## Lecture 7 <br> 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 $\phi$ is any normalized well behaved Function of the coordinates of the system particle that satisfy the Boundary condition of the problem then
$\int \varphi^{*} H \varphi d \tau \geq E_{0} \quad \varphi$ is normalized wavefunction
if the function $\varphi$ is not normalized then

$$
\frac{\int \varphi^{*} H \varphi d \tau}{\int \varphi^{*} \varphi d \tau} \geq E_{0}
$$

$\varphi$ is called trial function
$\int \varphi^{*} H \varphi d \tau$ called Variation Integral $=\mathrm{W}$

## 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 $\phi$
II. Then we vary the parameters so as to mininmize the variational integral W
III. The lowest one is the best $\quad \frac{\partial W}{\partial c}=0$

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, $\phi$, then the Expectation Value for the energy is greater than or equal to the exact ground state energy, $\mathrm{E}_{0}$.

$$
<E>=E_{\text {trial }}=\frac{\langle\varphi| H|\varphi\rangle}{\langle\varphi \mid \varphi\rangle}=\frac{\int \varphi^{*} H \varphi d \tau}{\int \varphi^{*} \varphi d \tau} \geq E_{0}
$$

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

Proof: $\left\langle E>-E_{0}=\frac{\int \varphi^{*} H \varphi d \tau}{\int \varphi^{*} \varphi d \tau}-E_{0} \frac{\int \varphi^{*} \varphi d \tau}{\int \varphi^{*}{ }_{\rho} d \tau} \geq 0\right.$

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

Assume that we know the exact solutions, $\psi_{n}: H \psi_{n}=E_{n} \psi_{n}$

It was discussed that the set of eigenfunctions, $\psi_{n}$, 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 $<\mathrm{E}>$ to get:

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

$$
\begin{aligned}
<E>-E_{0}=\frac{\int\left(\sum_{m} c_{m} \psi_{m}\right)^{*}\left(\sum_{n} c_{n}\left(E_{n}-E_{0}\right) \psi_{n}\right) d \tau}{\int\left(\sum_{m} c_{m} \psi_{m}\right)^{*} \sum_{n} c_{n} \psi_{n} d \tau}=\frac{\sum_{m} \sum_{n} c_{m}^{*} c_{n}\left(E_{n}-E_{0}\right) \int \psi_{m}^{*} \psi_{n} d \tau}{\sum_{m} \sum_{n} c_{m}^{*} c_{n} \int \psi_{m}^{*} \psi_{n} d \tau} \\
<E>-E_{0}=\frac{\sum_{m} \sum_{n} c_{m}^{*} c_{n}\left(E_{n}-E_{0}\right) \delta_{m n}}{\sum_{m} \sum_{n} c_{m}^{*} c_{n} \delta_{m n}} \text { because } \int \psi_{m}^{*} \psi_{n} d \tau=\delta_{m n} \\
\psi \text { orthonormality } \\
<E>-E_{0}=\frac{\sum_{n} c_{n}^{*} c_{n}\left(E_{n}-E_{0}\right)}{\sum_{n} c_{n}^{*} c_{n}} \geq 0 \text { because } \begin{array}{ll}
c_{n}^{*} c_{n} \geq 0 \\
& E_{n}-E_{0} \geq 0
\end{array}
\end{aligned}
$$

Therefore: $\langle E\rangle=E_{\text {trial }}=\frac{\langle\varphi| H|\varphi\rangle}{\langle\varphi \mid \varphi\rangle} \geq E_{0}$

## Applications of the Variational Method

## The Particle in a Box

We learned that, for a PIB:

$$
\begin{aligned}
& \psi_{n}=\sqrt{\frac{2}{a}} \sin \left(\frac{n \pi x}{a}\right) \\
& E_{n}=\frac{n^{2} h^{2}}{8 m a^{2}}
\end{aligned} \xrightarrow[\text { State }]{\text { Ground }} \begin{aligned}
& \psi_{1}=\sqrt{\frac{2}{a}} \sin \left(\frac{\pi x}{a}\right) \\
& E_{1}=\frac{h^{2}}{8 m a^{2}}=0.125 \frac{h^{2}}{m a^{2}}
\end{aligned}
$$

In a HW problem, you were asked to show that for the approximate PIB wavefunction $\psi_{\text {app }}=A x(a-x)$
The expectation value for $\left\langle\mathrm{p}^{2}\right\rangle$ is $\left\langle p^{2}\right\rangle=\frac{10 \hbar^{2}}{a^{2}}$
Let's calculate $\langle\mathrm{E}\rangle:\langle E\rangle=\left\langle\frac{p^{2}}{2 m}\right\rangle=\frac{\left\langle p^{2}\right\rangle}{2 m}=\frac{10 \hbar^{2}}{2 m a^{2}}=\frac{5 h^{2}}{4 \pi^{2} m a^{2}}=0.12665 \frac{h^{2}}{m a^{2}}$

Exact GS Energy: $E_{1}=0.125 \frac{h^{2}}{m a^{2}} \quad$ using $\psi_{1}=\sqrt{\frac{2}{a}} \sin \left(\frac{\pi x}{a}\right)$
Approx. GS Energy: $E_{a p p}=0.12665 \frac{h^{2}}{m a^{2}}$ using $\psi_{\text {app }}=A x(a-x)$
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: $\psi_{a p p}=A x^{2}(a-x)^{2}$
It can be shown (with a considerable amount of algebra) that:

$$
E_{a p p}=\frac{6 \hbar^{2}}{m a^{2}}=\frac{6 h^{2}}{4 \pi^{2}} \frac{1}{m a^{2}}=0.152 \frac{h^{2}}{m a^{2}} 21.6 \% \text { Error }
$$

