

The Variational Method

Introduction:

There are many problems of wave mechanics which can not be conveniently treated either by direct solution of wave equation (e.g. H-atom, S.H.O.) or by using other approximated methods (e.g. perturbation, WKB, ...). One of the most convenient and powerful methods of approximation is the variational method, which is only applicable to the ground state energy level of a system (the state of most interest to chemical and physical process). The variational method works best for the ground state and in some circumstances (to be described below) for some other low lying states.

If we know the Hamiltonian, H , of a system, one may construct wave function ϕ belonging to the same space; then the variational integral is defined as:

$$I(\phi) = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

Theorem: if one chooses a trial wavefunction, ϕ , then the Expectation Value for the energy is greater than or equal to the exact ground state energy, E_o , i.e. $\langle \phi | H | \phi \rangle \geq E_o$ if $\langle \phi | \phi \rangle = 1$

Proof: (we will use an orthonormal wavefunction ψ)

Assume that we know the exact solutions for $|\psi_n\rangle$, i.e.

$$H |\psi_n\rangle = E_n |\psi_n\rangle, \quad E_0 < E_1 < E_2 < \dots$$

It was known that the set of eigenfunctions, $|\psi_n\rangle$ of the Hamiltonian form a complete set of orthonormal functions. That is, any arbitrary function, $|\phi\rangle$, with the same boundary conditions can be expanded as a linear combination (an infinite number of terms) of eigenfunctions $|\psi_n\rangle$.

$$|\phi\rangle = \sum_{n=0}^{\infty} a_n |\psi_n\rangle \Rightarrow H |\phi\rangle = \sum_{n=0}^{\infty} a_n H |\psi_n\rangle = \sum_{n=0}^{\infty} a_n E_n |\psi_n\rangle$$

This can be substituted into the expression for $\langle H \rangle$ to get:

$$\langle \phi | H | \phi \rangle = \sum_{n=0}^{\infty} a_n \langle \phi | H | \psi_n \rangle = \sum_m \sum_n a_m^* a_n E_n \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{mn}} = \sum_n |a_n|^2 E_n \delta_{nn}$$

Let $E_n = E_o + (E_n - E_o)$, then $\langle \phi | H | \phi \rangle = E_o \sum_{n=0}^{\infty} |a_n|^2 + \sum_{n=0}^{\infty} |a_n|^2 (E_n - E_o)$.

But $\sum_{n=0}^{\infty} |a_n|^2 = 1$ for the normalized function $|\psi_n\rangle$, then

$$\langle \phi | H | \phi \rangle = E_o + \underbrace{\sum_n |a_n|^2 (E_n - E_o)}_{\substack{\geq 0 \\ > 0 \\ \text{positive quantities}}} \Rightarrow \langle \phi | H | \phi \rangle \geq E_o$$

Equal sign will hold only for the exact guessing of the trial function, i.e., you can celebrate getting the exact ground state energy.

Mathematically, the value E_0 is known as the lower limit to the sequence of the value $I(\phi)$, which obtained by assuming reasonable values for ϕ . Usually the variational integral is depend upon a parameter or a number of parameters, λ_i , which could be determined by the condition $\frac{dI}{d\lambda_i} = 0$.

The key in this approximation is a good guess of a trial wave function. You can make a good guess of a trial wave function by considering:

- 1- Is the parity conserved? Is the wave function even or odd?
- 2- How does the wave function approach zero? Model the asymptotes correctly.
- 3- Pick something you can integrate. Numerical integration is appropriate if analytic integration is not. The integral must converge in any instance.

Example: Use a trial function of the form $\varphi_{1s}(r) = Ne^{-ar}$ to calculate the ground state energy of the hydrogen atom. [Note that: $\hat{H} = -\frac{1}{2}\nabla_r^2 - \frac{1}{r}$, and $\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}$].

Solution: First calculate the normalization constant N (use $d\tau = r^2 \sin\theta d\theta d\phi dr$):

$$\langle \varphi_{1s} | \varphi_{1s} \rangle = \int |\varphi_{1s}(r)|^2 d\tau = N^2 \underbrace{\int_0^\infty r^2 e^{-2ar} dr}_{\frac{1}{4a^2}} \underbrace{\int_0^\pi \sin\theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

Using the standard integral: $\int_0^\infty r^2 e^{-br} dr = \frac{2}{b^3}$, we can have

$$4\pi |N|^2 \frac{1}{4a^3} = 1 \quad \Rightarrow \quad N = \frac{a^{3/2}}{\sqrt{\pi}}$$

Second calculate $I = \langle \varphi_{1s} | \hat{H} | \varphi_{1s} \rangle$ as follows:

$$\begin{aligned} \hat{H} |\varphi_{1s}\rangle &= -\frac{1}{2} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} |\varphi_{1s}\rangle \right] - \frac{|\varphi_{1s}\rangle}{r} = -\frac{a^{3/2}}{2\sqrt{\pi}} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 (-ae^{-ar}) \right] - \frac{\varphi_{1s}}{r} \\ &= \left[\frac{a}{r^2} (2r - r^2 a) - \frac{1}{r} \right] |\varphi_{1s}\rangle = \left[\frac{a-1}{r} - \frac{a^2}{2} \right] |\varphi_{1s}\rangle \end{aligned}$$

Then

$$\begin{aligned} I(a) &= \langle \varphi_{1s} | \hat{H} | \varphi_{1s} \rangle = 4\pi \int_0^\infty \varphi_{1s}^* \hat{H} \varphi_{1s} r^2 dr = 4a^3 \int_0^\infty \left[\frac{a-1}{r} - \frac{a^2}{2} \right] e^{-2ar} r^2 dr \\ &= 4a^3 \left[(a-1) \frac{1!}{(2a)^2} - \frac{a^2}{2} \frac{2!}{(2a)^3} \right] = \frac{a^2}{2} - a \end{aligned}$$

$$\text{Setting } \frac{dI(a)}{da} = 0 \quad \Rightarrow \quad \frac{\partial I}{\partial a} = \frac{\partial}{\partial a} \left[\frac{a^2}{2} - a \right] = a - 1 = 0 \quad \Rightarrow \quad a = 1$$

