Approximation Methods:

The variational principle

Rayleigh-Ritz variational method

Suppose you want to calculate the ground-state energy for a system describe By the Hamiltonian H, but you are unable to solve the (time-independent) Schrodinger equation. Pick any wave function and use

Theory

$$E_{g.s} \leq \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \equiv \langle H \rangle = \langle T \rangle + \langle V \rangle$$

Without proof

To find the ground state energy and wave function using the variation method, Use the following steps.

Step: 1

assume a wave function with a variational constants

$\psi(\mathrm{a,b,c,\cdots}) \longrightarrow$ Eq. I

Step: 2

calculate the following matrix elements

$$1\text{-} \int \left|\psi(\mathrm{a,b,c,\cdots})\right|^2 d\tau$$

$$2\text{-} \int \psi^*(\mathrm{a,b,c,\cdots}) T \psi(\mathrm{a,b,c,\cdots}) d\tau$$

$$3\text{-} \int \psi^*(\mathrm{a,b,c,\cdots}) V \psi(\mathrm{a,b,c,\cdots}) d\tau$$

$$4\text{-} \int \psi^*(\mathrm{a,b,c,\cdots}) H \psi(\mathrm{a,b,c,\cdots}) d\tau = 2 + 3$$

Step: 3

calculate

$$E(a,b,c,\cdots) = \frac{\int \psi^{*}(a,b,c,\cdots) H \psi(a,b,c,\cdots) d\tau}{\int \psi^{*}(a,b,c,\cdots) \psi(a,b,c,\cdots) d\tau} \longrightarrow \text{Eq. II}$$

Step: 4

minimize $E(a,b,c,\cdots)$ with respect to the variable a, b, c , ...

For example if we have only one variable we do the following

$$\frac{dE(a)}{da} = 0 \longrightarrow \text{Eq. III}$$

From the Eq. III determine the value of a, substituting by the value you Obtain in Eq. II to determine the energy and in Eq. I to determine the wave function

Example

Suppose we want to find the ground-state energy for the one-dimensional Harmonic oscillator:

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

Step: 1 we assume a trial wave function

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

Trial wave function

b is called “variational parameter”.

Step: 2

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx = |A|^2 \sqrt{\frac{\pi}{2b}} \Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}$$

$$\langle T \rangle = -\frac{\hbar^2}{2m} |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2}\left(e^{-bx^2}\right) dx = \frac{\hbar^2 b}{2m}$$

$$\langle V \rangle = \frac{1}{2} m\omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2 dx = \frac{m\omega^2}{8b}$$

