

Time-Independent (Stationary State) Perturbation Theory First Order (self study)

A. Introduction

So far, we have been looking at systems that we can solve completely analytically. The potential energies and Hamiltonians have been of a form that makes the Schrödinger equation solvable without any approximation techniques. What if we don't have such a "nice" Hamiltonian. In general, one must rely on numerical methods to solve the Schrödinger equation (a differential equation). However, if the Hamiltonian is not too different from one of the nice, solvable Hamiltonians, then we can use the results of perturbation theory to find approximate energies and eigenfunctions of the system. This theory is what we will develop here.

Perturbation theory works best when the system's total energy is "perturbed" by a small additional potential energy. The total Hamiltonian can be expressed as a sum of an unperturbed Hamiltonian (\hat{H}_o) and a perturbation (\hat{H}'):

$$\hat{H} = \hat{H}_o + \hat{H}' \quad (1)$$

The unperturbed Hamiltonian is one of the nice, solvable Hamiltonians while the perturbation is a relatively small adjustment to the total energy.

The plan is to expand the system Hamiltonian, and hence the system energy, into a sum of terms involving higher and higher powers of \hat{H}' , similar to a Taylor series expansion of a function around some value. Since the perturbation is small, we only have to keep the first few terms (typically two or three terms) to obtain a close approximation to the actual energy.

Because of the analogy to a Taylor series, it is useful to review a Taylor expansion for some function $f(x)$. Let's take the function

$$f(x) = (1+x)^{1/2}$$

The first three terms of the Taylor series expansion about $x=0$ are

$$f(x) = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \dots$$

We view x as the perturbation to the unperturbed value of $f(x)$ which is one. If x is very small compared to one, then the two terms added to one in the expansion are adequate to obtain the value of $f(x)$. The first term (involving x) added to one is the *first order correction* and the second term (involving x^2) is the *second order correction*. As an example, let $x = 0.2$. The value of $f(x = 0.2) = 1.0954451$. Using the first and second order correction, we obtain $f(0.2) = 1 + 0.1 - 0.005 = 1.095$. This approximate value is only 0.04% less than the actual value.

We will attempt to do a similar expansion to find the corrections to the unperturbed energy to obtain an approximate but very accurate value for the energy of the perturbed system.

B. Nondegenerate State Perturbation

The first procedure that we obtain will only work if a system is in a perturbed state that is very close to a nondegenerate, unperturbed eigenstate of the unperturbed Hamiltonian. This probably won't be obvious at first, but we will see later why this is so. We will discuss what to do if the unperturbed state is degenerate in a later section.

Let the unperturbed eigenstate be denoted by $|\psi_n^{(0)}\rangle$. The superscript of (0) means that this state is the unperturbed eigenstate of \hat{H}_o . Let's let the energy eigenvalue of this state be $E_n^{(0)}$ so that

$$\hat{H}_o |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \quad (2)$$

The subscript n refers to this one particular eigenstate of \hat{H}_o . Now for some time-saving notation. Let's just refer to the eigenstate by its label n ; we drop the ψ so that the eigenvalue equation (2) looks like

$$\boxed{\hat{H}_o |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle} \quad (3)$$

We assume that the actual eigenstate $|\psi\rangle$ of the total Hamiltonian is very close to the unperturbed state $|n^{(0)}\rangle$ and that it can be written as a series expansion of the form

$$\boxed{|\psi\rangle = |n^{(0)}\rangle + |a\rangle + |b\rangle + \dots} \quad (4)$$

where $|a\rangle$ is the first order correction and $|b\rangle$ the second order correction to $|n^{(0)}\rangle$. Likewise, we assume that the actual energy E is very close to the unperturbed energy $E_n^{(0)}$ and can be written as a series expansion of the form

$$\boxed{E = E_n^{(0)} + \epsilon_1 + \epsilon_2 + \dots} \quad (5)$$

where ϵ_1 is the first order correction and ϵ_2 the second order correction to $E_n^{(0)}$. The question is how to find these corrections, particularly the energy corrections since finding the energy is usually of primary importance.

