Lecture 7 Variation method

The variation method allow us to approximate the Ground State of the energy without solving the S.E.

The Variational Method

Theory:

For a system whose Hamiltonian operator H is time independent and whose lowest Energy Eigen value is E, if ϕ is any **normalized well behaved** Function of the coordinates of the system particle that satisfy the Boundary condition of the problem then

 $\int \varphi^* H \varphi d\tau \ge E_0 \qquad \qquad \varphi \text{ is normalized wavefunction}$

if the function φ is not normalized then

$$\frac{\int \varphi^* H \varphi d\tau}{\int \varphi^* \varphi d\tau} \ge E_0$$

 φ is called trial function

 $\int \varphi^* H \varphi d\tau$ called Variation Integral =W

The Variational Method

Procedure:

We try many trial function and the one give the Lower value of variational integral, the better Approximation we have for E1

In practice:

- I. We put several parameters into the trial function ϕ
- II. Then we vary the parameters so as to minimize the variational integral W
- III. The lowest one is the best

$$\frac{\partial W}{\partial c} = 0$$

The Real Utility of the Variation method is for problems to which we do not know the true solution, we will consider some example that we know energy (actual) to compare

The Variational Theorem

This theorem states that if one chooses an *approximate* wavefunction, ϕ , then the Expectation Value for the energy is greater than or equal to the exact ground state energy, E₀.

$$\langle E \rangle = E_{trial} = \frac{\left\langle \varphi \left| H \right| \varphi \right\rangle}{\left\langle \varphi \left| \varphi \right\rangle} = \frac{\int \varphi^* H \varphi d\tau}{\int \varphi^* \varphi d\tau} \ge E_0$$

Note: I will outline the proof, but you are responsible only for the result and its applications.

Proof:
$$\langle E \rangle - E_0 = \frac{\int \varphi^* H \varphi d\tau}{\int \varphi^* \varphi d\tau} - E_0 \frac{\int \varphi^* \varphi d\tau}{\int \varphi^* \varphi d\tau} \ge 0$$

 $\langle E \rangle - E_0 = \frac{\int \varphi^* (H - E_0) \varphi d\tau}{\int \varphi^* \varphi d\tau}$

Assume that we know the exact solutions, ψ_n : $H\psi_n = E_n\psi_n$

It was discussed that the set of eigenfunctions, ψ_n , of the Hamiltonian form a **complete set**. of orthonormal functions.

That is, any arbitrary function with the same boundary conditions can be expanded as a linear combination (an infinite number of terms) of eigenfunctions.

$$\varphi = \sum_{n=0}^{\infty} c_n \psi_n = \sum_n c_n \psi_n$$

This can be substituted into the expression for <E> to get:

$$< E > -E_{0} = \frac{\int \varphi^{*}(H - E_{0})\varphi d\tau}{\int \varphi^{*}\varphi d\tau} = \frac{\int \left(\sum_{m} c_{m}\psi_{m}\right)^{*}(H - E_{0})\left(\sum_{n} c_{n}\psi_{n}\right)d\tau}{\int \left(\sum_{m} c_{m}\psi_{m}\right)^{*}\sum_{n} c_{n}\psi_{n}d\tau}$$
$$< E > -E_{0} = \frac{\int \left(\sum_{m} c_{m}\psi_{m}\right)^{*}\left(\sum_{n} c_{n}(H - E_{0})\psi_{n}\right)d\tau}{\int \left(\sum_{m} c_{m}\psi_{m}\right)^{*}\sum_{n} c_{n}\psi_{n}d\tau}$$

$$< E > -E_{0} = \frac{\int \left(\sum_{m} c_{m} \psi_{m}\right)^{*} \left(\sum_{n} c_{n} \left(E_{n} - E_{0}\right) \psi_{n}\right) d\tau}{\int \left(\sum_{m} c_{m} \psi_{m}\right)^{*} \sum_{n} c_{n} \psi_{n} d\tau} = \frac{\sum_{m} \sum_{n} c_{m}^{*} c_{n} \left(E_{n} - E_{0}\right) \int \psi_{m}^{*} \psi_{n} d\tau}{\sum_{m} \sum_{n} c_{m}^{*} c_{n} \int \psi_{m}^{*} \psi_{n} d\tau}$$

$$< E > -E_{0} = \frac{\sum_{m=n}^{\infty} c_{m}^{*} c_{n} (E_{n} - E_{0}) \delta_{mn}}{\sum_{m=n}^{\infty} \sum_{n} c_{m}^{*} c_{n} \delta_{mn}}$$
 because $\int \psi_{m}^{*} \psi_{n} d\tau = \delta_{mn}$ ψ orthonormality

$$\langle E \rangle - E_0 = \frac{\sum_n c_n^* c_n (E_n - E_0)}{\sum_n c_n^* c_n} \geq \mathbf{O} \text{ because } c_n^* c_n \ge 0$$
$$E_n - E_0 \ge 0$$