$$\frac{d^2}{dx^2} e^{-bx^2} = -2b\left(e^{-bx^2} - 2bx^2 e^{-bx^2}\right)$$

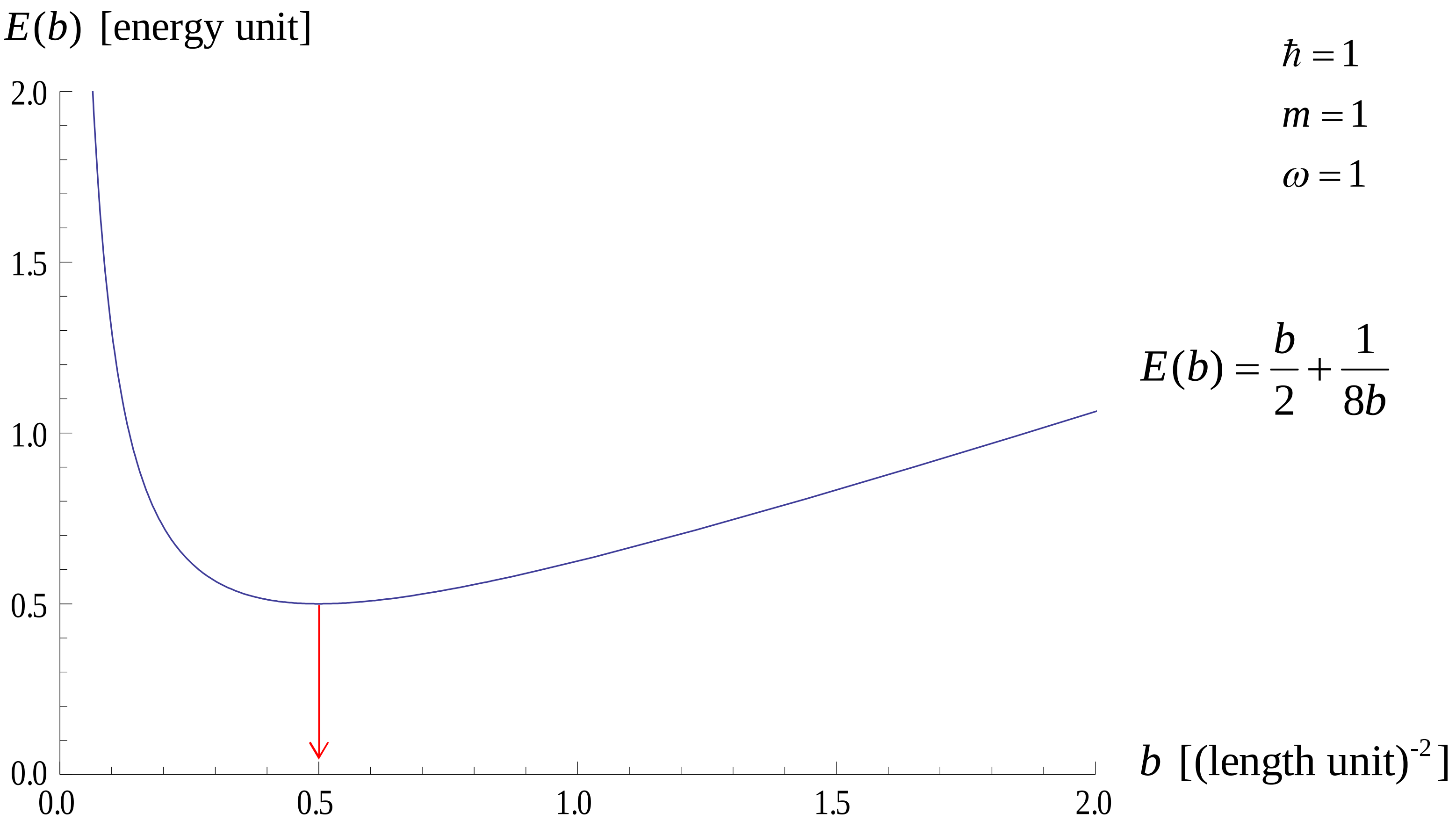
$$\langle T \rangle = -\frac{\hbar^2}{2m}\left(\frac{2b}{\pi}\right)^{1/2} (-2b). \int_{-\infty}^{\infty} \left(e^{-2bx^2} - 2bx^2 e^{-2bx^2}\right) dx$$

$$= \frac{\hbar^2}{2m}\left(\frac{2b}{\pi}\right)^{1/2} (2b).\left[\sqrt{\frac{\pi}{2b}} - (2b)\frac{\sqrt{\pi}}{2(2b)^{3/2}}\right]$$

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

Step: 3

$$E(b) = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$



$\hbar = 1$

$m = 1$

$\omega = 1$

$$E(b) = \frac{b}{2} + \frac{1}{8b}$$

Step: 4

$$\frac{d}{db}E(b)=\frac{\hbar^2}{2m}-\frac{m\omega^2}{8b^2}=0\Rightarrow \boxed{b=\frac{m\omega}{2\hbar}}$$

$$E_{\min}=E_{g.s}=\frac{\hbar^2}{2m}\left(\frac{m\omega}{2\hbar}\right)+\frac{m\omega^2}{8\left(\frac{m\omega}{2\hbar}\right)}=\frac{1}{2}\omega\hbar$$