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


$$
\psi_{a p p}^{(x \psi 1}=A \stackrel{\psi 2)}{x}(a-x) \quad E_{a p p}=0.12665 \frac{h^{2}}{m a^{2}}
$$


$\psi_{a p p} \stackrel{\left(x \psi_{3}\right.}{=} A x^{\psi_{1}}(a-x)^{2}$
$E_{a p p}=0.152 \frac{h^{2}}{m a^{2}}$

## 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:

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

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: ${ }^{a}$

$$
R=\frac{B}{A}=\frac{1.133}{a^{2}} \text { and } E_{a p p}=0.1250018 \frac{h^{2}}{m a^{2}} \quad \begin{aligned}
& \text { 0.0015\% Error } \\
& \text { Not bad!! }
\end{aligned}
$$

a) Quantum Chemistry, $7^{\text {th }}$ Ed., by I. N. Levine,


$$
\begin{aligned}
&(x ~ w 1 / ~ w 4) \\
& \psi_{a p p}=A\left[x(a-x)+R x^{2}(a-x)^{2}\right] \\
& E_{a p p}=0.1250018 \frac{h^{2}}{m a^{2}}
\end{aligned}
$$

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

## An Approximate Harmonic Oscillator Wavefunction

$\begin{aligned} \text { Exact HO Ground State: } H=-\frac{\hbar^{2}}{2 \mu} \frac{d^{2}}{d x^{2}}+\frac{1}{2} k x^{2} \quad & \psi_{0}=A e^{-\alpha x^{2} / 2} \\ E_{0} & =\frac{1}{2} \hbar \omega=0.5 \hbar \omega\end{aligned}$
Let's try an approximate wavefunction: $\psi_{a p p}=A \cos (\lambda x)-\frac{\pi}{2 \lambda} \leq x \leq \frac{\pi}{2 \lambda}$

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

One can use $\psi_{\text {app }}$ to calculate an estimate to the Ground State energy by:

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

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

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

Note: $\sqrt{2 C}=0.568$ (will be needed later in the calculation).
Because $E_{\text {app }}$ is a function of $\lambda^{2}$ (rather than $\lambda$ ), it is more convenient to consider the variational parameter to be $\Delta=\lambda^{2}$.

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

Note: $\sqrt{2 C}=0.568$ (will be needed later in the calculation).
The approximate GS energy is a function of the variational parameter, $\Delta$

One "could" find the best value of $\Delta$, which minimizes $\mathrm{E}_{\text {app }}$, by trial and error.

But there must be a better way!!!

$E_{\text {app }}=\frac{\hbar^{2} \Delta}{2 \mu}+C \frac{k}{\Delta} \quad$ where $\quad \Delta=\lambda^{2} \quad C=\frac{\pi^{2}}{24}-\frac{1}{4}=0.1612 \quad \sqrt{2 C}=0.568$
Sure!! At the minimum in $\mathrm{E}_{\text {app }}$ vs. $\Delta$, one has: $\frac{d E_{\text {app }}}{d \Delta}=0$

$$
\frac{d\left[\frac{\hbar^{2} \Delta}{2 \mu}+C \frac{k}{\Delta}\right]}{d \Delta}=0
$$

On
Board
$\Delta_{\text {best }}=\sqrt{2 C} \frac{\sqrt{k \mu}}{\hbar}=0.568 \frac{\sqrt{k \mu}}{\hbar}$
On
Board


It wasn't that great a wavefunction in the first place.
$E_{\text {best }}=0.284 \hbar \omega+0.284 \hbar \omega=0.568 \hbar \omega \quad 13.6 \%$ error (compared to $\mathrm{E}_{0}=0.5 \hbar \omega$ )
Note: We will use: $\frac{\sqrt{k \mu}}{\mu}=\sqrt{\frac{k}{\mu}}=\omega \quad$ and $\quad \frac{k}{\sqrt{k \mu}}=\sqrt{\frac{k}{\mu}}=\omega$

## 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 $f_{1}, f_{2}, \mathrm{c}, f_{n}$ :
So $\phi=c_{1} f_{1}+c_{2} f_{2}+c_{3} f_{3}+\ldots \ldots .+c_{n} f_{n}$

A linear variation function is a linear combination of $n$ linearly independent functions $f_{1}, f_{2}, \mathrm{c}, f_{n}$ :
So $\Phi=c_{1} f_{1}+c_{2} f_{2}+c_{3} f_{3}+\ldots \ldots .+c_{n} f_{n}+$
$\phi=\sum_{j=1}^{n} c_{j} f_{j} \quad \phi$ trial function is real. $\quad c_{j}$ Parameters to be determined
$\mathrm{f}_{\mathrm{j}}$ 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 $\quad S_{j k}=\int f_{j} f_{k} \partial t \quad$ called overlap integral
$\int \phi^{*} \phi \partial t=\sum_{j=1}^{n} c_{j} \sum_{k=1}^{n} c_{k} S_{j k}$
the variational integral $W=\frac{\int \phi^{*} H \phi \partial t}{\int \phi^{*} \phi \partial t}$
$\phi=\sum_{j=1}^{n} c_{j} f_{j} \quad \phi$ trial function is real. $\quad \mathrm{c}_{j}$ Parameters to be determined
$\mathrm{f}_{\mathrm{j}}$ called Basis set ( they must stasfy the boundary condition)
so the Variation function

