}{m} - \frac{m\omega_0^2}{\alpha^2}\right) = 0$$

or $$\frac{\hbar^2}{m} - \frac{m\omega_0^2}{\alpha^2} = 0$$

or $$\alpha^2 = \frac{m^2\omega_0^2}{\hbar^2}$$

i.e., $$\alpha = \alpha_0 = \frac{m\omega_0}{\hbar}.$$

Thus, the minimum value of $\langle H \rangle_\alpha$ is

$$\langle H \rangle_{min} = \langle H \rangle_{\alpha_0} = \frac{1}{4}\left(\frac{\alpha_0 \hbar^2}{m} + \frac{m\omega_0^2}{\alpha_0}\right)$$

$$= \frac{1}{4}\left(\frac{m\omega_0\hbar^2}{\hbar m} + \frac{m\omega_0^2\hbar}{m\omega_0}\right)$$

$$= \frac{1}{4}\left(\hbar\omega_0 + \hbar\omega_0\right) = \frac{1}{2}\hbar\omega_0 .$$

Therefore $$E_0 \leq \langle H \rangle_{\alpha_0}$$

or $$\boxed{E_0 \leq \frac{1}{2}\hbar\omega_0}$$

The variational estimate of the ground-state wavefunction is

$$\psi_{\alpha_0}(x) = \left(\frac{m\omega_0}{\pi\hbar}\right)^{1/4} e^{-m\omega_0 x^2/\hbar}.$$

First excited state of a one-dimensional harmonic oscillator.

The trial wavefunction has to be chosen such that it is orthogonal to the ground-state wavefunction. Since the ground state wavefunction is even, the trial wave function must be chosen as an odd function of x. In that case, the trial wavefunction will be orthogonal to the ground state wavefunction.

Let the trial wavefunction be

$$\psi(x) = B x e^{-\beta x^2/2}$$

where B is the normalization constant. Normalizing $\psi(x)$ we obtain

$$|B|^2 = \frac{2\beta^{3/2}}{\sqrt{\pi}} .$$

Hence the normalized trial wavefunction is

$$\psi(x) = \sqrt{\frac{2\beta^{3/2}}{\sqrt{\pi}}}\; x\, e^{-\beta x^2/2} .$$

Next, we have to calculate $\langle H \rangle$:

$$\langle H \rangle_\beta = \langle T \rangle_\beta + \langle V \rangle_\beta$$

where

$$\langle T\rangle_\beta = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\psi^*(x)\frac{d^2}{dx^2}\psi(x)\,dx$$

$$= \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\frac{d\psi^*}{dx}\frac{d\psi}{dx}\,dx \qquad \Big| \text{ Integrating by parts}$$

$$= \frac{\hbar^2 B^2}{2m}\int_{-\infty}^{\infty}\left[\frac{d}{dx}\left(x\,e^{-\beta x^2/2}\right)\right]^2 dx$$

$$= \frac{\hbar^2 B^2}{2m}\int_{-\infty}^{\infty}\left[e^{-\beta x^2/2} - \beta x^2 e^{-\beta x^2/2}\right]^2 dx$$

$$= \frac{\hbar^2 B^2}{2m}\int_{-\infty}^{\infty}\left(1 - 2\beta x^2 + \beta^2 x^4\right)e^{-\beta x^2}\,dx$$

$$= \frac{\hbar^2 B^2}{2m}\left[\sqrt{\frac{\pi}{\beta}} - 2\beta\cdot\frac{1}{2\beta}\sqrt{\frac{\pi}{\beta}} + \beta^2\frac{3}{4\beta^2}\sqrt{\frac{\pi}{\beta}}\right]$$

$$= \frac{\hbar^2 B^2}{2m}\cdot\sqrt{\frac{\pi}{\beta}}\left[1 - 1 + \frac{3}{4}\right]$$

$$= \frac{3}{4}\,\frac{\hbar^2 B^2}{2m}\sqrt{\frac{\pi}{\beta}}$$

$$= \frac{3}{4}\cdot\frac{\hbar^2}{2m}\,\frac{2}{\sqrt{\pi}}\beta^{3/2}\cdot\sqrt{\frac{\pi}{\beta}}$$

$$= \frac{3}{4}\,\frac{\beta\hbar^2}{m}\,.$$

and

$$\langle V \rangle = \int_{-\infty}^{\infty} \psi^*(x)\, V(x)\, \psi(x)\, dx$$

$$= \frac{1}{2} m \omega_0^2 B^2 \int_{-\infty}^{\infty} x\, e^{-\beta x^2/2}\, x^2\, x\, e^{-\beta x^2/2}\, dx$$