And substituting this result back into $W(a)$ gives

$$E_1 = I_{\min} = \frac{a^2}{2} - a = \frac{1}{2} - 1 = -\frac{1}{2} \text{ a.u.}$$

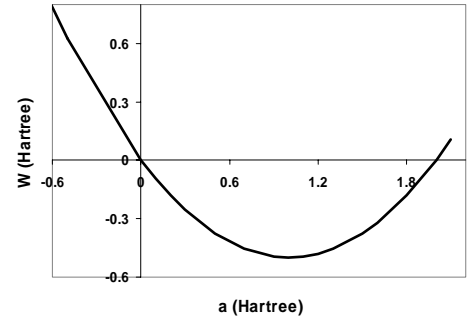
This happens to be the exact ground state energy of a hydrogen atom.

H.W1. Plot W versus a . to check the optimum value at $a=1$.

H.W2. Calculate $\langle T \rangle$ and $\langle V \rangle$ and find the relation between them.

H.W3. Calculate $\langle T \rangle$ and $\langle V \rangle$ and find the relation between them.

H.W4. Use a trial function of the form $\phi_{1s}(r) = Ne^{-ar^2}$ to calculate the ground state energy of the hydrogen atom.



Variational Method Treatment of Helium

Recall that we proved earlier that, if one has an approximate “trial” wavefunction, ϕ , then the expectation value for the energy must be either higher than or equal to the true ground state energy. It cannot be lower!!

$$\langle E \rangle = E_{\text{trial}} = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$$

This provides us with a very simple “recipe” for improving the energy. The lower the better!! When we calculated the He atom energy using the “Independent Particle Method”, we obtained an energy (-4.0 a.u.) which was lower than experiment (-2.9037 au). Isn’t this a violation of the Variational Theorem?? No, because we did not use the complete Hamiltonian in our calculation.

Example: Calculate the ground state energy for the Helium atom using the following trial function:

$$\psi_{1s}(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2)$$

where

$$\psi_{1s}(r_i) = N e^{-ar_i}, \quad N = \sqrt{\frac{a^3}{\pi}}, \quad i = 1, 2$$

a is a variational parameter and $\int |\psi_{1s}(r_i)|^2 dr_i = 1$

Answer:

Start with the Hamiltonian:

$$\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \tag{A.1}$$

And put it in a simple form:

$$\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{a}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{a}{r_2} + \frac{(a-2)}{r_1} + \frac{(a-2)}{r_2} + \frac{1}{r_{12}} \tag{A.2}$$

Use the Hydrogen atom Hamiltonian in a.u.:

$$\left(-\frac{1}{2}\nabla_i^2 - \frac{a}{r_i}\right)\psi(r_i) = -\frac{a^2}{2}\psi(r_i) \quad (\text{A.3})$$

One finds:

$$I(a) = \iint \psi_{1s}^*(r_1)\psi_{1s}^*(r_2) \left[-\frac{a^2}{2} - \frac{a^2}{2} + \frac{(a-2)}{r_1} + \frac{(a-2)}{r_2} + \frac{1}{r_{12}} \right] \psi_{1s}(r_1)\psi_{1s}(r_2) d\tau_1 d\tau_2$$

Taking into account the following integrations:

$$\int \frac{e^{-ar \pm i q \cdot r}}{r} d\mathbf{r} = \frac{4\pi}{a^2 + q^2};$$

$$\underbrace{\int |\psi_{1s}(r_2)|^2 d\tau_2}_{=1} \int \frac{e^{-2ar_1}}{r_1} d\tau_1 = \underbrace{\int |\psi_{1s}(r_1)|^2 d\tau_1}_{=1} \int \frac{e^{-2ar_2}}{r_2} d\tau_2 = \int \frac{e^{-2ar}}{r} d\tau = \frac{4\pi}{(2a)^2};$$

and

$$J(a) = \iint |\psi_{1s}(r_1)|^2 \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} |\psi_{1s}(r_2)|^2 d\tau_1 d\tau_2 = \frac{5a}{8}$$

one finds:

$$I(a) = -a^2 + \frac{2a^3(a-2)}{\pi} \int \frac{e^{-2ar}}{r} d\tau + J(a) = -a^2 + 2a(a-2) + \frac{5a}{8} = a^2 - \frac{27}{8}a$$

To find the optimum value for a , we use the relation $\frac{\partial W(a)}{\partial a} = 0$ to have $a = \frac{27}{16} \equiv Z - \frac{5}{16}$ and the

lowest energy is:

$$E_1 = I_{\min} = a^2 - \frac{27}{8}a = \left(\frac{27}{16}\right)^2 - \left(\frac{27}{8}\right)\left(\frac{27}{16}\right) = -\left(\frac{27}{16}\right)^2 = -2.8477 \text{ a.u.} = -77.45 \text{ eV}$$

The lower value for the “effective” atomic number ($a = Z' = \frac{27}{16} = 1.69$ vs. $Z=2$) reflects

“screening” due to the mutual repulsion of the electrons.

$E_{\text{trial}} = -2.8477$ a.u. (1.9% higher than experiment) $E_{\text{exp}} = -2.9037$ a.u.

The following table shows the theoretical and experimental values of ionization energy of the ground state energy for He-like atoms.

Z	Atom	Theo (eV)	Exp (eV)	%error
2	He	23.2	24.5	5.31
3	Li ⁺	74.1	75.6	1.98
4	Be ⁺⁺	152.2	153.6	0.91
6	C ⁴⁺	390	393	0.76
8	O ⁶⁺	737	738	0.14

As we can see, the error decreases with increasing Z. One can improve (i.e. lower the energy) by employing improved wavefunctions with additional variational parameters.