$$
\int \phi^{*} \phi \partial t=\int \sum_{j=1}^{n} c_{j} f_{j} \sum_{k=1}^{n} c_{k} f_{k}=\sum_{j=1}^{n} c_{j} \sum_{k=1}^{n} c_{k} \int f_{j} f_{k} \partial t
$$

the variational integral $\quad W=\frac{\int \phi^{*} H \phi \partial t}{\int \phi^{*} \phi \partial t}$ for the numenator

$$
\int \phi^{*} H \phi \partial t=\int \sum_{j=1}^{n} c_{j} f_{j} H \sum_{k=1}^{n} c_{k} f_{k}=\sum_{j=1}^{n} c_{j} \sum_{k=1}^{n} c_{k} \int f_{j} H f_{k} \partial t
$$

$$
\text { assume } \quad H_{j k}=\int f_{j} H f_{k} \partial t
$$

$$
\int \phi^{*} \phi \partial t=\sum_{j=1}^{n} c_{j} \sum_{k=1}^{n} c_{k} H_{j k} \quad \int \phi^{*} \phi \partial t=\sum_{j=1}^{n} c_{j} \sum_{k=1}^{n} c_{k} S_{j k}
$$

$$
W=\frac{\int \phi^{*} H \phi \partial t}{\int \phi^{*} \phi \partial t}=\frac{\sum_{j=1}^{n} c_{j} \sum_{k=1}^{n} c_{k} H_{j k}}{\sum_{j=1}^{n} c_{j} \sum_{k=1}^{n} c_{k} S_{j k}}
$$

So lets evaluate it.

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

we can minimize Win a way to approach a position of $\mathrm{E}_{1}\left[W \geq E_{1}\right]$.
The variational integral W is afunction of of the n independent variable $\mathrm{W}=\mathrm{W}\left(\mathrm{c}_{1}, c_{2}, c_{3} \ldots \ldots . c_{n}\right)$
minimize W mean $\frac{\partial W}{\partial c_{i}}=0$
the proof is not important lets go to the results
$\sum_{k=1}^{n}\left(H_{i k}-S_{i k} W\right) c_{k}=0 \quad i=1,2,3,4,5 \ldots \ldots . ., n$
It is a set of simultaneous Linear homogeneous equations in the unknown $c_{1}, c_{2}, c_{3}, \ldots c_{n} f_{n}$

$$
\phi=c_{1} f_{1}+c_{2} f_{2}+c_{3} f_{3}+c_{4} f_{4}+\ldots \ldots \ldots \ldots \ldots+c_{n} f_{n}=\sum_{j=1}^{n} c_{j} f_{j}
$$

## The solution of the equation is:

$$
\begin{aligned}
& \sum_{k=1}^{n}\left(H_{i k}-S_{i k} W\right) c_{k}=0 \quad i=1,2,3,4,5 \ldots \ldots ., n \\
& \left(H_{11}-S_{11} W\right) c_{1}+\left(H_{12}-S_{12} W\right) c_{2}+\left(H_{13}-S_{13} W\right) c_{1}+\ldots \ldots \ldots \ldots \ldots+\left(H_{1 n}-S_{1 n} W\right) c_{n}=0 \\
& \left(H_{21}-S_{21} W\right) c_{1}+\left(H_{22}-S_{22} W\right) c_{2}+\left(H_{23}-S_{23} W\right) c_{1}+\ldots \ldots \ldots \ldots \ldots+\left(H_{2 n}-S_{2 n} W\right) c_{n}=0 \\
& \left(H_{31}-S_{31} W\right) c_{1}+\left(H_{32}-S_{32} W\right) c_{2}+\left(H_{33}-S_{33} W\right) c_{1}+\ldots \ldots \ldots \ldots . .+\left(H_{3 n}-S_{3 n} W\right) c_{n}=0 \\
& \cdot \\
& \left(H_{11}-S_{11} W\right) c_{1}+\left(H_{12}-S_{12} W\right) c_{2}+\left(H_{13}-S_{13} W\right) c_{1}+\ldots \ldots \ldots \ldots \ldots+\left(H_{1 n}-S_{1 n} W\right) c_{n}=0 \\
& \left(\begin{array}{ccc}
H_{11}-S_{11} W & H_{12}-S_{22} W \ldots & H_{1 n}-S_{1 n} W \\
\vdots & \ddots & \vdots \\
H_{n 1}-S_{n 1} W & H_{n 2}-S_{n 2} W \ldots & H_{n n}-S_{n n} W
\end{array}\right)\left(\begin{array}{c}
c_{1} \\
\vdots \\
c_{n}
\end{array}\right)=0
\end{aligned}
$$

Matrix used to solve it ..........for $n=2$

$$
\left(\begin{array}{ll}
H_{11}-S_{11} W & H_{12}-S_{12} W \\
H_{21}-S_{21} W & H_{22}-S_{22} W
\end{array}\right)\binom{c_{1}}{c_{2}}=0 \quad \operatorname{det}\left(H_{i j}-S_{i j} W\right)=0
$$

## Example:

Add a functions to the function $x(1-x)$ 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:

$\phi=\sum_{j=1}^{n} c_{j} f_{j} \quad \mathrm{n}=4$ so $\quad \phi=\sum_{j=1}^{4} c_{j} f_{j}$
$f_{1}=x(l-x)$
$f_{2}=x^{2}(l-x)^{2} f_{2}$ is well behaved and obeys boundary conditions at $x=0$ 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 $x=1 / 2 l$, as well as at $x=0$ and $l$. A simple function with these properties is $f 3$ and f 4