To assist us in this endeavor, recall that what gives rise to these series expansions is the perturbation \hat{H}' of the Hamiltonian. If the perturbation is "turned off", then the correction terms vanish; if the perturbation is "turned on", then the correction terms appear. Let's introduce an integer variable q such that we write

$$\hat{H} = \hat{H}_o + q\hat{H}' \quad (6)$$

This q can have two values: if $q = 0$ then the perturbation is turned off, and if $q = 1$ then the perturbation is turned on. Using this q , we can rewrite (4) and (6) as

$$|\psi\rangle = |n^{(0)}\rangle + q|a\rangle + q^2|b\rangle + \dots \quad (7)$$

and

$$E = E_n^{(0)} + q\epsilon_1 + q^2\epsilon_2 + \dots \quad (8)$$

Notice, again, that if $q = 0$ the perturbation is off and we get the unperturbed eigenstate and energy, but if $q = 1$ the perturbation is on and we get the corrections to the eigenstate and energy. Notice also that the second order corrections involve the square of q . This is logical since we expect a second order term involving the square of \hat{H}' to give rise to the second order corrections to the eigenstate and energy.

Now the Schrödinger equation for the system is

$$\hat{H}|\psi\rangle = E|\psi\rangle \quad (9)$$

Substituting (6-6.8) into this equation gives

$$\boxed{\boxed{(\hat{H}_o + q\hat{H}')(|n^{(0)}\rangle + q|a\rangle + q^2|b\rangle + \dots)} = (E_n^{(0)} + q\epsilon_1 + q^2\epsilon_2 + \dots)(|n^{(0)}\rangle + q|a\rangle + q^2|b\rangle + \dots)} \quad (10)$$

Now we want any first order corrections to only depend on terms involving \hat{H}' , and second order corrections to only depend on terms involving \hat{H}'^2 , etc. This is accomplished if we simply require that the sum of terms involving q to a certain power on the left side of (10) equal the sum of terms involving q to that same power on the right side of the equation. This is sometimes referred to as “equating the powers” of q . Let’s do this for the first three powers of q .

Equating powers of q^0 gives:

$$\hat{H}_o |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle \quad (11)$$

This is simply the Schrodinger equation for the unperturbed Hamiltonian that we wrote in (2)

Equating powers of q^1 gives:

$$\boxed{\hat{H}_o |a\rangle + \hat{H}' |n^{(0)}\rangle = E_n^{(0)} |a\rangle + \epsilon_1 |n^{(0)}\rangle} \quad (12)$$

Equating powers of q^2 gives:

$$\boxed{\hat{H}_o |b\rangle + \hat{H}' |a\rangle = E_n^{(0)} |b\rangle + \epsilon_1 |a\rangle + \epsilon_2 |n^{(0)}\rangle} \quad (13)$$

We will stop here as a second order correction is sufficient for most systems of interest.

First Order Correction to Energy

We take the scalar product of the four vectors in (12) with the unperturbed eigenstate. Using Dirac notation, this looks like

$$\langle n^{(0)} | \hat{H}_o |a\rangle + \langle n^{(0)} | \hat{H}' |n^{(0)}\rangle = \langle n^{(0)} | E_n^{(0)} |a\rangle + \langle n^{(0)} | \epsilon_1 |n^{(0)}\rangle \quad (14)$$

Let’s look at the first scalar product in this equation in more detail. Recall that the adjoint of the Hamiltonian is equal to the Hamiltonian since it is an operator corresponding to a dynamic variable (total energy). So we can replace \hat{H} with \hat{H}^+ to get

$$\langle n^{(0)} | \hat{H}_o |a\rangle = \langle n^{(0)} | \hat{H}_o^+ |a\rangle \quad (15)$$