A Two Parameters Wavefunction

Let the two electrons have different values of Z_{eff} :

$$\phi = A \left[e^{-Z' r_1} e^{-Z'' r_2} + e^{-Z'' r_1} e^{-Z' r_2} \right]$$

(we must keep treatment of the radial part of the two electrons symmetrical, since the spin part is antisymmetrical)

If one computes E_{trial} as a function of Z' and Z'' and then finds the values of the two parameters that minimize the energy, one finds:

$$Z' = 1.19, \quad Z'' = 2.18, \quad E_{\text{trial}} = -2.876 \text{ au (1.0\% higher than experiment)}$$

The very different values of Z' and Z'' reflects **correlation** between the positions of the two electrons; i.e. if one electron is close to the nucleus, the other prefers to be far away.

Another Wavefunction Incorporating Electron Correlation

$$\phi = A \left[e^{-Z'(r_1+r_2)} (1 + b \cdot r_{12}) \right]$$

When E_{trial} is evaluated as a function of Z' and b , and the values of the two parameters are varied to minimize the energy, the results are:

$$Z' = 1.19, \quad b = 0.364 \text{ and } E_{\text{trial}} = -2.892 \text{ au (0.4\% higher than experiment).}$$

The second term, $(1 + b \cdot r_{12})$, accounts for electron correlation. It increases the probability (higher ϕ^2) of finding the two electrons further apart (higher r_{12}).

A Summary of Results

$$E_{\text{expt.}} = -2.9037 \text{ au}$$

Wavefunction	Energy	% Error
$A e^{-Z'(r_1+r_2)}$	-2.848	+1.9%
$A \left[e^{-Z' r_1} e^{-Z'' r_2} + e^{-Z'' r_1} e^{-Z' r_2} \right]$	-2.876	+1.0%
$A \left[e^{-Z'(r_1+r_2)} (1 + b \cdot r_{12}) \right]$	-2.892	+0.4%
$A \left[\left(e^{-Z' r_1} e^{-Z'' r_2} + e^{-Z'' r_1} e^{-Z' r_2} \right) \cdot (1 + b \cdot r_{12}) \right]$	-2.9014	+0.08%
$\phi = A \left[e^{-Z'(r_1+r_2)} (1 + \mathbf{g}(r_1, r_2, r_{12})) \right]$ (39 parameters)	-2.9037	~0%

Notes:

- 1- The computed energy is always higher than experiment.
- 2- One can compute an "approximate" energy to whatever degree of accuracy desired.
- 3- The choice of $a = Z$ reduces to the first-order perturbation theory in the previous section, which is therefore equivalent to a "non-optimum" variation calculation.
- 4- The physical meaning of a is that it represents the "effective charge" of the nucleus. The optimum a is less than Z (the true nuclear charge) because the electron experiences the screening effect of the other electron.

Example Ground state of Helium atom (two electrons 1,2)

$$\hat{H} = \frac{1}{2m}(\hat{p}_1^2 + \hat{p}_2^2) - 2e^2 \left(\frac{1}{\hat{r}_1} + \frac{1}{\hat{r}_2} \right) + \frac{e^2}{\hat{r}_{12}}$$

Without the last term $\frac{e^2}{r_{12}}$, the ground state wavefunction is just the product of wavefunctions $u_{100}(r_1)u_{100}(r_2)$

$$\psi(r_1, r_2) = \frac{Z^3}{\pi a_0^3} e^{-\left(\frac{Z}{a_0}\right)(r_1+r_2)} \quad \text{with } Z = 2 \quad \text{using } u_{100}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$$

We will take the above expression as a trial wavefunction and take Z as an adjustable parameter to minimize $\langle \psi | \hat{H} | \psi \rangle$.

First note that

$$\left\langle \psi \left| \frac{1}{2m}(\hat{p}_1^2 + \hat{p}_2^2) - 2e^2 \left(\frac{1}{\hat{r}_1} + \frac{1}{\hat{r}_2} \right) \right| \psi \right\rangle = 2 \left\langle u_{100} \left| \frac{\hat{p}^2}{2m} \right| u_{100} \right\rangle - 4 \left\langle u_{100} \left| \frac{e^2}{\hat{r}} \right| u_{100} \right\rangle$$

From the Virial theorem for the stationary states, we know

$$2\langle T \rangle = \langle \mathbf{r} \cdot \nabla V \rangle = \left\langle \frac{Ze^2}{r} \right\rangle$$

for hydrogenic atom $V = -\frac{Ze^2}{r}$. Therefore, $E = \langle T \rangle - \left\langle \frac{Ze^2}{r} \right\rangle = -\langle T \rangle$

$$\left\langle u_{100} \left| \frac{\hat{p}^2}{2m} \right| u_{100} \right\rangle = \langle T \rangle = -E_1 = \frac{Z^2 e^2}{2a_0}$$

$$\left\langle \frac{Ze^2}{r} \right\rangle = 2\langle T \rangle = \frac{Z^2 e^2}{a_0} \Rightarrow \left\langle \frac{e^2}{r} \right\rangle = \frac{Ze^2}{a_0}$$

Hence, we have

$$\left\langle \psi \left| \frac{1}{2m}(\hat{p}_1^2 + \hat{p}_2^2) - 2e^2 \left(\frac{1}{\hat{r}_1} + \frac{1}{\hat{r}_2} \right) \right| \psi \right\rangle = \frac{Z^2 e^2}{a_0} - \frac{4Ze^2}{a_0}$$

Now for the last term

$$\left\langle \psi \left| \frac{e^2}{\hat{r}_{12}} \right| \psi \right\rangle = \left(\frac{eZ^3}{\pi a_0^3} \right)^2 \int \int \frac{e^{-\frac{2Z}{a_0}(r_1+r_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

This can be evaluated by using the addition theorem for spherical harmonics.