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

$$
\begin{aligned}
& f_{1}=x(l-x) \text { multiply by }\left(\frac{1}{2} l-x\right) \text { to get } f_{3} \\
& f_{2}=x^{2}(l-x)^{2} \text { multiply by }\left(\frac{1}{2} l-x\right) \text { to get } f_{4} \\
& f_{3}=x(l-x)\left(\frac{1}{2} l-x\right) \\
& f_{4}=x^{2}(l-x)^{2}\left(\frac{1}{2} l-x\right)
\end{aligned}
$$

since $f_{1}$ and $f_{2}$ are even and $f_{3}$ and $f_{4}$ are odd so $S_{13}=\mathrm{S}_{31}=0 \quad S_{14}=\mathrm{S}_{41}=0 \quad S_{23}=\mathrm{S}_{32}=0 \quad S_{24}=\mathrm{S}_{42}=0$ and

$$
H_{13}=\mathrm{H}_{31}=0 \quad H_{14}=\mathrm{H}_{41}=0 \quad H_{23}=\mathrm{H}_{32}=0 \quad H_{24}=\mathrm{H}_{42}=0
$$

## The secular equation becomennce

$$
\left|\begin{array}{llll}
H_{11}-S_{11} W & H_{12}-S_{12} W & H_{13}-S_{13} W & H_{14}-S_{14} W \\
H_{21}-S_{21} W & H_{22}-S_{22} W & H_{23}-S_{23} W & H_{24}-S_{24} W \\
H_{31}-S_{31} W & H_{32}-S_{32} W & H_{33}-S_{33} W & H_{34}-S_{34} W \\
H_{41}-S_{41} W & H_{42}-S_{42} W & H_{43}-S_{43} W & H_{44}-S_{44} W
\end{array}\right|\left|\begin{array}{ll}
S_{13}=\mathrm{S}_{31}=0 & S_{14}=\mathrm{S}_{41}=0 \\
S_{23}=\mathrm{S}_{32}=0 & S_{24}=\mathrm{S}_{42}=0 \\
\text { and } \\
H_{13}=\mathrm{H}_{31}=0 & H_{14}=\mathrm{H}_{41}=0 \\
H_{23}=\mathrm{H}_{32}=0 & H_{24}=\mathrm{H}_{42}=0
\end{array}\right|
$$

so

$$
\begin{aligned}
& \left|\begin{array}{cccc}
H_{11}-S_{11} W & H_{12}-S_{12} W & 0 & 0 \\
H_{21}-S_{21} W & H_{22}-S_{22} W & 0 & 0 \\
0 & 0 & H_{33}-S_{33} W & H_{34}-S_{34} W \\
0 & 0 & H_{43}-S_{43} W & H_{44}-S_{44} W
\end{array}\right|=0 \text { so } \\
& \left(\begin{array}{ll}
H_{11}-S_{11} W & H_{12}-S_{12} W \\
H_{21}-S_{21} W & H_{22}-S_{22} W
\end{array}\right)\left[\begin{array}{l}
c_{1} \\
c_{2}
\end{array}\right]=0 \\
& \left(H_{11}-S_{11} W\right) c_{1}+\left(H_{12}-S_{12} W\right) c_{2}=0 \\
& \left(H_{21}-S_{21} W\right) c_{1}+\left(H_{22}-S_{22} W\right) c_{2}=0 \\
& \left(\begin{array}{ll}
H_{33}-S_{33} W & H_{34}-S_{34} W \\
H_{43}-S_{43} W & H_{44}-S_{44} W
\end{array}\right)\left[\begin{array}{l}
c_{3} \\
c_{4}
\end{array}\right]=0 \\
& \left(H_{33}-S_{33} W\right) c_{3}+\left(H_{34}-S_{34} W\right) c_{3}=0 \\
& \left(H_{43}-S_{43} W\right) c_{4}+\left(H_{44}-S_{44} W\right) c_{4}=0
\end{aligned}
$$

## Evaluate $\mathrm{H}_{11} \mathrm{~S}_{11} \ldots$ etc

$$
\begin{aligned}
& H_{11}=\left\langle f_{1} \vdots H \vdots f_{1}>=\int_{0}^{l} x(l-x)\left(-\frac{\hbar^{2}}{2 m} \frac{\partial^{2}}{\partial x^{2}}\right)[x(l-x)] \partial x=\frac{\hbar^{2} l^{3}}{6 m}\right. \\
& S_{11}=<f_{1} f_{1}>=\int_{0}^{l} x(l-x)[x(l-x)] \partial x=\frac{l^{5}}{30} \\
& H_{12}=H_{21}=\frac{\hbar^{2} l^{5}}{30 m} \quad S_{12}=S_{21}=\frac{l^{7}}{140} \quad H_{22}=\frac{\hbar^{2} l^{7}}{105 m} \quad S_{22}=\frac{l^{9}}{630} \\
& H_{33}=\frac{\hbar^{2} l^{5}}{40 m} \quad S_{33}=\frac{l^{7}}{840} \quad H_{44}=\frac{\hbar^{2} l^{9}}{1260 m} \quad S_{44}=\frac{l^{11}}{27720} \\
& H_{34}=H_{43}=\frac{\hbar^{2} l^{7}}{280 m} \quad S_{43}=S_{34}=\frac{l^{9}}{5040}
\end{aligned}
$$