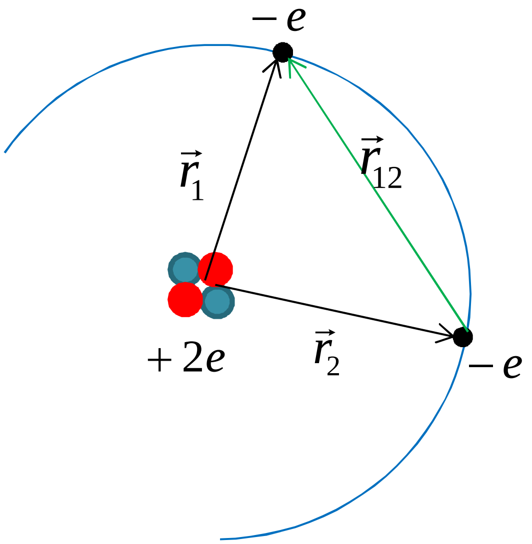
$$\psi_{g.s}(\mathrm{x})=\left(\frac{\mathrm{m}\omega}{\hbar\pi}\right)^{1/4}\exp\left(-\frac{\mathrm{m}\omega}{2\hbar}x^2\right)$$

Compare the above results with that we have obtain before.

Application:

The Ground state of Helium atom

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$



Our problem is to calculate the ground-state Energy E_g (the amount of energy require to strip Off the two electrons)

E_g has been measured very accuratly experimentaly as

$$\boxed{E_g = -78.975\ \text{eV}}$$

This is the number we would like To reproduce theoretically

This problem has no known exact solution !?

The problem comes from the electron-electron interaction.

$$V_{ee} = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\left|\vec{r}_1 - \vec{r}_2\right|}$$

If we neglect this potential the Hamiltonian will be separable

$$H = H_1 + H_2$$

If we apply the method of separation of variable which we learn before
We get

$$\psi_{g.s}^{Helium}(r_1, r_2) = \psi_{g.s}^{HLA}(r_1)\psi_{g.s}^{HLA}(r_1) = \frac{1}{\pi}\left[\frac{Z}{a_0}\right]^3 \exp\left[-\frac{Z}{a_0}(r_1 + r_2)\right]$$

$$E = E_1 + E_2$$

where $\psi(r_1)$ and $\psi(r_2)$ are the Hydrogen wave function

E_1 and E_2 are also Hydrogen energy with $Z = 2$.

From Hydrogen atom results we have $E_n = -13.6\frac{Z^2}{n^2}$

So if we neglect the electron - electron repulsive force the ground state energy of the Helium atom will be given by

$$E = E_{e_1}(Z=2) + E_{e_2}(Z=2) = -13.6\frac{2^2}{1^2} - 13.6\frac{2^2}{1^2} = \boxed{-108.8\ \text{eV}}$$

This value is larger than the experimental value by about

$$\frac{|108.8 - 78.975|}{78.975} \times 100 = 37.8\ \%$$

This results shows that the electron-electron repulsive force should be Taken into account.

Now we will used the variational principle to find a solution for Helium Atom taken into account the electron-electron interaction.

our trial wave function has the form

$$\psi(r_1, r_2) = Ae^{-\alpha(r_1 + r_2)}$$

As you will see in the H.W

$$A = \frac{1}{4\pi} \cdot \frac{(2\alpha)^3}{2}$$

$$\left\langle \nabla_1^2 \right\rangle = \int \psi^*(r_1, r_2) \nabla_1^2 \psi(r_1, r_2) dV_1 dV_2 = -\alpha^2$$

$$\left\langle \nabla_2^2 \right\rangle = \int \psi^*(r_1, r_2) \nabla_2^2 \psi(r_1, r_2) dV_1 dV_2 = -\alpha^2$$

$$\left\langle \frac{1}{r_1} \right\rangle = \alpha$$

$$\left\langle \frac{1}{r_2} \right\rangle = \alpha$$

$$\left\langle \frac{1}{|r_2 - r_1|} \right\rangle = \frac{5}{8}\alpha$$

the second step is to calculate $E(\alpha)$

$$E(\alpha)=\langle H\rangle=-\frac{\hbar^2}{2m}\langle\nabla_1^2\rangle-\frac{\hbar^2}{2m}\langle\nabla_2^2\rangle-\frac{e^2}{4\pi\varepsilon_0}\left(Z\left\langle\frac{1}{r_1}\right\rangle+Z\left\langle\frac{1}{r_2}\right\rangle-\left\langle\frac{1}{|\vec{r}_1-\vec{r}_2|}\right\rangle\right)$$