By definition of the adjoint, the right side of this equation can be written as

$$\langle n^{(0)} | \hat{H}_o^+ |a\rangle = (\langle a | \hat{H}_o |n^{(0)}\rangle)^* = E_n^{(0)} * (\langle a | n^{(0)}\rangle)^* = E_n^{(0)} * \langle n^{(0)} | a\rangle \quad (16)$$

Now the energy $E_n^{(0)}$ is real since we can measure it (or more formally, the eigenvalues of operators corresponding to dynamic variables are always real), so the complex conjugate of the energy is simply the energy. Thus, we have shown that

$$\langle n^{(0)} | \hat{H}_o |a\rangle = E_n^{(0)} \langle n^{(0)} | a\rangle \quad (17)$$

(Notice that we can think of \hat{H}_o as acting on the bra vector $\langle n^{(0)} |$ to give $E_n^{(0)}$. This is fine since the Hamiltonian is self-adjoint. Since any operator of a dynamic variable is self-adjoint, you can do the same for any operator inside a bracket.)

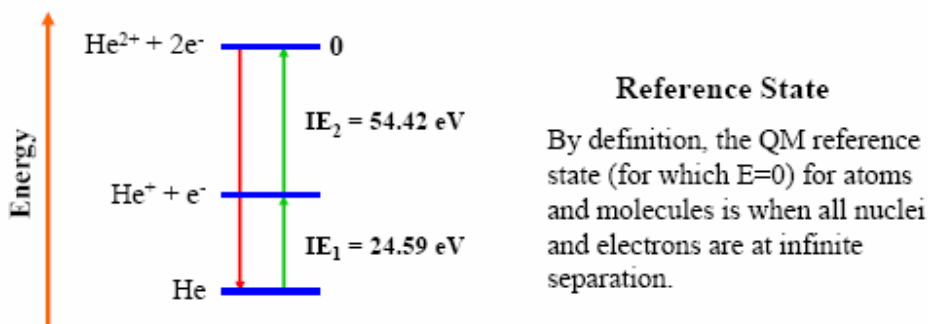
The energies inside the brackets of the two terms on the right of (14) can be simply taken outside the brackets to yield

$$E_n^{(0)} \langle n^{(0)} | a\rangle + \langle n^{(0)} | \hat{H}' |n^{(0)}\rangle = E_n^{(0)} \langle n^{(0)} | a\rangle + \epsilon_1 \langle n^{(0)} | n^{(0)}\rangle \quad (18)$$

Assuming that $|n^{(0)}\rangle$ is normalized, we can solve this equation for the first order correction to the energy:

$$\epsilon_1 = \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle \quad (19)$$

The Experimental Electronic Energy of He

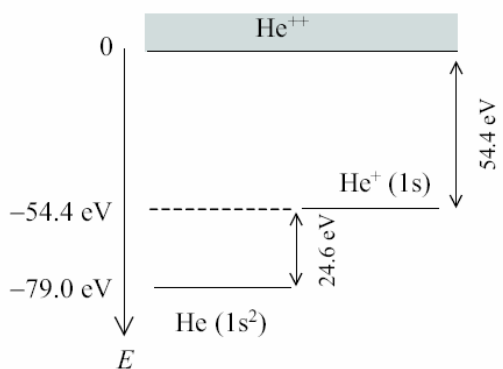


$$E_{\text{He}} = -[IE_1 + IE_2]$$

$$E_{\text{He}} = -[24.59 \text{ eV} + 54.42 \text{ eV}]$$

$$E_{\text{He}} = -79.01 \text{ eV}$$

or $E_{\text{He}} = -2.9037 \text{ au (hartrees)}$



Ground state	1s 1s ($\equiv 1s^2$)
First excited state	1s 2s
Second excited state	1s 2p
Third excited state	1s 3s
Fourth excited state	1s 3p
⋮	
Ionization limit	1s ∞l

Electron configurations for the states of the helium atom.