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{r_>} \sum_{l=0}^{\infty} \left(\frac{r_<}{r_>} \right)^l P_l(\cos \theta), \quad \theta : \text{angle between } \mathbf{r}_1 \text{ and } \mathbf{r}_2 \\ &= \frac{1}{r_>} \sum_{l=0}^{\infty} \left(\frac{r_<}{r_>} \right)^l \left(\frac{4\pi}{2l+1} \right) \sum_{m=-l}^l Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) \end{aligned}$$

Since

$$\int Y_{lm}(\theta, \phi) d\Omega = \sqrt{4\pi} \int Y_{00}^*(\theta, \phi) Y_{lm}(\theta, \phi) d\Omega = \sqrt{4\pi} \delta_{l0} \delta_{m0}$$

Therefore, integration over $d\Omega_1$ and $d\Omega_2$ leaves only $l = m = 0$ term nonvanishing. Thus, we get

$$\begin{aligned}
 \left\langle \frac{e^2}{r_{12}} \right\rangle &= \left(\frac{4\pi e Z^3}{\pi a_0^3} \right)^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{1}{r_{>}} e^{-\frac{2Z}{a_0}(r_1+r_2)} \\
 &= \left(\frac{4eZ^3}{a_0^3} \right)^2 \int_0^\infty r_1^2 dr_1 \left[\int_0^{r_1} r_2^2 dr_2 \frac{e^{-\frac{2Z}{a_0}(r_1+r_2)}}{r_1} + \int_{r_1}^\infty r_2^2 dr_2 \frac{e^{-\frac{2Z}{a_0}(r_1+r_2)}}{r_2} \right] \\
 &= \left(\frac{4eZ^3}{a_0^3} \right)^2 \int_0^\infty r_1^2 dr_1 \left[\frac{e^{-\frac{2Z}{a_0}r_1}}{r_1} \left\{ -e^{-\frac{2Z}{a_0}r_1} \left(\frac{a_0}{2Z} r_1^2 + 2 \frac{a_0^2}{4Z^2} r_1 + 2 \frac{a_0^3}{8Z^3} \right) + 2 \frac{a_0^3}{8Z^3} \right\} \right. \\
 &\quad \left. + e^{-\frac{2Z}{a_0}r_1} e^{-\frac{2Z}{a_0}r_1} \left(\frac{a_0}{2Z} r_1 + \frac{a_0^2}{4Z^2} \right) \right] \\
 &= \left(\frac{4eZ^3}{a_0^3} \right)^2 \left[\int_0^\infty dr_1 e^{-\frac{4Z}{a_0}r_1} \left(-\frac{a_0^2}{4Z^2} r_1^2 - \frac{a_0^3}{4Z^3} r_1 \right) + \int_0^\infty r_1 dr_1 e^{-\frac{2Z}{a_0}r_1} \frac{a_0^3}{4Z^3} \right] \\
 &= \left(\frac{4eZ^3}{a_0^3} \right)^2 \left[-2 \frac{a_0^2}{4Z^2} \left(\frac{a_0}{4Z} \right)^3 - \frac{a_0^3}{4Z^3} \left(\frac{a_0}{4Z} \right)^2 + \frac{a_0^3}{4Z^3} \left(\frac{a_0}{2Z} \right)^2 \right] \\
 &= \left(\frac{4eZ^3}{a_0^3} \right)^2 \left(\frac{a_0}{Z} \right)^5 \left[-\frac{1}{128} - \frac{1}{64} + \frac{1}{16} \right] = \frac{5}{8} \frac{Ze^2}{a_0}
 \end{aligned}$$

using

$$\int x^2 e^{-ax} dx = -e^{-ax} \left(\frac{x^2}{a} + \frac{2x}{a^2} + \frac{2}{a^3} \right) \quad \text{and} \quad \int x e^{-ax} dx = -e^{-ax} \left(\frac{x}{a} + \frac{1}{a^2} \right)$$

Hence, the total energy

$$\langle \hat{H} \rangle = \frac{Z^2 e^2}{a_0} - \frac{4Ze^2}{a_0} + \frac{5}{8} \frac{Ze^2}{a_0}$$

This is minimum when $\frac{d\langle \hat{H} \rangle}{dZ} = 0$

$$\frac{e^2}{a_0} \left(2Z - 4 + \frac{5}{8} \right) = 0 \quad \Rightarrow \quad Z = \frac{27}{16}$$

Therefore, the upperbound for the groundstate energy is

$$\frac{e^2}{a_0} \left[\left(\frac{27}{16} \right)^2 - \frac{27}{8} \frac{27}{16} \right] = - \left(\frac{27}{16} \right)^2 \frac{e^2}{a_0} \cong -2.85 \frac{e^2}{a_0}$$

This is the summation of the first and second ionization energy. The experimentally measured energy required for the double ionization from He atom is $-2.904 \frac{e^2}{a_0}$. The difference is only 1.9%.

Note

- $Z = \frac{27}{16} \cong 1.69 < 2$: screening between two electrons
- If we used perturbation theory by taking $\hat{H}_1 = \frac{e^2}{r_{12}}$, then the first order correction in energy is given by

$$\Delta E^{(1)} = \langle \psi_0 | \hat{H}_1 | \psi_0 \rangle = \frac{5}{8} \left[\frac{Ze^2}{a_0} \right]_{Z=2} = \frac{5}{4} \frac{e^2}{a_0}$$

Then,

$$E = E_0 + \Delta E^{(1)} = -2 \frac{2^2 e^2}{2a_0} + \frac{5 e^2}{4 a_0} = \frac{e^2}{a_0} \left(-4 + \frac{5}{4} \right) = -\frac{11 e^2}{4 a_0} = -2.75 \frac{e^2}{a_0}$$

In general, the first-order perturbation calculation is equivalent to a nonoptimal variational calculation because

$$E = E_0 + \langle n | \hat{H}_1 | n \rangle = \langle n | \hat{H}_0 | n \rangle + \langle n | \hat{H}_1 | n \rangle = \langle n | \hat{H}_0 + \hat{H}_1 | n \rangle = \langle n | \hat{H} | n \rangle$$

- The above calculation valid only for the spin singlet state of He atom. (Pauli exclusion principle)

Two identical particle system

Classical picture: Two particles are distinguishable.