Therefore:
$$\langle E \rangle = E_{trial} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} \ge E_0$$

Applications of the Variational Method

The Particle in a Box

We learned that, for a PIB:



In a HW problem, you were asked to show that for the approximate PIB wavefunction $\psi_{app} = Ax(a - x)$ The expectation value for $\langle p^2 \rangle = \frac{10\hbar^2}{a^2}$

Let's calculate :
$$\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle = \frac{\left\langle p^2 \right\rangle}{2m} = \frac{10\hbar^2}{2ma^2} = \frac{5\hbar^2}{4\pi^2 ma^2} = 0.12665 \frac{\hbar^2}{ma^2}$$

Exact GS Energy: $E_1 = 0.125 \frac{h^2}{ma^2}$ using $\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$ Approx. GS Energy: $E_{app} = 0.12665 \frac{h^2}{ma^2}$ using $\psi_{app} = Ax(a - x)$

The approximate wavefunction gives a ground state energy that is only 1.3% too high.

This is because the approximate wavefunction is a good one.



PIB: A Second Trial Wavefunction

If one considers a second trial wavefunction: $\psi_{app} = Ax^2(a-x)^2$

It can be shown (with a considerable amount of algebra) that:

$$E_{app} = \frac{6\hbar^2}{ma^2} = \frac{6\hbar^2}{4\pi^2} \frac{1}{ma^2} = 0.152 \frac{\hbar^2}{ma^2}$$
 21.6% Error

The much larger error using this second trial wavefunction is not surprising if one compares plots of the two approximate functions.



PIB: A Linear Combination of Combined Trial Wavefunctions

Let's try a trial wavefunction consisting of a linear combination of the two approximate functions which have been used:

$$\psi_{app} = Ax(a-x) + Bx^{2}(a-x)^{2}$$

or $\psi_{app} = A\left[x(a-x) + Rx^{2}(a-x)^{2}\right]$ where $R = \frac{B}{A}$

Because the Variational Theorem states that the approximate energy cannot be lower than the exact Ground State energy, one can vary the ratio of the two functions, R, to find the value that minimizes the approximate energy.

This can be done using a method (solving a Secular Determinant) that we will learn later in the course. The result is:^a

$$R = \frac{B}{A} = \frac{1.133}{a^2}$$
 and $E_{app} = 0.1250018 \frac{h^2}{ma^2}$ 0.0015% Error Not bad!!

a) Quantum Chemistry, 7th Ed., by I. N. Levine,



The agreement of $\psi_{approx.}$ with ψ_{exact} is actually even better than it looks. The two plots were perfectly superimposed and I had to add on a small constant to ψ_{exact} so that you could see the two curves.

An Approximate Harmonic Oscillator Wavefunction

Exact HO Ground State:
$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \qquad \psi_0 = Ae^{-\alpha x^2/2}$$
$$E_0 = \frac{1}{2}\hbar\omega = 0.5\hbar\omega$$

Let's try an approximate wavefunction: $\psi_{app} = A \cos(\lambda x) - \frac{\pi}{2\lambda} \le x \le \frac{\pi}{2\lambda}$



 λ is a variational parameter, which can be adjusted to give the lowest, i.e. the best energy.

One can use ψ_{app} to calculate an estimate to the Ground State energy by:

$$E_{app} = \langle E \rangle = \frac{\left\langle \psi_{app} \left| H \left| \psi_{app} \right\rangle \right\rangle}{\left\langle \psi_{app} \left| \psi_{app} \right\rangle \right\rangle} = \frac{\left\langle A\cos(\lambda x) \left| -\frac{h^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \left| A\cos(\lambda x) \right\rangle \right\rangle}{\left\langle A\cos(\lambda x) \left| A\cos(\lambda x) \right\rangle \right\rangle}$$

It can be shown that, when this expression is evaluated, one gets:

$$E_{app} = \frac{\hbar^2 \lambda^2}{2\mu} + \left(\frac{\pi^2}{24} - \frac{1}{4}\right) \frac{k}{\lambda^2} = \frac{\hbar^2 \Delta}{2\mu} + C \frac{k}{\Delta} \quad \text{where} \quad \begin{aligned} \Delta &= \lambda^2 \\ C &= \frac{\pi^2}{24} - \frac{1}{4} = 0.1612 \end{aligned}$$

Note: $\sqrt{2C} = 0.568$ (will be needed later in the calculation).