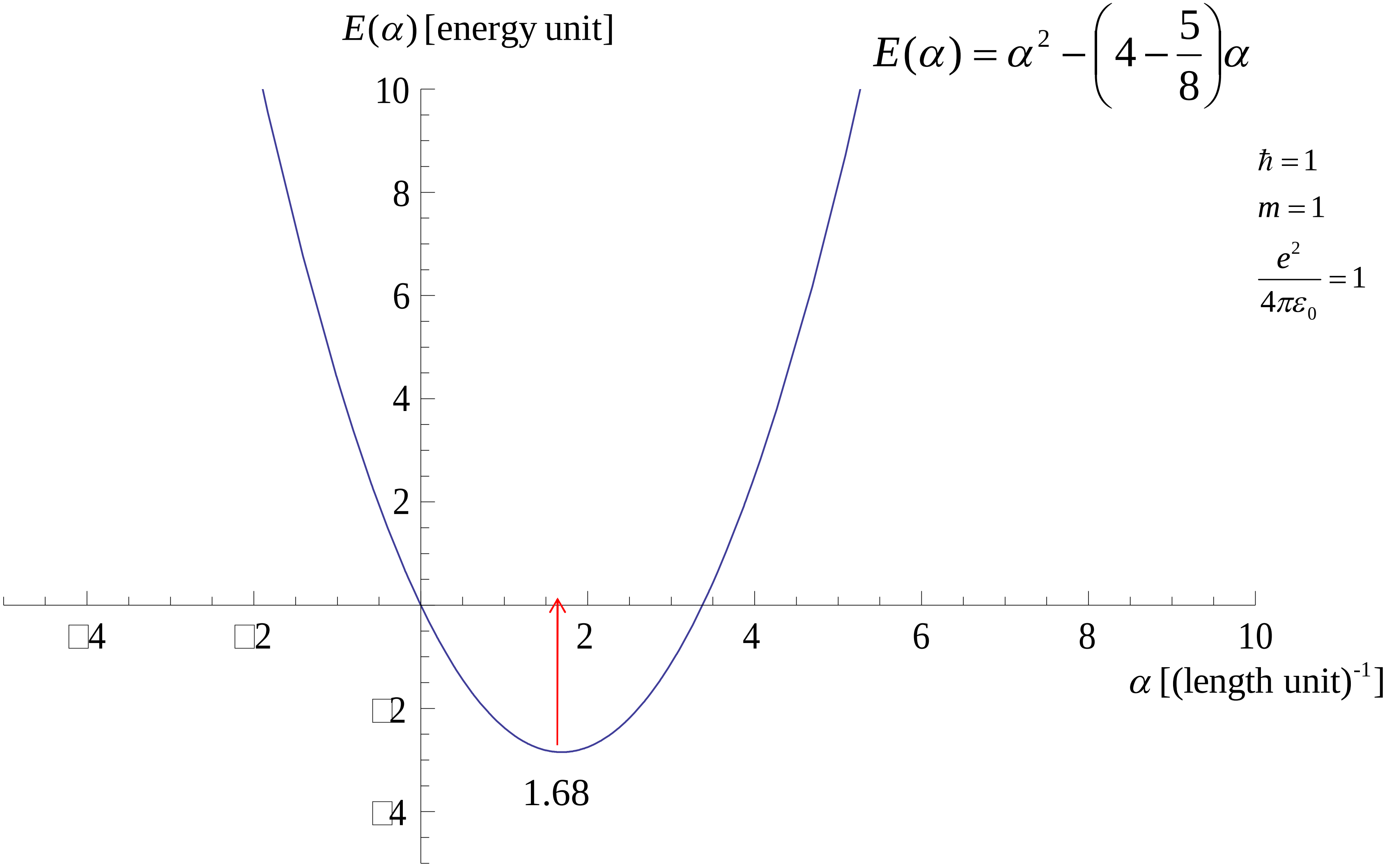
$$E(\alpha)=\frac{\hbar^2}{2m}\alpha^2+\frac{\hbar^2}{2m}\alpha^2-\frac{e^2}{4\pi\varepsilon_0}\left(Z\alpha+Z\alpha-\frac{5}{8}\alpha\right)$$

$$E(\alpha)=2\frac{\hbar^2}{2m}\alpha^2-\frac{e^2}{4\pi\varepsilon_0}\left(2Z-\frac{5}{8}\right)\alpha$$