Quantum picture: Two particles are indistinguishable.

$\psi(1, 2) = \psi(2, 1)$ – Boson

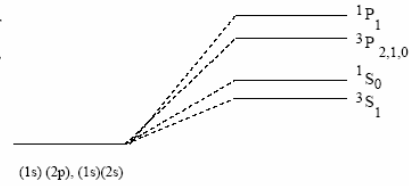
$\psi(1, 2) = -\psi(2, 1)$ – Fermion

$$\begin{aligned} \psi(1, 2) &= \frac{Z^3}{\pi a_0^3} e^{-\left(\frac{Z}{a_0}\right)(r_1+r_2)} \times \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ &= \text{orbital part (symmetric)} \times \text{spin part (antisymmetric)} \end{aligned}$$

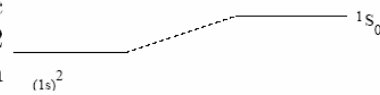
Ignoring electron-electron interaction, all 1s2s and 1s2p states have the same energy. The perturbation ($e^2/4\pi\epsilon_0r_{12}$) lifts that degeneracy, and we can treat it with degenerate perturbation theory. Rather than evaluating the integral in the 4x4 matrix exactly, we can use a physical argument: ($e^2/4\pi\epsilon_0r_{12}$) is not an external potential, and so applies no net torque or force on the electrons. The perturbation cannot change the angular momentum, so it cannot mix states with different l or m . The theta integral will be $\delta_{l'l'}$, and the phi integral $\delta_{mm'}$, total angular momentum remains a good quantum number: $L=0(1s2s)$ or $L=1(1s2p)$. Since the 2s state has finite probability of being at the nucleus, and the 2p has zero probability of being there, the 2s state is less well *screened* from the nuclear charge by the 1s and will have lower energy.

For a given spatial excited state the possible normalised spin wavefunction combinations, consistent with the anti-symmetry requirement are a spin triplet and a spin singlet.

$$\begin{aligned} \Phi_3 &= (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\uparrow\uparrow)/\sqrt{2} \\ &\quad (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\downarrow\downarrow)/\sqrt{2} \\ &\quad (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\uparrow\downarrow + \downarrow\uparrow)/2 \\ \Phi_1 &= (\phi_{nlm,n'l'm'} + \phi_{n'l'm',nlm})(\uparrow\downarrow - \downarrow\uparrow)/2 \end{aligned}$$



Where $|\phi_{nlm,n'l'm'}\rangle$ represents electron 1 in a hydrogenic state with quantum numbers n, l and m and electron 2 with $n', l',$ and m' . The subscripts on the Φ label spin multiplicity $(2S+1)$



Again whole effect of the potential is contained in the spatial part, the spin integral will be $\delta_{\sigma\sigma'}$. so off-diagonal matrix elements are all zero. We need to evaluate

$$J_{nl} = \langle \phi_{nlm,n'l'm'} | (e^2/4\pi\epsilon_0r_{12}) | \phi_{nlm,n'l'm'} \rangle - \text{the direct integral.}$$

$$K_{nl} = \langle \phi_{nlm,n'l'm'} | (e^2/4\pi\epsilon_0r_{12}) | \phi_{n'l'm',nlm} \rangle - \text{the exchange integral.}$$

with which perturbation theory gives an energy shift in the $1s^12s^1$ state of:

$$\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} (\langle \phi_{100,200} | 1/r_{12} | \phi_{100,200} \rangle + \langle \phi_{200,100} | 1/r_{12} | \phi_{200,100} \rangle \pm \langle \phi_{100,200} | 1/r_{12} | \phi_{200,100} \rangle \pm \langle \phi_{200,100} | 1/r_{12} | \phi_{100,200} \rangle)$$

where the + applies to the singlet state and the - to the triplet. The direct integral, electron-electron repulsion, increases the energy, but the exchange integral can either increase or decrease energy.

Thus the energy levels are split by different direct interactions into $L=0$ and $L=1$ and again through exchange interaction into singlet and triplet. The final degeneracies of states with one electron excited to $n=2$ are 3,1,9 and 3. The spectroscopic notation in the figure gives the quantum numbers as: $(nl)(n'l')^{2S+1}L_J$

Again, the most useful quantum number labels are the total spin and angular momentum: we could write the perturbation energy as $\Delta E = J_{nl} - (2S - 1)K_{nl}$, even though the perturbing potential does not act on the spin. The 'exchange force' selects preferred spin state via the requirement of overall antisymmetry.