Figure 7.2: The ionization energies of helium atom.

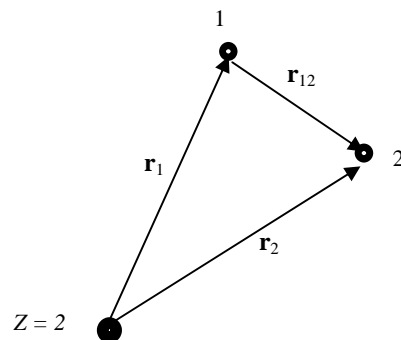
The Helium Atom Schrödinger Equation

In atomic units, the Helium Hamiltonian can be rewritten as:

$$H = H^{(0)} + H^{(1)}$$

Where

$$H^{(0)} = H_1(\vec{r}_1) + H_2(\vec{r}_2) = \left[-\frac{1}{2} \nabla_1^2(\vec{r}_1) - \frac{Z}{r_1} \right] + \left[-\frac{1}{2} \nabla_2^2(\vec{r}_2) - \frac{Z}{r_2} \right]$$



$$H^{(1)} = + \frac{1}{r_{12}} \text{(electron-electron repulsion)}$$

$H^{(0)}$ is exactly solvable, as we just showed in the independent particle method. $H^{(1)}$ is a small perturbation to the exactly solvable Hamiltonian. The energy due to $H^{(1)}$ can be estimated by First Order Perturbation Theory.

With the operator

$$\nabla_i^2(\vec{r}_i) = \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial}{\partial r_i} \right) + \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial}{\partial \theta_i} \left(\sin \theta_i \frac{\partial}{\partial \theta_i} \right) + \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \phi_i^2}$$

and the Schrödinger equation:

$$H \Psi(\vec{r}_1, \vec{r}_2) = E \Psi(\vec{r}_1, \vec{r}_2),$$

where Ψ depends upon the coordinates of both electrons. Now, can we separate variables? i.e. using the separable wavefunction:

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_2)$$

The answer is Nooooooooooooooooooooo!! The last term in the Hamiltonian messes us up.

The Independent Particle Model

$$H = \left[-\frac{1}{2} \nabla_1^2(\vec{r}_1) - \frac{Z}{r_1} \right] + \left[-\frac{1}{2} \nabla_2^2(\vec{r}_2) - \frac{Z}{r_2} \right] + \cancel{\frac{1}{r_{12}}}$$

If the $1/r_{12}$ term is causing all the problems, just throw it out.

$$H = \left[-\frac{1}{2} \nabla_1^2(\vec{r}_1) - \frac{Z}{r_1} \right] + \left[-\frac{1}{2} \nabla_2^2(\vec{r}_2) - \frac{Z}{r_2} \right] = H_1(\vec{r}_1) + H_2(\vec{r}_2)$$

Separation of Variables: Assume that

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_2) \Rightarrow [H_1(\vec{r}_1) + H_2(\vec{r}_2)] \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_2) = E \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_2)$$

$$\psi_2(\vec{r}_2) H_1(\vec{r}_1) \psi_1(\vec{r}_1) + \psi_1(\vec{r}_1) H_2(\vec{r}_2) \psi_2(\vec{r}_2) = E \psi_1(\vec{r}_1) \cdot \psi_2(\vec{r}_2)$$

$$\underbrace{\frac{1}{\psi_1(\vec{r}_1)} H_1(\vec{r}_1) \psi_1(\vec{r}_1)}_{=E_1} + \underbrace{\frac{1}{\psi_2(\vec{r}_2)} H_2(\vec{r}_2) \psi_2(\vec{r}_2)}_{=E_2} = E$$

$$H_1(\vec{r}_1) \psi_1(\vec{r}_1) = E \psi_1(\vec{r}_1) \quad \text{and} \quad H_2(\vec{r}_2) \psi_2(\vec{r}_2) = E \psi_2(\vec{r}_2)$$

$$\left[-\frac{1}{2} \nabla_1^2(\vec{r}_1) - \frac{Z}{r_1} \right] \psi_1(\vec{r}_1) = E_1 \psi_1(\vec{r}_1) \quad \text{and} \quad \left[-\frac{1}{2} \nabla_2^2(\vec{r}_2) - \frac{Z}{r_2} \right] \psi_2(\vec{r}_2) = E_2 \psi_2(\vec{r}_2)$$

These are just the one electron Schrödinger Equations for “hydrogen-like” atoms.