Because E_{app} is a function of λ^2 (rather than λ), it is more convenient to consider the variational parameter to be $\Delta = \lambda^2$.



Note: $\sqrt{2C} = 0.568$ (will be needed later in the calculation).

The approximate GS energy is a function of the variational parameter, $\boldsymbol{\Delta}$





 $E_{best} = 0.284\hbar\omega + 0.284\hbar\omega = 0.568\hbar\omega \quad 13.6\% \text{ error (compared to } E_0 = 0.5 \hbar\omega)$ Note: We will use: $\frac{\sqrt{k\mu}}{\mu} = \sqrt{\frac{k}{\mu}} = \omega \quad and \quad \frac{k}{\sqrt{k\mu}} = \sqrt{\frac{k}{\mu}} = \omega$ Slide 15

Linear Variation Functions

GO Back to Matrix, you need it

A special kind of variation function widely used in the study of molecules is the linear variation function. A **linear variation function** is a linear combination of *n* linearly independent functions f_1 , f_2 , c, f_n : So $\phi = c_1 f_1 + c_2 f_2 + c_3 f_3 + \dots + c_n f_n$ A **linear variation function** is a linear combination of *n* linearly independent functions f_1 , f_2 , c, f_n : So $\Phi = c_1 f_1 + c_2 f_2 + c_3 f_3 + \dots + c_n f_n$ f

$$\phi = \sum_{j=1}^{n} c_j f_j$$
 ϕ trial function is real. c_j Parameters to be determined

 f_j called Basis set (they must stasfy the boundary condition) so the Variation function

$$\int \phi^* \phi \partial t = \int \sum_{j=1}^n c_j f_j \sum_{k=1}^n c_k f_k = \sum_{j=1}^n c_j \sum_{k=1}^n c_k \int f_j f_k \partial t$$
assume
$$S_{jk} = \int f_j f_k \partial t$$
called overlap integra
$$\int \phi^* \phi \partial t = \sum_{j=1}^n c_j \sum_{k=1}^n c_k S_{jk}$$
the variational integral $W = \frac{\int \phi^* H \phi \partial t}{\int \phi^* \phi \partial t}$

Slide 17

 $\phi = \sum_{j=1}^{n} c_j f_j$ ϕ trial function is real. c_j Parameters to be determined

 $f_{\rm j}\,$ called Basis set (they must stasfy the boundary condition) so the Variation function

$$\begin{split} \int \phi^* \phi \partial t &= \int \sum_{j=1}^n c_j f_j \sum_{k=1}^n c_k f_k = \sum_{j=1}^n c_j \sum_{k=1}^n c_k \int f_j f_k \partial t \\ the \text{ variational integral} \qquad W &= \frac{\int \phi^* H \phi \partial t}{\int \phi^* \phi \partial t} \quad \text{for the numenator} \\ \int \phi^* H \phi \partial t &= \int \sum_{j=1}^n c_j f_j H \sum_{k=1}^n c_k f_k = \sum_{j=1}^n c_j \sum_{k=1}^n c_k \int f_j H f_k \partial t \\ \text{assume} \qquad H_{jk} &= \int f_j H f_k \partial t \\ \int \phi^* \phi \partial t &= \sum_{j=1}^n c_j \sum_{k=1}^n c_k H_{jk} \qquad \qquad \int \phi^* \phi \partial t = \sum_{j=1}^n c_j \sum_{k=1}^n c_k S_{jk} \\ W &= \frac{\int \phi^* H \phi \partial t}{\int \phi^* \phi \partial t} = \frac{\sum_{j=1}^n c_j \sum_{k=1}^n c_k F_{jk}}{\sum_{j=1}^n c_j \sum_{k=1}^n c_k S_{jk}} \end{split}$$

Slide 18

So lets evaluate it.....