using the expansion

$$\frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_2^l}{r_1^{l+1}} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2)$$

r_2 and r_1 are, respectively, the smaller and larger values of r_1 and r_2 . i.e. if $r_1 < r_2$, then $r_2 = r_1$ and $r_1 = r_2$.
for $l=0, m=0$

$$\begin{aligned} E^{(1)} &= 16Z^6 \int_0^{\infty} dr_1 r_1^2 e^{-2Zr_1} \int_0^{\infty} dr_2 r_2^2 \frac{e^{-2Zr_2}}{r_1} \\ &= 16Z^6 \int_0^{\infty} dr_1 r_1 e^{-2Zr_1} \int_0^{r_1} dr_2 r_2^2 e^{-2Zr_2} \\ &\quad + 16Z^6 \int_0^{\infty} dr_1 r_1^2 e^{-2Zr_1} \int_{r_1}^{\infty} dr_2 r_2 e^{-2Zr_2} \\ &= -4Z^3 \int_0^{\infty} dr_1 r_1 e^{-2Zr_1} [e^{-2Zr_1} (2Zr_1^2 + 2Zr_1 + 1) - 1] \\ &\quad + 4Z^4 \int_0^{\infty} dr_1 r_1^2 e^{-2Zr_1} [e^{-2Zr_1} (2Zr_1 + 1)] \\ &= -4Z^6 \int_0^{\infty} dr_1 e^{-4Zr_1} \left[\frac{r_1^2}{Z^2} + \frac{r_1}{Z} \right] + 4Z^3 \int_0^{\infty} dr_1 r_1 e^{-2Zr_1} \\ &= \frac{5}{8} Z \end{aligned}$$

$$R = \langle \psi_{1s}^{(0)} | \frac{1}{r_{12}} | \psi_{1s}^{(0)} \rangle = \left(\frac{Z^3}{\pi} \right)^2 \int d\bar{r}_1 d\bar{r}_2 \frac{e^{-2Z(r_1+r_2)}}{|\bar{r}_1 - \bar{r}_2|}$$

using

$$\frac{1}{|\bar{r}_1 - \bar{r}_2|} = \frac{4\pi}{(2\pi)^3} \int \frac{d\bar{k}}{k^2} e^{i\bar{k} \cdot (\bar{r}_1 - \bar{r}_2)}$$

$$\therefore R = \frac{Z^6}{\pi^2} \cdot \frac{4\pi}{(2\pi)^3} \int \frac{d\bar{k}}{k^2} \int d\bar{r}_1 e^{i\bar{k} \cdot \bar{r}_1 - 2Zr_1} \int d\bar{r}_2 e^{-i\bar{k} \cdot \bar{r}_2 - 2Zr_2}$$

using the standard integral $A = \int e^{\pm i\bar{k} \cdot \bar{r} - br} d\bar{r} = \frac{8\pi b}{(q^2 + b^2)^2}$

$$\therefore R = \frac{Z^6}{\pi^2} \cdot \frac{4\pi}{(2\pi)^3} \int \frac{(16\pi Z)^2}{(k^2 + 4Z^2)^4} \cdot \frac{d\bar{k}}{k^2}$$

$$= \frac{Z^8 \times 8 \times 16}{\pi^2} \int \frac{d\bar{k}}{k^2 (k^2 + 4Z^2)^4} \quad d\bar{k} = 4\pi k^2 dk$$

$$B = 4\pi \int_0^\infty \frac{dk}{(k^2 + 4Z^2)^4} = 4\pi \int_0^\infty \frac{2Z dx}{(x^2 + 1)^4 (4Z^2)^4} \quad x = \frac{k}{2Z}$$

$$= \frac{8\pi}{16 \times 16 Z^7} \int_0^\infty \frac{dx}{(1+x^2)^4}$$

$$R = \frac{5}{8} Z$$

$$\int_0^\infty \frac{dx}{(1+x^2)^4} = \frac{5!!}{2(6!!)} \pi = \frac{1 \times 3 \times 5}{2(2 \times 4 \times 6)} \pi = \frac{5\pi}{32}$$

using $\psi(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$

For the integral

$$I = \int \psi^2(\vec{r}_1, \vec{r}_2) \frac{1}{r_{12}} d\vec{r}_1 d\vec{r}_2,$$

we can use the elliptical coordinates

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}, \quad \text{and}$$

$$d\vec{r}_1 d\vec{r}_2 = \pi^2 (s^2 - t^2) u ds dt du$$

$$-u \leq t \leq u, \quad 0 \leq u \leq s \leq \infty$$

$$\therefore I = \pi^2 \left(\frac{Z^3}{\pi} \right)^2 \int_0^\infty ds \int_0^s du \int_{-u}^u dt e^{-2Zs} \frac{s^2 - t^2}{u} \cdot u$$

$$= \frac{5}{8} Z$$

Example: consider the ground state of the hydrogen atom. Although we know that we can solve this problem exactly, let's assume that we cannot and use the variational method. We will compare our variational result to the exact result. Because $l=0$ in the ground state, the Hamiltonian operator is:

$$\hat{H} = -\frac{1}{2}\nabla_r^2 - \frac{1}{r}, \quad \nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}. \quad (1)$$

Even if we did not know the exact solution, we would expect that the wave function decays to zero with increasing r . Consequently, as a trial function, we will try a Gaussian of the form $\phi(r) = Ne^{-\alpha r^2}$ where α is a variational parameter. By a straight forward calculation we can show.

$$4\pi \int_0^{\infty} \phi^*(r)\hat{H}\phi(r)r^2 dr = \frac{3\hbar^2\pi^{3/2}}{4\sqrt{2}m_e\alpha^{1/2}} - \frac{e^2}{4\varepsilon_0\alpha}$$

and that

$$4\pi \int_0^{\infty} \phi^*(r)\phi(r)r^2 dr = \left(\frac{\pi}{2\alpha}\right)^{3/2}$$

Therefore from equation $E_{trial} = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$:

$$E(\alpha) = \frac{3\hbar^2\alpha}{2m_e} - \frac{e^2\alpha^{1/2}}{2^{1/2}\varepsilon_0\pi^{3/2}} \quad (2)$$

We now minimize $E(\alpha)$ with respect to α by differentiating with respect to α and setting the result equal to zero. We solve the equation:

$$\frac{dE(\alpha)}{d\alpha} = \frac{3\hbar^2}{2m_e} - \frac{e^2}{\alpha^{1/2}\varepsilon_0(2\pi)^{3/2}} = 0$$

For α to give

$$\alpha = \frac{m_e^2 e^4}{18\varepsilon_0^2 \pi^3 \hbar^4} \quad (3)$$

As the value of α that minimize $E(\alpha)$. Substituting equation 3 back in equation 2

$$E_{min} = -\frac{4}{3\pi} \left(\frac{m_e e^4}{16\varepsilon_0^2 \pi^2 \hbar^2} \right) = -0.424 \left(\frac{m_e e^4}{16\varepsilon_0^2 \pi^2 \hbar^2} \right) \quad (4)$$

Compared with exact value

$$E_o = -\frac{1}{2} \left(\frac{m_e e^4}{16\varepsilon_0^2 \pi^2 \hbar^2} \right) = -0.500 \left(\frac{m_e e^4}{16\varepsilon_0^2 \pi^2 \hbar^2} \right) \quad (5)$$

Note that $E_{min} > E_o$ as the variational theorem assures us.