Wavefunctions

$$\psi_1^{n_1 l_1 m_1}(\vec{r}_1) = A \cdot R_{n_1 l_1}(r_1) \cdot Y_{l_1 m_1}(\theta_1, \phi_1), \quad \psi_2^{n_2 l_2 m_2}(\vec{r}_2) = A \cdot R_{n_2 l_2}(r_2) \cdot Y_{l_2 m_2}(\theta_2, \phi_2)$$

Ground State Wavefunctions (1s: $n = 1, \ell = 0, m = 0$)

$$\psi_1^{100}(\vec{r}_1) = A \cdot e^{-Zr_1} \quad \text{and} \quad \psi_2^{100}(\vec{r}_2) = A \cdot e^{-Zr_2}$$

Energies

$$E_1 = -\frac{Z^2}{2n_1^2} \text{ a.u.} \quad \text{and} \quad E_2 = -\frac{Z^2}{2n_2^2} \text{ a.u.} \quad \Rightarrow \quad E = E_1 + E_2 = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2}$$

Ground State Energy ($n_1 = n_2 = 1$)

$$E = E_1 + E_2 = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 = -4 \text{ a.u.}$$

Z = 2 for He, $E_{\text{exp}} = -2.9037 \text{ a.u.}$

Our calculated Ground State Energy is 38% lower than experiment. This is because, by throwing out the $\frac{1}{r_{12}}$ term in the Hamiltonian, we ignored the electron-electron repulsive energy, which is positive.

Problem: Each of the two 1s electrons in helium atom may be described by a hydrogenic wave

function $\psi_{1s}(r_i) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr_i}$ in the absence of the other electron. Here Z, the atomic number, is 2. Prove that the mutual potential energy, Coulomb's (direct) integral, of the two electrons, given by:

$$J(1s, 1s, Z) = I(Z) = \Delta E = \iint \psi_{1s}^*(r_1) \psi_{1s}^*(r_2) \frac{1}{r_{12}} \psi_{1s}(r_1) \psi_{1s}(r_2) d\tau_1 d\tau_2$$

$$= \iint \frac{|\psi_{1s}^*(r_1)|^2 |\psi_{1s}^*(r_2)|^2}{r_{12}} d\tau_1 d\tau_2 = \frac{5}{8} Z$$

Note: $d\tau_i = r_i^2 \sin \theta_i d\theta_i d\phi_i dr_i$, $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$.

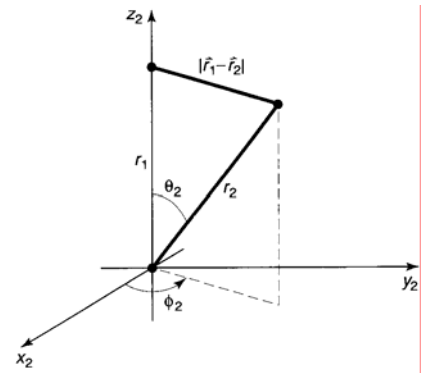
Answer: For the Coulomb's integral $I(Z)$, use (see Figure)

$$|\mathbf{r}_2 - \mathbf{r}_1| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta}, \quad \theta_2 = \theta.$$

Start with

$$|\mathbf{r}_2 - \mathbf{r}_1| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta}$$

And use $d\tau_i = r_i^2 \sin \theta_i d\theta_i d\phi_i dr_i$.