$$W = \frac{\int \phi^* H \phi \partial t}{\int \phi^* \phi \partial t} = \frac{\sum_{j=1}^n c_j \sum_{k=1}^n c_k H_{jk}}{\sum_{j=1}^n c_j \sum_{k=1}^n c_j \sum_{k=1}^n c_k S_{jk}} \quad \text{and so } W \sum_{j=1}^n c_j \sum_{k=1}^n c_k S_{jk} = \sum_{j=1}^n c_j \sum_{k=1}^n c_k H_{jk}$$

we can minimize Win a way to approach a position of $E_1[W \ge E_1]$. The variational integral W is afunction of of the **n** independent variable $W=W(c_1, c_2, c_3, \dots, c_n)$ minimize W mean $\frac{\partial W}{\partial c_i} = 0$

the proof is not important lets go to the results

$$\sum_{k=1}^{n} (H_{ik} - S_{ik}W)c_{k} = 0$$

i = 1,2,3,4,5.....,*n*
It is a set of simultaneous Linear homogeneous
equations in the unknown $c_{1,}$ $c_{2,}c_{3,}...c_{n}f_{n}$
 $\phi = c_{1}f_{1} + c_{2}f_{2} + c_{3}f_{3} + c_{4}f_{4} ++c_{n}f_{n} = \sum_{i=1}^{n} c_{i}f_{i}$

Slide 19

The solution of the equation is:

$$\sum_{k=1}^{n} (H_{ik} - S_{ik}W)c_{k} = 0 \qquad i = 1, 2, 3, 4, 5, \dots, n$$

$$(H_{11} - S_{11}W)c_{1} + (H_{12} - S_{12}W)c_{2} + (H_{13} - S_{13}W)c_{1} + \dots + (H_{1n} - S_{1n}W)c_{n} = 0$$

$$(H_{21} - S_{21}W)c_{1} + (H_{22} - S_{22}W)c_{2} + (H_{23} - S_{23}W)c_{1} + \dots + (H_{2n} - S_{2n}W)c_{n} = 0$$

$$(H_{31} - S_{31}W)c_{1} + (H_{32} - S_{32}W)c_{2} + (H_{33} - S_{33}W)c_{1} + \dots + (H_{3n} - S_{3n}W)c_{n} = 0$$

$$\begin{pmatrix} H_{11} - S_{11}W \end{pmatrix} c_1 + \begin{pmatrix} H_{12} - S_{12}W \end{pmatrix} c_2 + \begin{pmatrix} H_{13} - S_{13}W \end{pmatrix} c_1 + \dots + \begin{pmatrix} H_{1n} - S_{1n}W \end{pmatrix} c_n = 0$$

$$\begin{pmatrix} H_{11} - S_{11}W & H_{12} - S_{22}W \dots & H_{1n} - S_{1n}W \\ \vdots & \ddots & \vdots \\ H_{n1} - S_{n1}W & H_{n2} - S_{n2}W \dots & H_{nn} - S_{nn}W \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix} = 0$$

Matrix used to solve itfor n = 2

•

$$\begin{pmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \qquad \det(H_{ij} - S_{ij}W) = 0$$
 Slide 2

Example:

Add a functions to the function x(I-x) to form a linear variation function for a particle in 1-D box of length I .Find the approximate energies and wave function of the lowest four states? Answer:

$$\phi = \sum_{j=1}^{n} c_j f_j \qquad n = 4 \text{ so} \qquad \phi = \sum_{j=1}^{4} c_j f_j$$

$$f_1 = x(l-x)$$

$$f_2 = x^2(l-x)^2 \quad f_2 \text{ is well behaved and obeys boundary conditions at } x = 0 \text{ and } x = l$$

There are an infinite number of possible well-behaved functions that could be used for f_2 , f_3 , and f_4 . The function f_2 obeys the boundary conditions of vanishing at x = 0 and x = l.

we shall add in two functions that are odd. An odd function must vanish at the origin and vanish at the box midpoint $x = \frac{1}{2}l$, as well as at x = 0 and l. A simple function with these properties is f3 and f4