$$= \frac{1}{2} m \omega_0^2 B^2 \int_{-\infty}^{\infty} x^4 e^{-\beta x^2}\, dx$$

$$= \frac{1}{2} m \omega_0^2 B^2 \cdot \frac{3}{4\beta^2} \sqrt{\frac{\pi}{\beta}}$$

$$= \frac{1}{2} m \omega_0^2 \cdot \frac{2}{\sqrt{\pi}} \beta^{3/2} \cdot \frac{3}{4\beta^2} \sqrt{\frac{\pi}{\beta}}$$

$$= \frac{3}{4} \frac{m \omega_0^2}{\beta}$$

$$\therefore \quad \langle H \rangle_\beta = \frac{3}{4} \left(\frac{\hbar^2 \beta}{m} + \frac{m \omega_0^2}{\beta} \right)$$

Next, we minimize $\langle H \rangle_\beta$ by choosing the appropriate value for β. We set

$$\frac{\partial}{\partial \beta} \langle H \rangle_\beta = 0$$

or $$\frac{\hbar^2}{m} - \frac{m \omega_0^2}{\beta^2} = 0$$

or $$\beta^2 = \frac{m^2 \omega_0^2}{\hbar^2}.$$

Since β is a positive parameter, we have

$$\beta = \beta_0 = \frac{m\omega_0}{\hbar} .$$

Thus, the minimized value of $\langle H \rangle_\beta$ is

$$\langle H \rangle_{min} = \langle H \rangle_{\beta_0}$$

$$= \frac{3}{4} \left[\frac{\hbar^2 \, m\omega_0/\hbar}{m} + \frac{m\omega_0^2}{m\omega_0/\hbar} \right]$$

$$= \frac{3}{4} \left[\hbar\omega_0 + \hbar\omega_0 \right]$$

$$= \frac{3}{2} \hbar\omega_0 .$$

Therefore,

$$E_1 \leq \langle H \rangle_{min}$$

i.e.,

$$\boxed{E_1 \leq \frac{3}{2} \hbar\omega_0}$$

Note :

$$\int_{-\infty}^{\infty} e^{-\beta x^2} dx = \sqrt{\frac{\pi}{\beta}}$$

$$\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{2\beta} \sqrt{\frac{\pi}{\beta}}$$

$$\int_{-\infty}^{\infty} x^4 e^{-\beta x^2} dx = \frac{3}{4\beta^2} \sqrt{\frac{\pi}{\beta}}$$

In general,

$$\int_{-\infty}^{\infty} x^{2n} e^{-\beta x^2} dx = \frac{1 \cdot 2 \cdot 3 \cdot \cdots \cdot (2n-1)}{2^n \beta^n} \sqrt{\frac{\pi}{\beta}}$$

for $n = 0, 1, 2, 3, \ldots$,

Example.

Variational method for estimating the ground state energy of hydrogen atom.

The ground state is spherically symmetric. Therefore, let us choose a trial wavefunction of the form

$$\psi(\vec{r}) = A e^{-\beta r}.$$

We normalize $\psi(\vec{r})$, i.e.,

$$\int \psi^*(\vec{r})\,\psi(\vec{r})\,d^3r = 1$$

or $\displaystyle |A|^2 \int_0^\infty e^{-2\beta r} r^2\,dr \int_\Omega d\Omega = 1$ | $d\Omega = \sin\theta\,d\theta\,d\varphi$

or, $\displaystyle 4\pi |A|^2 \int_0^\infty e^{-2\beta r} r^2\,dr = 1$

or, $\displaystyle 4\pi |A|^2 \frac{2!}{(2\beta)^3} = 1$ | $\displaystyle\int_0^\infty x^n e^{-\beta x}\,dx = \frac{n!}{\beta^{n+1}}$ for $n = 0, 1, 2, \ldots$

or $\displaystyle |A|^2 = \frac{\beta^3}{\pi}$

Choosing A to be real and positive we have

$$A = \sqrt{\frac{\beta^3}{\pi}}.$$

The normalized trial wave function for the ground state is then

$$\psi(\vec{r}) = \sqrt{\frac{\beta^3}{\pi}}\, e^{-\beta r}.$$

Now, the Hamiltonian for the hydrogen atom is

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

Therefore

$$\langle H\rangle = \left\langle -\frac{\hbar^2}{2m}\nabla^2\right\rangle + \left\langle -\frac{e^2}{4\pi\epsilon_0 r}\right\rangle = \langle T\rangle + \langle V\rangle$$