## So

## Energy states

$\left(\begin{array}{ll}\frac{\hbar^{2} l^{3}}{6 m}-\frac{l^{5}}{30} W & \frac{\hbar^{2} l^{5}}{30 m}-\frac{l^{7}}{140} W \\ \frac{\hbar^{2} l^{5}}{30 m}-\frac{l^{7}}{140} W & \frac{\hbar^{2} l^{7}}{105 m}-\frac{l^{9}}{630} W\end{array}\right)=0$ so
$W=\left(\frac{\hbar^{2}}{m l^{2}}\right)(28 \pm \sqrt{532})=\binom{0.1250018 h^{2} / m l^{2}}{1.293495 h^{2} / m l^{2}}$ and from $\mathrm{c}_{3}$ and $\mathrm{c}_{4}$ matrix
$W=\left(\frac{\hbar^{2}}{m l^{2}}\right)(60 \pm \sqrt{1620})=\binom{0.500293 h^{2} / m l^{2}}{2.5393425 h^{2} / m l^{2}}$
so the $\left(m l^{2} / h^{2}\right) W$ values are:
$0.1250018,0.500293,1.293495$ and 2.5393425 are compared to
$0.125 \quad, 0.5 \quad, 1.125$ and 2
for the four lewst stated in exact solution of PIB

## Wave functions

Substitution of $W=0.1250018 h^{2} / \mathrm{ml}^{2}$ in
$\left(H_{11}-S_{11} W\right) c_{1}+\left(H_{12}-S_{12} W\right) c_{2}=0$

$$
\left(H_{21}-S_{21} W\right) c_{1}+\left(H_{22}-S_{22} W\right) c_{2}=0
$$

give
$0.023095 c_{1}-0.02038 \quad c_{2} l^{2}=0$
$-0.061144 c_{1}+0.053960 c_{2} l^{2}=0$
assume $\mathrm{c}_{1}=\mathrm{k}$ so for eqn $10.023095 c_{1}-0.02038 \quad c_{2} l^{2}=0$ willbe
$0.023095 k=0.02038 \quad c_{2} l^{2} \Rightarrow c_{2}=1.132 \mathrm{k} / l^{2}$
to find $\mathrm{k}\left\langle\phi_{1} / \phi_{1}\right\rangle=1$ and so $\left\langle\left(\mathrm{c}_{1} f_{1}+c_{2} f_{2}\right) /\left(\mathrm{c}_{1} f_{1}+c_{2} f_{2}\right)\right\rangle$
$=<\left(k f_{1}+1.132 k / l^{2}\right) /\left(k f_{1}+1.132 k / l^{2}\right)=1$
$k=4.404 / l^{5 / 2}$
$\phi_{1}=\mathrm{c}_{1} f_{1}+c_{2} f_{2}=4.404 f_{1} l^{5 / 2}+4.990 f_{1}{ }^{9 / 2}$
$\phi_{1}=l^{-1 / 2}\left[4.404(x / l)(1-(x / l))+4.990(x / l)^{2}(1-(x / l))^{2}\right]$
using $\mathrm{W} 2, \mathrm{~W} 3$ and W 4 we will get the follwing normailzed function in which $\mathrm{X}=\frac{x}{l}$

## The four wavefunctions

$$
\begin{aligned}
& X=\frac{x}{l} \\
& \phi_{1}=l^{-1 / 2}\left[4.404 X(1-X)+4.990 X^{2}(1-X)^{2}\right] \\
& \phi_{2}=l^{-1 / 2}\left[16.78 X(1-X)(1-X)\left(\frac{1}{2}-X\right)+71.85 X^{2}(1-X)^{2}\left(\frac{1}{2}-X\right)\right] \\
& \phi_{3}=l^{-1 / 2}\left[28.65 X(1-X)(1-X)-132.7 X^{2}(1-X)^{2}\right] \\
& \phi_{4}=l^{-1 / 2}\left[98.99 X(1-X)\left(\frac{1}{2}-X\right)-572.3 X^{2}(1-X)^{2}\left(\frac{1}{2}-X\right)\right]
\end{aligned}
$$

## Application

1. Time-Independent Perturbation Theory
2. Variation method

## The Helium Atom Schrödinger Equation

## The Hamiltonian

$$
\begin{aligned}
H= & \frac{p_{1}^{2}\left(\vec{r}_{1}\right)}{2 m}+\frac{p_{2}^{2}\left(\vec{r}_{2}\right)}{2 m}-\frac{Z e^{2}}{4 \pi \varepsilon_{0} r_{1}}-\frac{Z e^{2}}{4 \pi \varepsilon_{0} r_{2}}+\frac{e^{2}}{4 \pi \varepsilon_{0} r_{12}} \\
& \mathrm{KE}(1) \quad \mathrm{KE}(2) \quad \mathrm{PE}(1) \quad \mathrm{PE}(2) \mathrm{PE}(12) \\
H= & -\frac{\hbar^{2}}{2 m} \nabla_{1}^{2}\left(\vec{r}_{1}\right)-\frac{\hbar^{2}}{2 m} \nabla_{2}^{2}\left(\vec{r}_{2}\right)-\frac{Z e^{2}}{4 \pi \varepsilon_{0} r_{1}}-\frac{Z e^{2}}{4 \pi \varepsilon_{0} r_{2}}+\frac{e^{2}}{4 \pi \varepsilon_{0} r_{12}}
\end{aligned}
$$