We got f3 and f4 by multiply f2 and f3 by (1/2 I - x)

$$f_{1} = x(l-x) \quad \text{multiply by } (\frac{1}{2}l-x) \text{ to get } f_{3}$$

$$f_{2} = x^{2}(l-x)^{2} \quad \text{multiply by } (\frac{1}{2}l-x) \text{ to get } f_{4}$$

$$f_{3} = x(l-x)\left(\frac{1}{2}l-x\right)$$

$$f_{4} = x^{2}(l-x)^{2}\left(\frac{1}{2}l-x\right)$$
since f_{1} and f_{2} are even and f_{3} and f_{4} are odd so
$$S_{13} = S_{31} = 0 \quad S_{14} = S_{41} = 0 \quad S_{23} = S_{32} = 0 \quad S_{24} = S_{42} = 0$$
and

$$H_{13} = H_{31} = 0$$
 $H_{14} = H_{41} = 0$ $H_{23} = H_{32} = 0$ $H_{24} = H_{42} = 0$

$\begin{array}{c} \textbf{The secular equation becomeince}} \\ H_{11} - S_{11}W & H_{12} - S_{12}W & H_{13} - S_{13}W & H_{14} - S_{14}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W & H_{23} - S_{23}W & H_{24} - S_{24}W \\ H_{31} - S_{31}W & H_{32} - S_{32}W & H_{33} - S_{33}W & H_{34} - S_{34}W \\ H_{41} - S_{41}W & H_{42} - S_{42}W & H_{43} - S_{43}W & H_{44} - S_{44}W \\ \end{array} \\ \begin{array}{c} \textbf{S}_{13} = \textbf{S}_{31} = 0 & S_{14} = \textbf{S}_{41} = 0 \\ S_{23} = \textbf{S}_{32} = 0 & S_{24} = \textbf{S}_{42} = 0 \\ \textbf{and} \\ H_{13} = \textbf{H}_{31} = 0 & H_{14} = \textbf{H}_{41} = 0 \\ H_{23} = \textbf{H}_{32} = 0 & H_{24} = \textbf{H}_{42} = 0 \end{array} \right)$

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W & 0 & 0 \\ H_{21} - S_{21}W & H_{22} - S_{22}W & 0 & 0 \\ 0 & 0 & H_{33} - S_{33}W & H_{34} - S_{34}W \\ 0 & 0 & H_{43} - S_{43}W & H_{44} - S_{44}W \end{vmatrix} = 0 \text{ so}$$

$$\begin{pmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W \end{pmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 & \begin{pmatrix} H_{33} - S_{33}W & H_{34} - S_{34}W \\ H_{43} - S_{43}W & H_{44} - S_{44}W \end{pmatrix} \begin{bmatrix} c_3 \\ c_4 \end{bmatrix} = 0 \\ (H_{11} - S_{11}W)c_1 + (H_{12} - S_{12}W)c_2 = 0 & (H_{33} - S_{33}W)c_3 + (H_{34} - S_{34}W)c_3 = 0 \\ (H_{21} - S_{21}W)c_1 + (H_{22} - S_{22}W)c_2 = 0 & (H_{43} - S_{43}W)c_4 + (H_{44} - S_{44}W)c_4 = 0 \end{aligned}$$

Evaluate H₁₁ S₁₁....etc



Energy states

$$\begin{pmatrix} \frac{\hbar^2 l^3}{6m} - \frac{l^5}{30} W & \frac{\hbar^2 l^5}{30m} - \frac{l^7}{140} W\\ \frac{\hbar^2 l^5}{30m} - \frac{l^7}{140} W & \frac{\hbar^2 l^7}{105m} - \frac{l^9}{630} W \end{pmatrix} = 0 \quad so$$

$$W = \left(\frac{\hbar^2}{ml^2}\right) \left(28 \pm \sqrt{532}\right) = \left(\begin{array}{c} 0.1250018 \ h^2/ml^2\\ 1.293495 \ h^2/ml^2\end{array}\right) \text{ and from } c_3 \text{ and } c_4 \text{ matrix}$$
$$W = \left(\frac{\hbar^2}{ml^2}\right) \left(60 \pm \sqrt{1620}\right) = \left(\begin{array}{c} 0.500293 \ h^2/ml^2\\ 2.5393425 \ h^2/ml^2\end{array}\right)$$
so the $\left(ml^2/h^2\right) W$ values are :
 0.1250018 , 0.500293 , 1.293495 and 2.5393425 are compared to
 0.125 , 0.5 , 1.125 and 2