$$I = \frac{Z^6}{\pi^2} \int_0^\infty e^{-2Zr_1} r_1^2 dr_1 \underbrace{\int_0^{2\pi} d\Omega_1}_{4\pi} \int_0^\infty e^{-2Zr_2} r_2^2 dr_2 \underbrace{\int_0^{2\pi} d\phi_2}_{2\pi} \int_0^\pi \frac{\sin \theta d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta}}$$

$$= 8Z^6 \int_0^\infty e^{-2Zr_1} r_1^2 dr_1 \int_0^\infty e^{-2Zr_2} r_2^2 dr_2 \int_0^\pi \frac{\sin \theta d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta}}$$

Use the substitution $x = \cos \theta$, $dx = -\sin \theta d\theta$, and integrate for θ we have

$$\begin{aligned} \int_0^\pi \frac{\sin \theta d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta}} &= \int_{-1}^{+1} \frac{dx}{\sqrt{r_1^2 + r_2^2 - 2x r_1 r_2}} = \left. \frac{\sqrt{r_1^2 + r_2^2 - 2x r_1 r_2}}{r_1 r_2} \right|_{-1}^{+1} \\ &= \frac{1}{r_1 r_2} \left(\sqrt{r_1^2 + r_2^2 + 2r_1 r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1 r_2} \right) \\ &= \frac{1}{r_1 r_2} \left[(r_1 + r_2) - |r_1 - r_2| \right] = \begin{cases} \frac{1}{r_1 r_2} \left[(r_1 + r_2) - (r_1 - r_2) \right] = \frac{2}{r_1}, & r_1 > r_2 \\ \frac{1}{r_1 r_2} \left[(r_1 + r_2) - (r_2 - r_1) \right] = \frac{2}{r_2}, & r_2 > r_1 \end{cases} \end{aligned}$$

Then we find:

$$I = 16Z^6 \int_0^\infty e^{-2Z r_1} r_1^2 dr_1 \left[\frac{1}{r_1} \int_0^{r_1} e^{-2Z r_2} r_2^2 dr_2 + \int_{r_1}^\infty e^{-2Z r_2} r_2 dr_2 \right] = 16Z^6 \int_0^\infty e^{-2Z r_1} r_1^2 dr_1 [I_1 + I_2]$$

With the integrals

$$\begin{aligned} I_1 &= \frac{1}{r_1} \int_0^{r_1} e^{-2Z r_2} r_2^2 dr_2 = \frac{1}{4Z^3 r_1} \left\{ e^{-2Z r_1} (-1 - 2Z r_1 - 2Z^2 r_1^2) + 1 \right\}, \\ I_2 &= \int_{r_1}^\infty e^{-2Z r_2} r_2 dr_2 = \frac{e^{-2Z r_1}}{4Z^2} (1 + 2Z r_1) \end{aligned}$$

Finally:

$$\begin{aligned} I &= 16Z^6 \int_0^\infty e^{-2Z r_1} r_1^2 dr_1 \left[\frac{e^{-2Z r_1}}{4Z^3 r_1} (-1 + e^{2Z r_1} - r_1 Z) \right] \\ &= 4Z^3 \int_0^\infty e^{-4Z r_1} (-1 + e^{2Z r_1} - r_1 Z) r_1 dr_1 = 4Z^3 \left(\frac{5}{32Z^2} \right) = \frac{5}{8} Z \end{aligned}$$

Therefore, using First Order Perturbation Theory, the total electronic energy of the Helium atom is:

$$E = E^{(0)} + \Delta E = -\frac{Z^2}{2} - \frac{Z^2}{2} + \frac{5}{8} Z = -2^2 + \frac{5}{8} \cdot 2 = -2.75 \text{ a.u.}$$

This result is 5.3% above (less negative) the experimental energy of -2.9037 a.u. However, remember that we made only the *First Order* Perturbation Theory correction to the energy.