Consider the expectation value of kinetic energy:

$$\langle T\rangle = -\frac{\hbar^2}{2m}\langle\nabla^2\rangle = -\frac{\hbar^2}{2m}\int \psi^*(r)\,\nabla^2\psi(r)\,d^3r.$$

Use the vector identity

$$\vec{\nabla}\cdot(\psi^*\vec{\nabla}\psi) = \psi^*\nabla^2\psi + \vec{\nabla}\psi^*\cdot\vec{\nabla}\psi$$

$$\therefore \int \psi^*\nabla^2\psi\, d^3r = \int \vec{\nabla}\cdot(\psi^*\vec{\nabla}\psi)\,d^3r - \int \vec{\nabla}\psi^*\cdot\vec{\nabla}\psi\, d^3r.$$

The first integral on the right can be converted to a surface integral using Gauss's theorem, and since the surface is at infinity, the integrand vanishes since ψ vanishes for $r \to \infty$.

Hence we have

$$\langle T \rangle = -\frac{\hbar^2}{2m} \int \psi^* \nabla^2 \psi \, d^3 r$$

$$= \frac{\hbar^2}{2m} \int \vec{\nabla}\psi^* \cdot \vec{\nabla}\psi \, d^3 r. = \frac{\hbar^2}{2m} \int |\nabla \vec{\psi}|^2 d^3 r.$$

Now, ψ is only a function of $r \equiv |\vec{r}|$. Therefore

$$\vec{\nabla}\psi = \hat{r} \frac{d}{dr} \psi = -\hat{r} \beta \psi(r).$$

Hence

$$|\vec{\nabla}\psi|^2 = \beta^2 \psi^2(r).$$

Thus

$$\langle T \rangle = \frac{\hbar^2 \beta^2}{2m} \underbrace{\int \psi^2(r) d^3 r}_{=1}$$

or

$$\langle T \rangle = \frac{\hbar^2 \beta^2}{2m}.$$

Next, we calculate the expectation value of the potential energy.

$$\langle V \rangle = \left\langle -\frac{e^2}{4\pi\epsilon_0 r} \right\rangle = -\frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle$$

$$= -\frac{e^2}{4\pi\epsilon_0} \int \psi^*(r)\, \frac{1}{r}\, \psi(r)\, d^3r$$

Since ψ and ψ^* do not depend upon θ or ϕ, we can easily integrate over θ and ϕ to get 4π. Hence $d^3r = 4\pi r^2 dr$. Then

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0} (4\pi) \int_0^\infty \psi^2(r)\, r\, dr$$

$$= -\frac{e^2}{4\pi\epsilon_0} 4\pi \cdot \frac{\beta^3}{\pi} \int_0^\infty e^{-2\beta r} r\, dr$$

$$= -\frac{e^2}{4\pi\epsilon_0} 4\pi \frac{\beta^3}{\pi} \cdot \frac{1}{4\beta^2}$$

$$= -\frac{\beta e^2}{4\pi\epsilon_0}.$$

$$\int_0^\infty e^{-\alpha x} x^n dx = \frac{n!}{\alpha^{n+1}}$$
$n = 0, 1, 2, \ldots$

Hence, we obtain

$$\langle H \rangle_\beta = \frac{\hbar^2 \beta^2}{2m} - \frac{\beta e^2}{4\pi\epsilon_0} .$$

We now ~~minimi~~ minimize $\langle H \rangle_\beta$.

$$\left. \frac{\partial}{\partial \beta} \langle H \rangle_\beta \right|_{\beta = \beta_0} = 0$$

or $$\frac{\hbar^2 \beta_0}{m} - \frac{e^2}{4\pi\epsilon_0} = 0$$

or $$\beta_0 = \frac{m e^2}{4\pi\epsilon_0 \hbar^2} = \frac{1}{a_0}$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = \text{Bohr radius}$$