for the four lewst stated in exact solution of PIB

Wave functions

Substitution of $W = 0.1250018 h^2 / ml^2$ in $(H_{11} - S_{11}W)c_1 + (H_{12} - S_{12}W)c_2 = 0$ $(H_{21} - S_{21}W)c_1 + (H_{22} - S_{22}W)c_2 = 0$ give $-0.061144c_1 + 0.053960c_2l^2 = 0 \dots (2)$ assume $c_1 = k$ so for eqn 1 $0.023095c_1 - 0.02038$ $c_2l^2 = 0$ will be $0.023095k = 0.02038 \quad c_2 l^2 \implies c_2 = 1.132 \text{k}/l^2$ to find k $\langle \phi_1 / \phi_1 \rangle = 1$ and so $\langle (c_1 f_1 + c_2 f_2) / (c_1 f_1 + c_2 f_2) \rangle$ $= \langle (kf_1 + 1.132k/l^2) / (kf_1 + 1.132k/l^2) = 1$ $k = 4.404/l^{5/2}$ $\phi_1 = c_1 f_1 + c_2 f_2 = 4.404 f_1 l^{5/2} + 4.990 f_1 l^{9/2}$ $\phi_{1} = l^{-1/2} \left[4.404 \left(\frac{x}{l} \right) \left(1 - \left(\frac{x}{l} \right) \right) + 4.990 \left(\frac{x}{l} \right)^{2} \left(1 - \left(\frac{x}{l} \right) \right)^{2} \right]$

using W2,W3 and W4 we will get the following normalized function in which $X = \frac{x}{1}$

The four wavefunctions

$$X = \frac{x}{l}$$

$$\phi_{1} = l^{-1/2} \left[4.404X \left(1 - X \right) + 4.990X^{2} \left(1 - X \right)^{2} \right]$$

$$\phi_{2} = l^{-1/2} \left[16.78X \left(1 - X \right) \left(1 - X \right) \left(\frac{1}{2} - X \right) + 71.85X^{2} \left(1 - X \right)^{2} \left(\frac{1}{2} - X \right) \right]$$

$$\phi_{3} = l^{-1/2} \left[28.65X \left(1 - X \right) \left(1 - X \right) - 132.7X^{2} \left(1 - X \right)^{2} \right]$$

$$\phi_{4} = l^{-1/2} \left[98.99X \left(1 - X \right) \left(\frac{1}{2} - X \right) - 572.3X^{2} \left(1 - X \right)^{2} \left(\frac{1}{2} - X \right) \right]$$

Application

Time-Independent Perturbation Theory Variation method

The Helium Atom Schrödinger Equation



The Schrödinger Equation

$$H = -\frac{1}{2}\nabla_1^2(\vec{r_1}) - \frac{1}{2}\nabla_2^2(\vec{r_2}) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} - \frac{Z}{r_2} - \frac{Z}{r_1} - \frac{Z}{r_1} - \frac{Z}{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2} - \frac{Z}{r_1} - \frac{Z}{r_1} - \frac{Z}{r_2} - \frac{Z}{r_1} - \frac{Z}{r_1} - \frac{Z}{r_2} - \frac{Z}{r_1} - \frac{Z}{r_1} - \frac{Z}{r_2} - \frac{Z}{r_1} - \frac{Z}{r_1}$$

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

$$H\Psi\left(\vec{r}_{1},\vec{r}_{2}\right)=E\Psi\left(\vec{r}_{1},\vec{r}_{2}\right)$$

 Ψ depends upon the coordinates of both electrons



Can we separate variables?

 $\Psi(\vec{r}_{1},\vec{r}_{2}) = \psi_{1}(\vec{r}_{1}) \cdot \psi_{2}(\vec{r}_{2})$

Nope!! The last term in the Hamiltonian messes us up.

The Experimental Electronic Energy of He



Reference State

By definition, the QM reference state (for which E=0) for atoms and molecules is when all nuclei and electrons are at infinite separation.

 $E_{He} = -[IE_1 + IE_2]$ $E_{He} = -[24.59 \text{ eV} + 54.42 \text{ eV}]$ $E_{He} = -79.01 \text{ eV}$ or $E_{He} = -2.9037 \text{ au} \text{ (hartrees)}$