Merzbacher Exercise 8.4

The wave function is:

$$\psi(x) = Ne^{-\lambda x^2}$$

And the potential is:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0 e^{-\alpha x^2}, \quad (V_0, \alpha > 0)$$

The normalization condition gives:

$$\langle \psi | \psi \rangle = N^2 \int_{-\infty}^{\infty} e^{-2\lambda x^2} dx = N^2 \sqrt{\frac{\pi}{2\lambda}} = 1 \quad \Rightarrow \quad N = \left(\frac{2\lambda}{\pi} \right)^{1/4}$$

$$T\psi = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi = \frac{\hbar^2}{2m} e^{-\lambda x^2} \lambda(1 - 2x^2 \lambda)$$

$$\langle \psi | T | \psi \rangle = -\frac{\hbar^2}{2m} N^2 \int_{-\infty}^{\infty} e^{-2\lambda x^2} \lambda(1 - 2x^2 \lambda) dx = \frac{\hbar^2}{2m} \lambda$$

$$\langle \psi | V | \psi \rangle = -N^2 \int_{-\infty}^{\infty} V_0 e^{-\alpha x^2} e^{-2\lambda x^2} dx = -V_0 \sqrt{\frac{2\lambda}{2\lambda + \alpha}}$$

And

$$W = \langle \psi | T | \psi \rangle + \langle \psi | V | \psi \rangle = \frac{\hbar^2}{2m} \lambda - V_0 \sqrt{\frac{2\lambda}{2\lambda + \alpha}}$$

Using $\hbar = V_0 = \alpha = 1$, then the condition

$$\frac{\partial W}{\partial \lambda} = 0, \quad \text{gives } \lambda_1 = 0.374, \quad \lambda_2 = -1.109$$

and

$$W(\lambda) = -1.903$$

Merzbacher Exercise 8.5

The wave function is:

$$\psi(x) = \begin{cases} C \left(1 - \frac{|x|}{a}\right), & |x| \leq a \\ 0, & |x| \geq a \end{cases}$$

And the potential is:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2$$

The normalization condition gives:

$$\begin{aligned} \langle \psi | \psi \rangle &= C^2 \int_{-a}^a \left(1 - \frac{|x|}{a}\right)^2 dx \\ &= C^2 \left\{ \underbrace{\int_{-a}^0 \left(1 + \frac{x}{a}\right)^2 dx}_{a/3} + \underbrace{\int_0^a \left(1 - \frac{x}{a}\right)^2 dx}_{a/3} \right\} \\ &= C^2 \left\{ \frac{2a}{3} \right\} = 1 \quad \Rightarrow \quad C = \sqrt{\frac{3}{2a}} \end{aligned}$$

Note that: we will use the integral:

$$\int_{-\infty}^{\infty} \psi^* \frac{d^2\psi}{dx^2} dx = \underbrace{\psi^* \frac{d\psi}{dx}}_{=0} \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \left(\frac{d\psi}{dx}\right)^2 dx$$

The expectation of T and V gives:

$$\begin{aligned} \langle \psi | T | \psi \rangle &= -\frac{\hbar^2}{2m} C^2 \int_{-a}^a \left(1 - \frac{|x|}{a}\right) \frac{d^2}{dx^2} \left(1 - \frac{|x|}{a}\right) dx \\ &= -\frac{\hbar^2}{2m} \frac{3}{2a} \underbrace{\int_{-a}^a \left(\frac{d}{dx} \left(1 - \frac{|x|}{a}\right)\right)^2 dx}_{-2/a} = \frac{3\hbar^2}{2ma^2} \\ \langle \psi | V | \psi \rangle &= \frac{1}{2} k \int_{-a}^a \left(1 - \frac{|x|}{a}\right) x^2 \left(1 - \frac{|x|}{a}\right) dx, \quad k = m\omega^2 \\ &= \frac{1}{2} k C^2 \left\{ \underbrace{\int_{-a}^0 x^2 \left(1 + \frac{x}{a}\right)^2 dx}_{a^3/30} + \underbrace{\int_0^a x^2 \left(1 - \frac{x}{a}\right)^2 dx}_{a^3/30} \right\} \\ &= \frac{1}{2} \frac{3}{2a} \frac{2a^3}{30} k = \frac{a^2}{20} k \end{aligned}$$

And

$$W = \langle \psi | T | \psi \rangle + \langle \psi | V | \psi \rangle = \frac{3\hbar^2}{2ma^2} + \frac{a^2}{20}k,$$

The condition

$$\frac{\partial W}{\partial a} = 0, \quad \text{gives } a^4 = \frac{30\hbar^2}{m^2\omega^2} \Rightarrow a = \left(\frac{30\hbar}{mk} \right)^{1/4}$$

and

$$W = 0.5447\hbar\omega > 0.5\hbar\omega, \quad \text{as expected}$$

1- Apply the variational method to the determination of the ground state energy of the hydrogen atom, using $\psi(r,b) = A r e^{-br}$ as a trial function. Here, A is the normalization constant and b is the variational parameter.