Thus, the minimum value of $\langle H \rangle$ is

$$\langle H \rangle_{min} = \langle H \rangle_{\beta_0} = \frac{\hbar^2 \beta_0^2}{2m} - \frac{\beta_0 e^2}{4\pi\epsilon_0}$$

$$= \frac{\hbar^2}{2 m a_0^2} - \frac{e^2}{4\pi\epsilon_0 a_0}$$

$$= \left(\frac{\hbar^2}{2 m a_0} - \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{a_0}$$

or

$$\langle H \rangle_{min} = \left(\frac{\hbar^2}{2m \cdot \left(\frac{4\pi\epsilon_0 \hbar^2}{me^2}\right)^2} - \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{a_0}$$

$$= \frac{1}{4\pi\epsilon_0} \left(\frac{e^2}{2} - e^2 \right) \frac{1}{a_0}$$

$$= - \frac{e^2}{(4\pi\epsilon_0) 2a_0}$$

Therefore

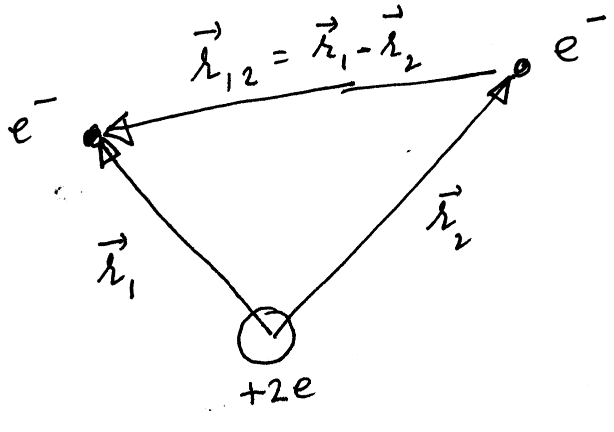
$$E_0 \leq - \frac{e^2}{(4\pi\epsilon_0) 2a_0} .$$

The variational estimate of the ground state wave function is

$$\psi = \left(\frac{\beta^3}{\pi} \right)^{1/2} e^{-\beta r} = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} .$$

In this example, variational estimates of the ground state energy and ground state wave function coincide with the exact values.

Ground state of Helium atom using variational method.



The Hamiltonian is

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

Next, we have to choose an appropriate trial wave function. We note that, for a helium ion, the exact ground state wave function is

$$\psi_{100}(\vec{r}) = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-Zr/a_0} \qquad (Z = 2)$$

where
$$a_0 = \text{Bohr radius} = \frac{4\pi\epsilon_0 \hbar^2}{me^2}.$$

If we neglect the interaction $e^2/4\pi\epsilon_0 r_{12}$ between the two electrons of the helium atom, the wavefunction of the helium atom can be written as

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)$$

$$= \frac{Z^3}{\pi a_0^3}\, e^{-Z(r_1 + r_2)/a_0}$$

Of course $\psi(\vec{r}_1, \vec{r}_2)$ cannot be the exact wavefunction of the helium atom since we have left out the electron-electron interaction. However, we can use $\psi(\vec{r}_1, \vec{r}_2)$ as the trial wavefunction, and to take the mutal interaction between the two electrons into account, we will take Z appearing in $\psi(\vec{r}_1, \vec{r}_2)$ to be a free parameter (not $Z = 2$). However $Z = 2$ appearing in the Hamiltonian is kept unchanged.

Next, we calculate the expectation value of H using the trial wavefunction $\psi(\vec{r}_1, \vec{r}_2)$.

The expectation value of the Hamiltonian is

$$\langle H \rangle_Z = \int \psi^* H \psi \, d^3 r_1 \, d^3 r_2$$

$$= \int \psi^*(\vec{r}_1, \vec{r}_2) \left[-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right.$$

$$\left. + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \psi(\vec{r}_1, \vec{r}_2) \, d^3 r_1 \, d^3 r_2 \, .$$

<u>Expectation values of ∇_1^2 and ∇_2^2</u>

$$\langle \nabla_1^2 \rangle = \int \psi^*(\vec{r}_1, \vec{r}_2) \, \nabla_1^2 \, \psi(\vec{r}_1, \vec{r}_2) \, d^3 r_1 \, d^3 r_2$$

$$= \int \psi_{100}^*(\vec{r}_1) \, \nabla_1^2 \, \psi_{100}(\vec{r}_1) \, d^3 r_1$$

$$= \frac{Z^3}{\pi a_0^3} \int e^{-Zr/a_0} \, \nabla^2 \, e^{-Zr/a_0} \, d^3 r$$

$$= -\frac{Z^3}{\pi a_0^3} \int \left(\vec{\nabla} e^{-Zr/a_0} \right) \cdot \left(\vec{\nabla} e^{-Zr/a_0} \right) r^2 \, dr \, d\Omega$$

$$= -\frac{Z^3}{\pi a_0^3} \cdot (4\pi) \frac{Z^2}{a_0^2} \int_0^\infty e^{-2Zr/a_0} \, r^2 \, dr$$

$$= -\frac{Z^3}{\pi a_0^3} \cdot (4\pi) \frac{Z^2}{a_0^2} \cdot \frac{2}{(2Z/a_0)^3} = -\frac{Z^2}{a_0^2} \, .$$