+Ze

Atomic Units: $\hbar=m=e=4 \pi \varepsilon_{0}=1$

$$
H=-\frac{1}{2} \nabla_{1}^{2}\left(\vec{r}_{1}\right)-\frac{1}{2} \nabla_{2}^{2}\left(\vec{r}_{2}\right)-\frac{Z}{r_{1}}-\frac{Z}{r_{2}}+\frac{1}{r_{12}}
$$

$$
\begin{aligned}
& \nabla_{1}^{2}\left(\vec{r}_{1}\right)=\frac{1}{r_{1}^{2}} \frac{\partial}{\partial r_{1}}\left(r_{1}^{2} \frac{\partial}{\partial r_{1}}\right)+\frac{1}{r_{1}^{2} \sin ^{2} \theta_{1}} \frac{\partial}{\partial \theta_{1}}\left(\sin \theta_{1} \frac{\partial}{\partial \theta_{1}}\right)+\frac{1}{r_{1}^{2} \sin ^{2} \theta_{1}} \frac{\partial^{2}}{\partial \varphi_{1}^{2}} \\
& \nabla_{2}^{2}\left(\vec{r}_{2}\right)=\frac{1}{r_{2}^{2}} \frac{\partial}{\partial r_{2}}\left(r_{2}^{2} \frac{\partial}{\partial r_{2}}\right)+\frac{1}{r_{2}^{2} \sin ^{2} \theta_{2}} \frac{\partial}{\partial \theta_{2}}\left(\sin \theta_{2} \frac{\partial}{\partial \theta_{2}}\right)+\frac{1}{r_{2}^{2} \sin ^{2} \theta_{2}} \frac{\partial^{2}}{\partial \varphi_{2}^{2}}
\end{aligned}
$$

## The Schrödinger Equation

$$
\begin{array}{r}
H=-\frac{1}{2} \nabla_{1}^{2}\left(\vec{r}_{1}\right)-\frac{1}{2} \nabla_{2}^{2}\left(\vec{r}_{2}\right)-\frac{Z}{r_{1}}-\frac{Z}{r_{2}}+\frac{1}{r_{12}} \xrightarrow{H} \longrightarrow \begin{array}{c}
H \Psi\left(\vec{r}_{1}, \vec{r}_{2}\right)=E \Psi\left(\vec{r}_{1}, \vec{r}_{2}\right) \\
\\
\text { 世 depends upon the } \\
\text { coordinates of both electrons }
\end{array} \\
\left.H=H_{1}\left(\vec{r}_{1}\right)+H_{2}\left(\vec{r}_{2}\right)+\frac{1}{r_{12}}\left(\vec{r}_{1}\right)-\frac{Z}{r_{1}}\right]+\left[-\frac{1}{2} \nabla_{2}^{2}\left(\vec{r}_{2}\right)-\frac{Z}{r_{2}}\right]+\frac{1}{r_{12}}
\end{array} \quad \begin{aligned}
& \text { Can we separate variables? } \\
& \text { Electron } \\
& \text { Repulsion }
\end{aligned} \quad \begin{aligned}
& \Psi\left(\vec{r}_{1}, \vec{r}_{2}\right)=\psi_{1}\left(\vec{r}_{1}\right) \cdot \psi_{2}\left(\vec{r}_{2}\right) \\
& \text { Nope!! The last term in the } \\
& \text { Hamiltonian messes us up. }
\end{aligned}
$$

## The Experimental Electronic Energy of He



## Reference State

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

$$
E_{H e}=-\left[I E_{1}+I E_{2}\right]
$$

$$
\mathrm{E}_{\mathrm{He}}=-[24.59 \mathrm{eV}+54.42 \mathrm{eV}]
$$

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

$$
\text { or } \mathrm{E}_{\mathrm{He}}=-2.9037 \text { au (hartrees) }
$$

## The Independent Particle Model

$$
H=\left[-\frac{1}{2} \nabla_{1}^{2}\left(\vec{r}_{1}\right)-\frac{Z}{r_{1}}\right]+\left[-\frac{1}{2} \nabla_{2}^{2}\left(\vec{r}_{2}\right)-\frac{Z}{r_{2}}\right]+\frac{1}{1}
$$

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

$$
H=\left[-\frac{1}{2} \nabla_{1}^{2}\left(\vec{r}_{1}\right)-\frac{Z}{r_{1}}\right]+\left[-\frac{1}{2} \nabla_{2}^{2}\left(\vec{r}_{2}\right)-\frac{Z}{r_{2}}\right]=H_{1}\left(\vec{r}_{1}\right)+H_{2}\left(\vec{r}_{2}\right)
$$

Separation of Variables: Assume that $\Psi\left(\vec{r}_{1}, \vec{r}_{2}\right)=\psi_{1}\left(\vec{r}_{1}\right) \cdot \psi_{2}\left(\vec{r}_{2}\right)$

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

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

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

We already solved this problem in Chapter 6.

## Wavefunctions

$\psi_{1}^{n_{l} l_{1} m_{1}}\left(\vec{r}_{1}\right)=A \cdot R_{n_{1} l_{1}}\left(r_{1}\right) \cdot Y_{l_{1} m_{1}}\left(\theta_{1}, \varphi_{1}\right) \quad \psi_{2}^{n_{2} l_{2} m_{2}}\left(\vec{r}_{2}\right)=A \cdot R_{n_{2} l_{2}}\left(r_{2}\right) \cdot Y_{l_{2} m_{2}}\left(\theta_{2}, \varphi_{2}\right)$

## Ground State Wavefunctions

(1s: $n=1, l=0, m=0$ )

$$
\psi_{1}^{100}\left(\vec{r}_{1}\right)=A \cdot e^{-Z r_{1}} \quad \psi_{2}^{100}\left(\vec{r}_{2}\right)=A \cdot e^{-Z r_{2}}
$$