Here we solve for
the general Z value

$$\frac{d}{d\alpha}E(\alpha)=4\frac{\hbar^2}{2m}\alpha-\frac{e^2}{4\pi\varepsilon_0}\left(2Z-\frac{5}{8}\right)=0$$

The value of α that satisfy the above relation,
we call it $\alpha_{\min}$



$$E(\alpha) = \alpha^2 - \left(4 - \frac{5}{8}\right)\alpha$$

$$\hbar = 1$$

$$m = 1$$

$$\frac{e^2}{4\pi\varepsilon_0} = 1$$

$$2\frac{\hbar^2}{m}\alpha_{\min} = \frac{e^2}{4\pi\varepsilon_0}\left(2Z - \frac{5}{8}\right)$$

$$\alpha_{\min} = \frac{m}{2\hbar^2}\frac{e^2}{4\pi\varepsilon_0}\left(2Z - \frac{5}{8}\right)$$

$$\Rightarrow \boxed{\alpha_{\min} = \frac{1}{2a_0}\left(2Z - \frac{5}{8}\right)}$$

$$a_0 = \frac{\hbar^2}{m}\frac{(4\pi\varepsilon_0)}{e^2} \equiv \text{Bohr radius}$$

$$E_{g.s}(\alpha = \alpha_{\min}) = \frac{\hbar^2}{m}\left[\frac{1}{2a_0}(2Z - \frac{5}{8})\right]^2 - \frac{e^2}{(4\pi\varepsilon_0)}(2Z - \frac{5}{8})\left[\frac{1}{2a_0}(2Z - \frac{5}{8})\right]$$

$$E_{g.s}(\alpha = \alpha_{\min}) = \frac{1}{2a_0}\left(2Z - \frac{5}{8}\right)^2\left[\frac{\hbar^2}{m}\frac{1}{(2a_0)} - \frac{e^2}{(4\pi\varepsilon_0)}\right]$$

$$E_{g.s}(\alpha=\alpha_{\min})=\left(2Z-\frac{5}{8}\right)^2\left[\frac{1}{2}\left(\frac{\hbar^2}{2ma_0^2}\right)-\frac{e^2}{(4\pi\varepsilon_0)}\frac{1}{(2a_0)}\right]$$

$$\boxed{\frac{e^2}{(4\pi\varepsilon_0)}=\frac{\hbar^2}{ma_0}}$$

$$E_{g.s}(\alpha=\alpha_{\min})=\left(2Z-\frac{5}{8}\right)^2\left[\frac{1}{2}(13.6)-13.6\right]=-6.8\left(2Z-\frac{5}{8}\right)^2$$

For $Z=2$

$$\boxed{E_{g.s}=-6.8\left(4-\frac{5}{8}\right)^2=-77.5\ \text{eV}}$$

This value is smaller than the experimental value by about

$$\frac{|78.975-77.5|}{78.975}\times 100\cong 2\ \%$$

$$\psi_{g.s}(r_1, r_2) = \frac{1}{\pi}\left[\frac{27}{16a_0}\right]^3 \exp\left[-\frac{27}{16a_0}(r_1 + r_2)\right]$$

Compare with wave function with

$$\psi_{g.s}^{Helium}(r_1, r_2) = \psi_{g.s}^{HLA}(r_1)\psi_{g.s}^{HLA}(r_1) = \frac{1}{\pi}\left[\frac{Z}{a_0}\right]^3 \exp\left[-\frac{Z}{a_0}(r_1 + r_2)\right]$$

We just replace Z by $\frac{27}{16} = 1.69 \ < 2 \quad !?$

Each electron partially screens the nucleus from the other one, reducing its Charge from 2 down to 1.69 .