The expectation value of ∇_2^2 is the same as that of ∇_1^2 because the trial wavefunction is symmetric under the interchange of r_1 and r_2. Thus

$$\langle \nabla_1^2 \rangle = \langle \nabla_2^2 \rangle = - \frac{Z^2}{a_0^2} .$$

Therefore

$$\left\langle -\frac{\hbar^2}{2m} \nabla_1^2 \right\rangle = \left\langle -\frac{\hbar^2}{2m} \nabla_2^2 \right\rangle = \frac{\hbar^2 Z^2}{2 m a_0^2}$$

$$= \frac{\hbar^2 Z^2}{2m . \frac{4\pi \epsilon_0 \hbar^2}{m e^2} . a_0}$$

$$= \frac{Z^2 e^2}{(4\pi\epsilon_0) 2 a_0} . \qquad \cdots\cdots (2)$$

Expectation values of $\frac{1}{r_1}$ and $\frac{1}{r_2}$

We first note that expectation values of $1/r_1$ and $1/r_2$ are equal since the trial wavefunction is symmetric under the interchange of r_1 and r_2. Now

$$\left\langle \frac{1}{r_1} \right\rangle = \int \psi^*(\vec{r}_1, \vec{r}_2)\, \frac{1}{r_1}\, \psi(\vec{r}_1, \vec{r}_2)\, d^3r_1\, d^3r_2$$

$$= \int \psi^*_{100}(\vec{r}_1)\, \frac{1}{r_1}\, \psi_{100}(\vec{r}_1)\, d^3r_1$$

$$= \frac{Z^3}{\pi a_0^3} \int e^{-Zr/a_0}\, \frac{1}{r}\, e^{-Zr/a_0}\, r^2\, d\Omega\, dr$$

$$= \frac{Z^3}{\pi a_0^3}(4\pi) \int_0^\infty e^{-2Zr/a_0}\, r\, dr$$

$$= \frac{Z^3}{\pi a_0^3}(4\pi)\, \frac{1}{(2Z/a_0)^2}$$

$$= \frac{Z}{a_0}$$

Hence

$$\left\langle -\frac{2e^2}{4\pi\epsilon_0 r_1} \right\rangle = \left\langle -\frac{2e^2}{4\pi\epsilon_0 r_2} \right\rangle = -\frac{2e^2 Z}{4\pi\epsilon_0 a_0} \quad \cdots (3)$$

Expectation value of $\dfrac{e^2}{4\pi\epsilon_0 r_{12}}$.

$$\left\langle \frac{e^2}{4\pi\epsilon_0 r_{12}} \right\rangle = \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r_{12}} \right\rangle$$

$$= \frac{e^2}{4\pi\epsilon_0} \int \psi^*(\vec{r}_1, \vec{r}_2) \frac{1}{r_{12}} \psi(\vec{r}_1, \vec{r}_2)\, d^3r_1\, d^3r_2$$

$$= \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int e^{-2Z(r_1+r_2)/a_0} \frac{1}{r_{12}}\, d^3r_1\, d^3r_2$$

We will now make a change of variable :

Let

$$\frac{2Z}{a_0}\vec{r}_1 = \vec{\rho}_1 \quad , \quad \frac{2Z}{a_0}\vec{r}_2 = \vec{\rho}_2$$

Therefore

$$\frac{2Z}{a_0}(\vec{r}_1 - \vec{r}_2) = \vec{\rho}_1 - \vec{\rho}_2$$

i.e.,
$$\frac{2Z}{a_0}\vec{r}_{12} = \vec{\rho}_{12}$$

Hence

$$\left\langle \frac{e^2}{4\pi\epsilon_0 \rho_{12}} \right\rangle$$

$$= \frac{e^2}{4\pi\epsilon_0} \cdot \frac{Z^6}{\pi^2 a_0^6} \quad \frac{2Z}{a_0} \cdot \left(\frac{a_0}{2Z}\right)^6 \iint \frac{e^{-(\rho_1+\rho_2)}}{\rho_{12}} d^3\rho_1 d^3\rho_2$$

$$= \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{Z}{32\pi^2 a_0} \underbrace{\iint \frac{e^{-(\rho_1+\rho_2)}}{\rho_{12}} d^3\rho_1 d^3\rho_2}_{20\pi^2}$$

$$= \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{Z}{32\cancel{\pi^2} a_0} \cdot 20\cancel{\pi^2}$$

$$= \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{5Z}{8 a_0} \quad \cdots\cdots\cdots (4)$$