Remember that in atomic units, $\mathrm{a}_{0}=1$ bohr

## Energies

$$
\begin{gathered}
E_{1}=-\frac{Z^{2}}{2 n_{1}^{2}} \quad E_{2}=-\frac{Z^{2}}{2 n_{2}^{2}} \\
E=E_{1}+E_{2}=-\frac{Z^{2}}{2 n_{1}^{2}}-\frac{Z^{2}}{2 n_{2}^{2}} \\
\text { Ground State Energy } \\
\left(\mathbf{n}_{1}=\mathbf{n}_{2}=1\right)
\end{gathered} \begin{gathered}
E=E_{1}+E_{2}=-\frac{Z^{2}}{2}-\frac{Z^{2}}{2}=-Z^{2}=-4 \text { a.u. (hartrees) } \\
Z=2 \text { for He } \\
E_{\text {exp }}=-2.9037 \text { a.u. (hartrees) }
\end{gathered}
$$

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

$$
H=\left[-\frac{1}{2} \nabla_{1}^{2}\left(\vec{r}_{1}\right)-\frac{Z}{r_{1}}\right]+\left[-\frac{1}{2} \nabla_{2}^{2}\left(\vec{r}_{2}\right)-\frac{Z}{r_{2}}\right]+\frac{1}{r_{12}}
$$

The Helium Hamiltonian can be rewritten as:

$$
\begin{gathered}
H=H^{(0)}+H^{(1)} \\
\text { where } H^{(0)}=\left[-\frac{1}{2} \nabla_{1}^{2}\left(\vec{r}_{1}\right)-\frac{Z}{r_{1}}\right]+\left[-\frac{1}{2} \nabla_{2}^{2}\left(\vec{r}_{2}\right)-\frac{Z}{r_{2}}\right] \\
H^{(1)}=+\frac{1}{r_{12}}
\end{gathered}
$$

$H^{(0)}$ is exactly solvable, as we just showed in the independent particle method.
$\mathrm{H}^{(1)}$ is a small perturbation to the exactly solvable Hamiltonian.
The energy due to $\mathrm{H}^{(1)}$ 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:

$$
E=E_{1}+E_{2}=-\frac{Z^{2}}{2}-\frac{Z^{2}}{2}=-Z^{2} \quad \text { a.u. }=-4.00 \text { a.u. }
$$

The "Zeroth Order" wavefunction is the product of $\mathrm{He}^{+}$ 1s wavefunctions for electrons 1 and 2

$$
\begin{gathered}
\psi^{(0)}=\psi_{1}^{100}\left(\vec{r}_{1}\right) \cdot \psi_{2}^{100}\left(\vec{r}_{2}\right)=\left[\left(\frac{Z^{3}}{\pi}\right)^{1 / 2} e^{-Z r_{1}}\right] \cdot\left[\left(\frac{Z^{3}}{\pi}\right)^{1 / 2} e^{-Z r_{2}}\right] \\
\psi^{(0)}=\frac{Z^{3}}{\pi} e^{-Z\left(r_{1}+r_{2}\right)}=A e^{-Z\left(r_{1}+r_{2}\right)}
\end{gathered}
$$

## First Order Perturbation Theory Correction to the Energy

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

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

For the He atom: $H^{(1)}=+\frac{1}{r_{12}} \quad$ and $\quad \psi^{(0)}=\frac{Z^{3}}{\pi} e^{-Z\left(r_{1}+r_{2}\right)}=A e^{-Z\left(r_{1}+r_{2}\right)}$
Therefore: $\Delta E=A^{2} \int d \vec{r}_{1} \int d \vec{r}_{2} e^{-2 Z r_{r}} e^{-2 Z r_{2}} \frac{1}{r_{12}} \quad$ where $\quad \begin{aligned} & d \vec{r}_{1} \equiv r_{1}^{2} \sin \left(\theta_{1}\right) d r_{d} d \theta_{1} d \varphi_{1} \\ & \\ & d \vec{r}_{2} \equiv r_{2}^{2} \sin \left(\theta_{2}\right) d r_{2} d \theta_{2} d \varphi_{2}\end{aligned}$
The evaluation of this integral is rather difficult, and in outlined in several texts.

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

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:

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

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 | \% Error |
| :---: | :--- | :---: |
| 0 | -4.0 a. u. | $-38 \%$ |
| 1 | -2.75 | +5 |
| 2 | -2.91 | -0.2 |
| 13 | -2.9037 | $\sim 0$ |

## Variational Method Treatment of Helium

Recall that we proved earlier in this Chapter that, if one has an approximate "trial" wavefunction, $\phi$, then the expectation value for the energy must be either higher than or equal to the true ground state energy. It cannot be lower!!

$$
<E\rangle=E_{\text {trial }}=\frac{\langle\varphi| H|\varphi\rangle}{\langle\varphi \mid \varphi\rangle}=\frac{\int \varphi^{*} H \varphi d \tau}{\int \varphi^{*} \varphi d \tau} \geq E_{0}
$$

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 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 $1 \mathrm{~s} \mathrm{He}+$ functions.

$$
\varphi=\psi_{1}^{100}\left(\vec{r}_{1}\right) \cdot \psi_{2}^{100}\left(\vec{r}_{2}\right)=\left(\frac{Z^{3}}{\pi}\right)^{1 / 2} e^{-Z r_{1}} e^{-Z r_{2}}=\left(\frac{Z^{3}}{\pi}\right)^{1 / 2} e^{-Z\left(r_{1}+r_{2}\right)}
$$

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

$$
\begin{aligned}
& \text { for } H=-\frac{1}{2} \nabla_{1}^{2}-\frac{1}{2} \nabla_{2}^{2}-\frac{Z}{r_{1}}-\frac{Z}{r_{2}}+\frac{1}{r_{12}} \quad \mathrm{Z}=2 \text { for } \mathrm{He} \\
& \text { and } \varphi=\left(\frac{Z^{\prime 3}}{\pi}\right)^{1 / 2} e^{-Z^{\prime}\left(r_{1}+r_{2}\right)}
\end{aligned}
$$

$$
E_{\text {trial }}=\frac{\langle\varphi| H|\varphi\rangle}{\langle\varphi \mid \varphi\rangle}=\frac{Z^{\prime 2}}{\underset{\mathrm{KE}(1)}{2}+\frac{Z^{\prime 2}}{2}-Z Z^{\prime}-Z Z^{\prime}+\frac{5}{8} Z^{\prime}}
$$

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

$\mathrm{He}: Z=2$

(Z E)

We want to find the value of $Z^{\prime}$ which minimizes the energy, $\mathrm{E}_{\text {trial }}$.