Order	Energy (a.u.)	% Error
0	-4.0	-38%
1	-2.75	+5
2	-2.91	-0.2
13	-2.9037	~0

Homework: Prove that

$$\begin{aligned} J(1s, 2s, Z) &= \frac{17}{81} Z, & J(1s, 2p, Z) &= \frac{203}{3^5} Z \\ K(1s, 2s, Z) &= \frac{18}{3^6} Z, & K(1s, 2p, Z) &= \frac{7 \times 2^4}{3^8} Z \end{aligned}$$

$$\psi[\mathbf{r}_1, \mathbf{r}_2] := \frac{1}{\pi} e^{-\mathbf{r}_1 - \mathbf{r}_2}$$

$$\text{normalizer} = (4\pi)^2 \int_0^\infty \int_0^\infty r_1^2 r_2^2 \psi[\mathbf{r}_1, \mathbf{r}_2]^2 d\mathbf{r}_1 d\mathbf{r}_2$$

1

$$16\pi^2 \int_0^\infty \left(\int_0^{r_2} r_1^2 \psi[\mathbf{r}_1, \mathbf{r}_2]^2 d\mathbf{r}_1 + \int_{r_2}^\infty r_1 r_2 \psi[\mathbf{r}_1, \mathbf{r}_2]^2 d\mathbf{r}_1 \right) r_2 d\mathbf{r}_2$$

$\frac{5}{8}$

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 $\phi_{1s}(r) = Ne^{-ar}$ 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 $d\tau = r^2 \sin\theta d\theta d\phi dr$):

$$\langle \phi_{1s} | \phi_{1s} \rangle = \int |\phi_{1s}(r)|^2 d\tau = N^2 \underbrace{\int_0^\infty r^2 e^{-2ar} dr}_{\frac{1}{4a^3}} \underbrace{\int_0^\pi \sin\theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

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

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

Then

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

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

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 $a=1$.

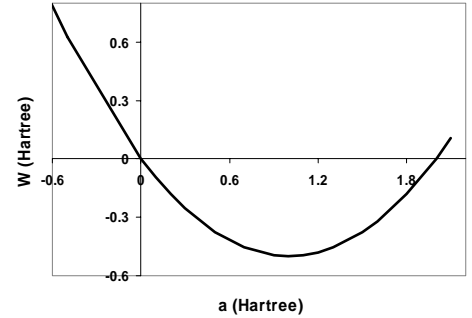
H.W2. Calculate $\langle T \rangle$ and $\langle V \rangle$ and find the relation between them.

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.

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.

H.W5. Use a trial function of the form $\phi_{1s}(r) = N r e^{-ar^2}$ 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:

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

Taking into account the following integrations: $\int \frac{e^{-ar \pm i \mathbf{q} \cdot \mathbf{r}}}{r} d\mathbf{r} = \frac{4\pi}{a^2 + q^2}$;

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

And (H.W. prove the following integral)

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

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.

Two-Parameter 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.

Elliptic coordinates

Calculate the integral

$$I(1s, 1s, Z) = \int |\psi(r_1, r_2)|^2 \frac{1}{r_{12}} d\tau_1 d\tau_2 = \iint |\psi_{1s}(r_1)|^2 \frac{1}{|r_2 - r_1|} |\psi_{1s}(r_2)|^2 d\tau_1 d\tau_2,$$

where $\psi(r_1, r_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$ using the elliptic coordinate.