Substituting Eqs. (2), (3) and (4) in Eq. (1) we get

$$\langle H \rangle_Z = \frac{Z^2 e^2}{4\pi\epsilon_0 a_0} - \frac{4 Z e^2}{4\pi\epsilon_0 a_0} + \frac{5 Z e^2}{(4\pi\epsilon_0)\, 8 a_0}$$

$$= \frac{e^2}{(4\pi\epsilon_0) a_0} \left(Z^2 - 4Z + \frac{5Z}{8} \right)$$

$$= \frac{e^2}{4\pi\epsilon_0 a_0} \left(Z^2 - \frac{27 Z}{8} \right)$$

Next, we minimize $\langle H \rangle_Z$ by varying Z.

$$\frac{\partial}{\partial Z} \langle H \rangle_Z = 0$$

$$2Z - \frac{27}{8} = 0$$

$$\therefore \quad Z = \frac{27}{16}.$$

Thus the lowest upper bound for the ground state energy of the helium atom is

$$E_0 \leq \langle H \rangle_{min}$$

$$= \langle H \rangle_{Z=27/16}$$

$$= \frac{e^2}{4\pi\epsilon_0 a_0}\left[\left(\frac{27}{16}\right)^2 - \frac{27}{8}\cdot\frac{27}{16}\right]$$

$$= -\left(\frac{27}{16}\right)^2 \frac{e^2}{4\pi\epsilon_0 a_0}$$

$$= -2\left(\frac{27}{16}\right)^2 \frac{e^2}{4\pi\epsilon_0 2a_0}$$

$$= -5.7\,\frac{e^2}{4\pi\epsilon_0 2a_0}$$

i.e

$$\left(E_0\right)_{\text{variational method}} = -5.7\,\frac{e^2}{4\pi\epsilon_0 2a_0}.$$

Experimental value for the ground state energy of the helium ~~atom is~~ atom is

$$\left(E_0\right)_{expt} = -5.81\,\frac{e^2}{4\pi\epsilon_0 2a_0}.$$

The disagreement is only 2%.

In the variational calculation, the hydrogenic wavefunction gives the best value for the ground state energy of the helium atom when $Z = 27/16$ rather than $Z = 2$. This indicates that each electron screens the nucleus from the other electron. Therefore, the effective nuclear charge is reduced.

Note:

The variational method is in general more accurate for estimation of energy than for the wave function. Suppose we choose a trial ground state $|\psi\rangle$ which differs from the exact ground state $|\psi_0\rangle$ by $|\delta\psi\rangle$, i.e.,

$$|\psi\rangle = |\psi_0\rangle\langle\psi_0|\psi\rangle + |\delta\psi\rangle. \quad \text{------} (1)$$

i.e.,
$$|\psi\rangle = c_0|\psi_0\rangle + |\delta\psi\rangle \quad \text{------} (2)$$

where
$$c_0 = \langle\psi_0|\psi\rangle \quad \text{------} (3)$$

is the component of the trial wave function along the exact ground state $|\psi_0\rangle$. The deviation of $|\psi\rangle$ from $|\psi_0\rangle$ i.e., $|\delta\psi\rangle$, is orthogonal to the exact ground state $|\psi_0\rangle$ as can be seen by taking the scalar product of (1) with $\langle\psi_0|$ and noting that $\langle\psi_0|\psi_0\rangle = 1$.

Now, the variational estimate to the ground state energy is

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

i.e.,

$$E = \frac{\left(c_0^* \langle \psi_0 | + \langle \delta\psi |\right) H \left(c_0 | \psi_0 \rangle + | \delta\psi \rangle\right)}{\left(c_0^* \langle \psi_0 | + \langle \delta\psi |\right)\left(c_0 | \psi_0 \rangle + | \delta\psi \rangle\right)}$$

or,

$$E = \frac{|c_0|^2 \langle \psi_0 | H | \psi_0 \rangle + c_0^* \langle \psi_0 | H | \delta\psi \rangle + c_0 \langle \delta\psi | H | \psi_0 \rangle + o(\delta\psi^2)}{|c_0|^2 \langle \psi_0 | \psi_0 \rangle + c_0^* \langle \psi_0 | \delta\psi \rangle + c_0 \langle \delta\psi | \psi_0 \rangle + o(\delta\psi^2)}$$