- a. calculate N .
- b. calculate $\langle T \rangle$.
- c. calculate $\langle V \rangle$.
- d. calculate $W(b)$.
- e. calculate b .
- f. calculate E_{\min} .

Discuss your final result, for example: compared with the exact, the behavior of the wave function. [Hint: $\hat{T} = -\frac{1}{2} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right]$, $V(r) = -\frac{1}{r}$]

Answer:

```

Ψ1 = N r e-r α

e-r α N r

rΨ1 = r Ψ1

e-r α N r2

rΨ2 = (r Ψ1)2

e-2 r α N2 r4

cc = Integrate[rΨ2, {r, 0, ∞}, Assumptions → α > 0]

3 N2
4 α5

(*calculate the normalization constant *)
Nn = Solve[ ( ∫02 π dφ ) * ( ∫0π sin[θ] dθ ) * (cc) == 1, N ]

{ {N → - $\frac{\alpha^{5/2}}{\sqrt{3 \pi}}$  }, {N →  $\frac{\alpha^{5/2}}{\sqrt{3 \pi}}$  } }

Nnorm = Nn[[ 2 ]]

{N →  $\frac{\alpha^{5/2}}{\sqrt{3 \pi}}$  }

T = - $\frac{1}{2 r^2}$  ∂r (r2 ∂rΨ1) // Simplify

-  $\frac{e^{-r \alpha} N (2 - 4 r \alpha + r^2 \alpha^2)}{2 r}$ 

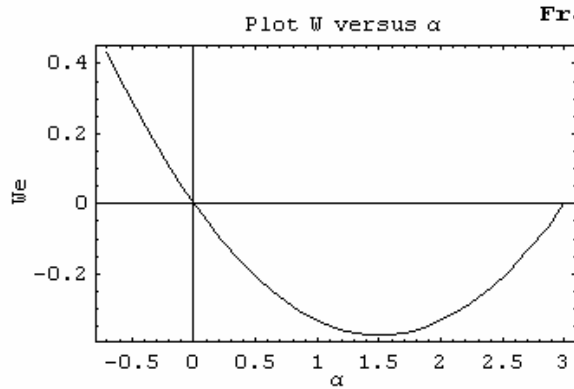
AveragT = Integrate[r2 Ψ1*T, {r, 0, ∞}, Assumptions → α > 0] / cc

 $\frac{\alpha^2}{6}$ 

```

```

AveragV = Integrate[ $r^2 \Psi_1 * \frac{-1}{r} \Psi_1$ , { $r$ , 0,  $\infty$ }, Assumptions  $\rightarrow \alpha > 0$ ] / cc
-  $\frac{\alpha}{2}$ 
W = AveragT + AveragV // Simplify
 $\frac{1}{6} (-3 + \alpha) \alpha$ 
p3 = Plot[ $W$ , { $\alpha$ , -0.7, 3}, Frame  $\rightarrow$  True, PlotLabel  $\rightarrow$  " Plot W versus  $\alpha$ ",
FrameLabel  $\rightarrow$  { $\alpha$ ,  $W_e$ }]
    
```



- Graphics -

```

varparam3 = Solve[ $\partial_{\alpha} W = 0$ ,  $\alpha$ ]
    
```

$$\left\{ \left\{ \alpha \rightarrow \frac{3}{2} \right\} \right\}$$

```

Vcoeff = varparam3[1]
    
```

$$\left\{ \alpha \rightarrow \frac{3}{2} \right\}$$

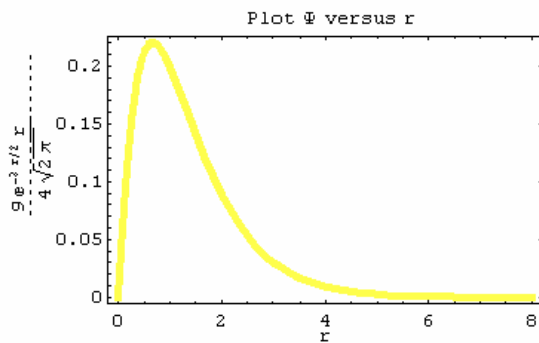
W /. Vcoeff // N

-0.375

Ψ = Ψ1 /. Nnorm /. Vcoeff

$$\frac{9 e^{-3 r/2} r}{4 \sqrt{2 \pi}}$$

**p2 = Plot[Ψ, {r, 0, 8}, Frame → True, PlotStyle → {RGBColor[1, 1, 0.3], Thickness[0.018]},
 PlotLabel → " Plot Ψ versus r", FrameLabel → {r, Ψ}]**

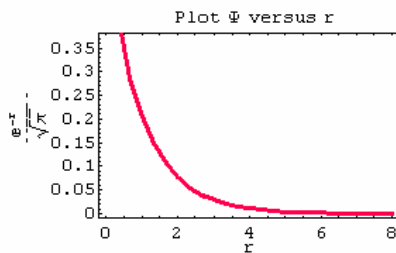


- Graphics -

Ψexact = N e^{-r} /. {N → 1/√π}

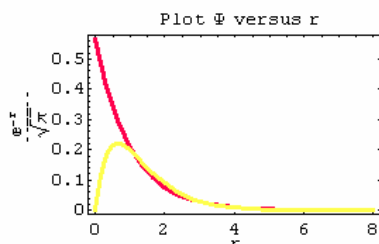
$$\frac{e^{-r}}{\sqrt{\pi}}$$

**p1 = Plot[Ψexact, {r, 0, 8}, Frame → True, PlotStyle → {RGBColor[1, 0, 0.3], Thickness[0.018]},
 PlotLabel → " Plot Ψ versus r", FrameLabel → {r, Ψexact}]**



- Graphics -

Show[p1, p2]



Comment:

-0.375 > -0.5 which satisfy the variational approximation claim. The difference is mainly due to the behavior of the wave function at the origin.