The elliptic coordinates is defined by the variables:

$$\begin{aligned} s &= r_1 + r_2, & t &= r_1 - r_2, & u &= r_{12}; \\ -u &\leq t \leq u, & 0 &\leq u \leq s \leq \infty; \\ d\tau_1 d\tau_2 &= \pi^2 (s^2 - t^2) u ds dt du \end{aligned}$$

Then for the wave function: $\psi(r_1, r_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$, we can have:

$$\begin{aligned} I &= \int |\psi(r_1, r_2)|^2 \frac{1}{r_{12}} d\tau_1 d\tau_2 = \pi^2 \left(\frac{Z^3}{\pi} \right)^2 \int_0^\infty ds \int_0^s du \int_{-u}^u e^{-2Zs} \left(\frac{s^2 - t^2}{u} \right) dt \\ &= \frac{5}{8} Z \end{aligned}$$

H.W. Using the elliptic coordinates calculate $I(1s, 2s, Z)$, $K(1s, 2s, Z)$

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 $\ell=0$ 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.
- calculate N .
 - calculate $\langle T \rangle$.
 - calculate $\langle V \rangle$.
 - calculate $W(b)$.
 - calculate b .
 - 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

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

```

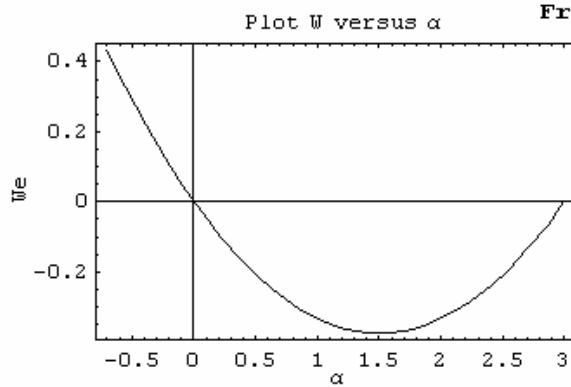
$$\text{AveragV} = \text{Integrate}\left[r^2 \Psi_1 * \frac{-1}{r} \Psi_1, \{r, 0, \infty\}, \text{Assumptions} \rightarrow \alpha > 0\right] / \text{cc}$$

$$-\frac{\alpha}{2}$$

$$\text{W} = \text{AveragT} + \text{AveragV} // \text{Simplify}$$

$$\frac{1}{6} (-3 + \alpha) \alpha$$

$$\text{p3} = \text{Plot}[\text{W}, \{\alpha, -0.7, 3\}, \text{Frame} \rightarrow \text{True}, \text{PlotLabel} \rightarrow \text{" Plot W versus } \alpha \text{"}, \text{FrameLabel} \rightarrow \{\alpha, \text{We}\}]$$



- Graphics -

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

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

$$\text{Vcoeff} = \text{varparam3}[[1]]$$

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

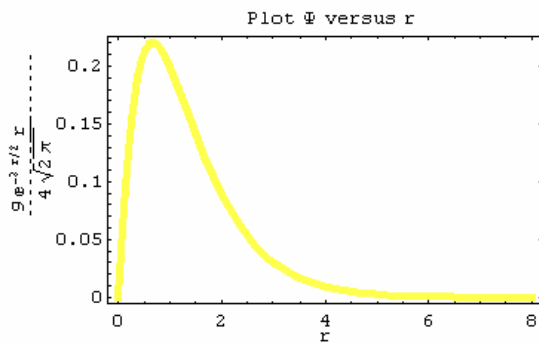
W /. Vcoeff // N

-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}]**

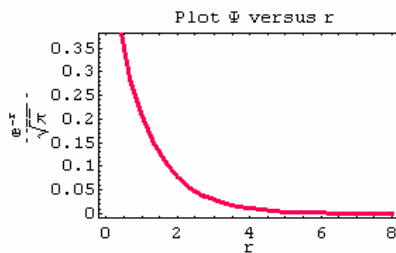


- Graphics -

Ψexact = N e^{-x} /. {N → 1/sqrt(π)}

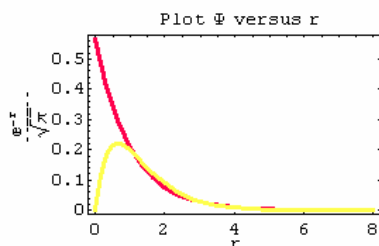
$$\frac{e^{-x}}{\sqrt{\pi}}$$

**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.