$$= \frac{|c_0|^2 E_0 + o(\delta\psi^2)}{|c_0|^2 + o(\delta\psi^2)}$$

$$= E_0 + o(\delta\psi^2)$$

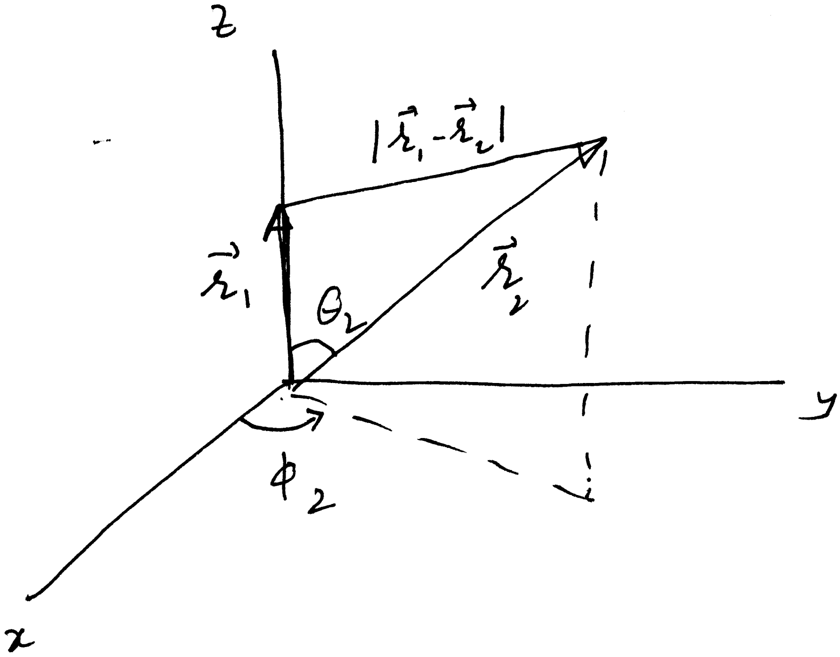
i.e., E differs from E_0 in second order in $\delta\psi$. Hence E is an accurate estimate of E_0.

Appendix

We show that

$$I \equiv \iint \frac{e^{-(r_1+r_2)}}{r_{12}} d^3r_1 d^3r_2 = 20\pi^2 . \quad \cdots (1)$$

We will do the r_2 integral first. For this purpose $\vec{r}_1$ is fixed and we ~~alig~~ align the coordinate system so that $\vec{r}_1$ lies along the z-axis.



Now

$$I = \int e^{-r_1} d^3r_1 \int \frac{e^{-r_2}}{|\vec{r}_1-\vec{r}_2|} d^3r^2$$

$$= \int e^{-r_1} d^3r_1 \, J \quad \cdots\cdots (2)$$

where

$$J = \int \frac{e^{-r_2}}{|\vec{r}_1 - \vec{r}_2|} d^3 r_2$$

$$= \int \frac{e^{-r_2} r_2^2 dr_2 \sin\theta_2 d\theta_2 d\varphi_2}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}}$$

$$= 2\pi \int_0^\infty e^{-r_2} r_2^2 dr_2 \underbrace{\int_0^\pi \frac{\sin\theta_2 d\theta_2}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}}}_{K} \quad \cdots (3)$$

We now do the θ_2 integral.

$$K = \int_0^\pi \frac{\sin\theta_2 d\theta_2}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}}$$

Let

$$Z = r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2$$

$$\therefore \quad dZ = 2 r_1 r_2 \sin\theta_2 d\theta_2 .$$

Hence

$$K = \int_{\theta_2 = 0}^{\theta_2 = \pi} \frac{dZ}{2 r_1 r_2} Z^{-1/2}$$

$$\propto \quad K = \frac{1}{2r_1 r_2} \int_{\theta_2=0}^{\theta_2=\pi} Z^{-1/2}\, dZ$$

$$= \frac{1}{2r_1r_2} \cdot \frac{1}{(-\frac{1}{2}+1)} Z^{1/2} \Big|_{\theta_2=0}^{\theta_2=\pi} \qquad \int x^n\,dx = \frac{x^{n+1}}{n+1}$$

$$= \frac{1}{\cancel{2} r_1 r_2} \cdot \cancel{2}\, Z^{1/2} \Big|_{\theta_2=0}^{\theta_2=\pi}$$

$$= \left(\frac{1}{r_1 r_2}\right) \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}\,\Big|_{\theta_2=0}^{\theta_2=\pi}$$