The Independent Particle Model

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

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

 $\left[H_{1}(\vec{r}_{1}) + H_{2}(\vec{r}_{2})\right]\psi_{1}(\vec{r}_{1}) \cdot \psi_{2}(\vec{r}_{2}) = E\psi_{1}(\vec{r}) \cdot \psi_{2}(\vec{r}_{2})$

$$H_{1}(\vec{r}_{1})\psi_{1}(\vec{r}_{1}) = E_{1}\psi_{1}(\vec{r}_{1}) \quad \text{and} \quad H_{2}(\vec{r}_{2})\psi_{2}(\vec{r}_{2}) = E_{2}\psi_{2}(\vec{r}_{2})$$
$$\left[-\frac{1}{2}\nabla_{1}^{2}(\vec{r}_{1}) - \frac{Z}{r_{1}}\right]\psi_{1}(\vec{r}_{1}) = E_{1}\psi_{1}(\vec{r}_{1}) \quad \left[-\frac{1}{2}\nabla_{2}^{2}(\vec{r}_{2}) - \frac{Z}{r_{2}}\right]\psi_{2}(\vec{r}_{2}) = E_{2}\psi_{2}(\vec{r}_{2})$$

Hey!!! These are just the one electron Schrödinger Equations for "hydrogenlike" atoms. For Z=2, we have He⁺.

We already solved this problem in Chapter 6.

Wavefunctions

 $\psi_1^{n_1l_1m_1}(\vec{r_1}) = A \cdot R_{n_1l_1}(r_1) \cdot Y_{l_1m_1}(\theta_1, \varphi_1) \qquad \qquad \psi_2^{n_2l_2m_2}(\vec{r_2}) = A \cdot R_{n_2l_2}(r_2) \cdot Y_{l_2m_2}(\theta_2, \varphi_2)$ Ground State Wavefunctions

(1s: n=1,I=0,m=0)

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

Remember that in atomic units, $a_0 = 1$ bohr

Energies



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

 $Z = 2 \text{ for He}$

 $E_{exp} = -2.9037 \ a.u. (hartrees)$

Our calculated Ground State Energy is 38% lower than experiment.

This is because, by throwing out the $1/r_{12}$ term in the Hamiltonian, we ignored the electron-electron repulsive energy, which is positive.

Perturbation Theory Treatment of Helium

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

The Helium Hamiltonian can be rewritten as:

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

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

 $H^{(1)} = +\frac{1}{r_{12}}$

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.

Zeroth Order Energy and Wavefunction

 $H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$

The "Zeroth Order" Ground State energy is:

$$E = E_1 + E_2 = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 \quad a.u. = -4.00a.u.$$

The "Zeroth Order" wavefunction is the product of He⁺ 1s wavefunctions for electrons 1 and 2

$$\psi^{(0)} = \psi_1^{100}(\vec{r_1}) \cdot \psi_2^{100}(\vec{r_2}) = \left[\left(\frac{Z^3}{\pi} \right)^{1/2} e^{-Zr_1} \right] \cdot \left[\left(\frac{Z^3}{\pi} \right)^{1/2} e^{-Zr_2} \right]$$

$$\psi^{(0)} = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} = A e^{-Z(r_1+r_2)}$$

First Order Perturbation Theory Correction to the Energy

In Chapter 5, we learned that the correction to the energy, ΔE [or $E^{(1)}$] is:

 $\Delta E = E^{(1)} = \int \psi^{(0)} * H^{(1)} \psi^{(0)} d\tau$

For the He atom: $H^{(1)} = +\frac{1}{r_{12}}$ and $\psi^{(0)} = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} = A e^{-Z(r_1+r_2)}$ Therefore: $\Delta E = A^2 \int d\vec{r_1} \int d\vec{r_2} e^{-2Zr_1} e^{-2Zr_2} \frac{1}{r_{12}}$ where $d\vec{r_1} \equiv r_1^2 \sin(\theta_1) dr_1 d\theta_1 d\varphi_1$ $d\vec{r_2} \equiv r_2^2 \sin(\theta_2) dr_2 d\theta_2 d\varphi_2$

The evaluation of this integral is rather difficult, and in outlined in several texts. ζ

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

e.g. Introduction to Quantum Mechanics in Chemistry, by M. A. Ratner and G. C. Schatz, Appendix B.

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

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

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

Variational Method Treatment of Helium

Recall that we proved earlier in this Chapter 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!!

$$< E >= E_{trial} = rac{\left\langle \varphi \left| H \left| \varphi \right\rangle \right\rangle}{\left\langle \varphi \left| \varphi \right\rangle \right\rangle} = rac{\int \varphi^* H \varphi d \tau}{\int \varphi^* \varphi d \tau} \ge E_0$$

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 au) 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.