$$= \frac{1}{r_1r_2}\left[\sqrt{r_1^2+r_2^2+2r_1r_2} - \sqrt{r_1^2+r_2^2-2r_1r_2}\right]$$

$$= \frac{1}{r_1r_2}\left[(r_1+r_2) - |r_1-r_2|\right]$$

$$= \begin{cases} \frac{1}{r_1r_2}\left[r_1+r_2-(r_1-r_2)\right] & \text{if } r_2 < r_1 \\ \frac{1}{r_1r_2}\left[r_1+r_2-(r_2-r_1)\right] & \text{if } r_2 > r_1 \end{cases}$$

or $$K = \begin{cases} \frac{1}{r_1 r_2} 2r_2 & \text{if } r_2 < r_1 \\ \frac{1}{r_1 r_2} 2r_1 & \text{if } r_2 > r_1 \end{cases}$$

~~or~~ $\cancel{K = \left\{ \frac{2}{\rho_1} \text{ if } \rho \right.}$

or $$K = \begin{cases} \frac{2}{r_1} & \text{if } r_2 < r_1 \\ \frac{2}{r_2} & \text{if } r_2 > r_1 . \end{cases} \quad \text{---} (4)$$

Substitute Eq. (4) in Eq. (3). We get

$$J = (2\pi) \int_0^{\infty} e^{-r_2} r_2^2 \, dr_2 \begin{cases} \frac{2}{r_1} & \text{if } r_2 < r_1 \\ \frac{2}{r_2} & \text{if } r_2 > r_1 \end{cases}$$

$$= 4\pi \left[\frac{1}{r_1} \int_0^{r_1} e^{-r_2} r_2^2 \, dr_2 + \int_{r_1}^{\infty} e^{-r_2} r_2 \, dr_2 \right] \quad \text{---} (5)$$

Now

$$\int e^{-x}\,dx = -e^{-x}$$

$$\int x e^{-x}\,dx = -(1+x)e^{-x}$$

$$\int x^2 e^{-x}\,dx = -(2+2x+x^2)e^{-x}$$

Using these standard integrals, Eq. (5) becomes

$$J\cancel{K} = 4\pi\left[\frac{1}{r_1}\left\{-(2+2r_2+r_2^2)e^{-r_2}\right\}_0^{r_1} + \left\{-(1+r_2)e^{-r_2}\right\}_{r_1}^{\infty}\right]$$

$$= 4\pi\left[-\frac{1}{r_1}(2+2r_1+r_1^2)e^{-r_1} + \frac{2}{r_1} + (1+r_1)e^{-r_1}\right]$$

$$= \frac{4\pi}{r_1}\left[(-2-2r_1-\cancel{r_1^2})e^{-r_1} + 2 + (r_1+\cancel{r_1^2})e^{-r_1}\right]$$

$$= \frac{4\pi}{r_1}\left[-2e^{-r_1} - r_1 e^{-r_1} + 2\right]$$

$$= \frac{4\pi}{r_1}\left[-(r_1+2)e^{-r_1} + 2\right] \qquad \cdots\cdots (6)$$

Finally substitute Eq. (6) in Eq. (2). We get

$$I = \int_0^\infty e^{-r_1} r_1^2 \, dr_1 \underbrace{\int d\Omega_1}_{=4\pi} \cdot \frac{4\pi}{r_1}\left[2 - (r_1+2)e^{-r_1}\right]$$

$$= 16\pi^2 \int_0^\infty dr_1 \, e^{-r_1} r_1 \left[2 - (r_1+2)e^{-r_1}\right]$$

$$= 16\pi^2 \left[2 \underbrace{\int_0^\infty e^{-r_1} r_1 \, dr_1}_{=1} - \int_0^\infty e^{-2r_1}(r_1^2 + 2r_1)\, dr_1 \right]$$

$$= 16\pi^2 \left[2 \times 1 - \left\{ \frac{2}{8} + 2 \cdot \frac{1}{4} \right\} \right]$$

$$= 16\pi^2 \left[2 - \left\{ \frac{2}{8} + \frac{1}{2} \right\} \right]$$

$$= 16\pi^2 \left[2 - \frac{3}{4} \right] = 16\pi^2 \times \frac{5}{4} = 20\pi^2$$

Hence

$$\boxed{\iint \frac{e^{-(r_1+r_2)}}{r_{12}} \, d^3r_1 \, d^3r_2 = 20\pi^2.}$$

—— X —— END