A Trial Wavefunction for Helium

Recall that when we assumed an Independent Particle model for Helium, we obtained a wavefunction which is the product of two 1s He⁺ functions.

$$\varphi = \psi_1^{100}(\vec{r}_1) \cdot \psi_2^{100}(\vec{r}_2) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr_1} e^{-Zr_2} = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Z(r_1+r_2)}$$

For a trial wavefunction on which to apply the Variational Method, we can use an "effective" atomic number, Z', rather than Z=2.

By using methods similar to those above (Independent Particle Model + First Order Perturbation Theory Integral), it can be shown that

for
$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$
 Z = 2 for He
and $\varphi = \left(\frac{Z'}{\pi}\right)^{1/2} e^{-Z'(r_1 + r_2)}$

$$E_{trial} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} = \frac{Z'^2}{2} + \frac{Z'^2}{2} - ZZ' - ZZ' + \frac{5}{8}Z'$$

KE(1) KE(2) PE(1) PE(2) PE(12)

$$E_{trial} = Z'^2 - 2ZZ' + \frac{5}{8}Z' = Z'^2 - 4Z' + \frac{5}{8}Z' = Z'^2 - \frac{27}{8}Z'$$

He: $Z = 2$



We want to find the value of Z' which minimizes the energy, E_{trial} .

Once again, we can either use trial-and-error (Yecch!!) or basic Calculus.



 $E_{trial} = -2.848 \ au$ (1.9% higher than experiment)

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

The lower value for the "effective" atomic number (Z'=1.69 vs. Z=2) reflects "screening" due to the mutual repulsion of the electrons.

Better Variational Wavefunctions

One can improve (i.e. lower the energy) by employing improved wavefunctions with additional variational parameters.

A Two Parameter Wavefunction

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

 $\varphi = A \left[e^{-Z'r_1} e^{-Z'r_2} + e^{-Z'r_1} e^{-Z'r_2} \right]$ (we must keep treatment of the two electrons symmetrical)

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 $E_{trial} = -2.876$ au (1.0% higher than experiment) Z'' = 2.18

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

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

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 $E_{trial} = -2.892$ au (0.4% higher than experiment) b = 0.364

The second term, $1+br_{12}$, accounts for electron correlation.

It increases the probability (higher ϕ^2) of finding the two electrons further apart (higher r_{12}).

A Three Parameter Wavefunction

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

We have incorporated both ways of including electron correlation.

When E_{trial} is evaluated as a function of Z', Z" and b, and the values of the 3 parameters are varied to minimize the energy, the results are:

Z' = 1.435 $E_{trial} = -2.9014$ au (0.08% higher than experiment) Z'' = 2.209 b = 0.292

Even More Parameters

When we used a wavefunction of the form: $\varphi = A \left[e^{-Z'(r_1 + r_2)} \left(1 + b \cdot r_{12} \right) \right]$

The variational energy was within 0.4% of experiment.

We can improve upon this significantly by generalizing ϕ to:

$$\varphi = A \left[e^{-Z'(r_1 + r_2)} \left(1 + g(r_1, r_2, r_{12}) \right) \right]$$

 $g(r_1, r_2, r_{12})$ is a polynomial function of the 3 interparticle distances.

Hylleras (1929) used a 9 term polynomial (10 total parameters) to get: $E_{trial} = -2.9036$ au (0.003% higher than experiment)

Kinoshita (1957) used a 38 term polynomial (39 total parameters) to get: $E_{trial} = -2.9037$ au (~0% Error)

To my knowledge, the record to date was a 1078 parameter wavefunction [Pekeris (1959)]

A Summary of Results			
$E_{expt.} = -2.90$	E _{expt.} = -2.9037 au		
Wavefunction	Energy	% Error	
$A e^{-Z(r_1+r_2)}$	-2.75 au	+5.3%	
$A e^{-Z'(r_1+r_2)}$	-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%	
$A\left[e^{-Z'(r_1+r_2)}\left(1+b\cdot r_{12}\right)\right]$	-2.892	+0.4%	
$A\left[\left(e^{-Z'r_{1}}e^{-Z'r_{2}}+e^{-Z'r_{1}}e^{-Z'r_{2}}\right)\cdot\left(1+b\cdot r_{12}\right)\right]$	-2.9014	+0.08%	
$\varphi = A \left[e^{-Z'(r_1 + r_2)} \left(1 + g(r_1, r_2, r_{12}) \right) \right]$	-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.