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

$$
E_{\text {trial }}=Z^{\prime 2}-\frac{27}{8} Z^{\prime}
$$

At minimum: $\frac{d E_{\text {trial }}}{d Z^{\prime}}=0=2 Z^{\prime}-\frac{27}{8}$
For lowest $E_{\text {trial }}: \quad Z^{\prime}=\frac{27}{16}=1.6875$


$$
\begin{aligned}
& E_{\text {trial }}=\left(\frac{27}{16}\right)^{2}-\frac{27}{8} \cdot \frac{27}{16} \\
& E_{\text {trial }}=-2.848 \text { au }(1.9 \% \text { higher than experiment })
\end{aligned}
$$

vs. $E_{\text {expt }}=-2.9037 a u$
The lower value for the "effective" atomic number ( $Z$ ' $=1.69 \mathrm{vs} . ~ Z=2$ ) 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 $Z_{\text {eff }}$ :

$$
\varphi=A\left[e^{-Z_{1}^{\prime} r_{1}} e^{-Z_{2} r_{2}}+e^{-Z_{1}^{\prime \prime} r_{1}} e^{-Z^{\prime} r_{2}}\right] \text { (we must keep treatment of the }
$$ two electrons symmetrical)

If one computes $E_{\text {trial }}$ as a function of $Z^{\prime}$ and $Z$ " and then finds the values of the two parameters that minimize the energy, one finds:

$$
Z_{Z}^{\prime}=1.19 \quad E_{\text {trial }}=-2.876 \text { au (1.0\% higher than experiment) }
$$

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

$$
\varphi=A\left[e^{-Z^{\prime}\left(r_{1}+r_{2}\right)}\left(1+b \cdot r_{12}\right)\right]
$$

When $E_{\text {trial }}$ 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:

$$
\begin{aligned}
& Z^{\prime}=1.19 \quad E_{\text {trial }}=-2.892 \text { au }(0.4 \% \text { higher than experiment }) \\
& b=0.364
\end{aligned}
$$

The second term, $1+\mathrm{br}_{12}$, accounts for electron correlation.
It increases the probability (higher $\phi^{2}$ ) of finding the two electrons further apart (higher $\mathrm{r}_{12}$ ).

## A Three Parameter Wavefunction

$$
\varphi=A\left[\left(e^{-Z r_{1}} e^{-Z " r_{2}}+e^{-Z^{\prime \prime} r_{1}} e^{-Z r_{2}}\right) \bullet\left(1+b \cdot r_{12}\right)\right]
$$

We have incorporated both ways of including electron correlation.

When $E_{\text {trial }}$ is evaluated as a function of $Z^{\prime}, Z^{\prime \prime}$ and $b$, and the values of the 3 parameters are varied to minimize the energy, the results are:

$$
\begin{aligned}
& Z^{\prime}=1.435 \quad E_{\text {trial }}=-2.9014 \mathrm{au}(0.08 \% \text { higher than experiment }) \\
& Z^{\prime \prime}=2.209 \\
& b=0.292
\end{aligned}
$$

## Even More Parameters

When we used a wavefunction of the form: $\varphi=A\left[e^{-Z\left(\gamma_{1}+t_{2}\right)}\left(1+b \cdot r_{12}\right)\right]$
The variational energy was within $0.4 \%$ of experiment.
We can improve upon this significantly by generalizing $\phi$ to:

$$
\varphi=A\left[e^{-Z^{\prime}\left(r_{1}+r_{2}\right)}\left(1+g\left(r_{1}, r_{2}, r_{12}\right)\right]\right.
$$

$g\left(r_{1}, r_{2}, r_{12}\right)$ is a polynomial function of the 3 interparticle distances.
Hylleras (1929) used a 9 term polynomial ( 10 total parameters) to get: $\mathrm{E}_{\text {trial }}=-2.9036$ au ( $0.003 \%$ higher than experiment)

Kinoshita (1957) used a 38 term polynomial ( 39 total parameters) to get: $\mathrm{E}_{\text {trial }}=-2.9037$ au ( $\sim 0 \%$ Error)
To my knowledge, the record to date was a 1078 parameter wavefunction [Pekeris (1959)]

## A Summary of Results

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

## Wavefunction <br> Energy <br> \% Error

| $A e^{-Z\left(r_{1}+r_{2}\right)}$ | -2.75 au | $+5.3 \%$ |
| :--- | :--- | :--- |
| $A e^{-Z\left(r_{i}+r_{2}\right)}$ | -2.848 | $+1.9 \%$ |

$A\left[e^{-Z^{\prime} r_{2}} e^{-Z^{\prime \prime} r_{2}}+e^{-Z^{\prime \prime} r_{1}} e^{-Z^{\prime} r_{2}}\right] \quad-2.876 \quad+1.0 \%$
$A\left[e^{-Z^{\left(r_{1}+r_{2}\right)}}\left(1+b \cdot r_{12}\right)\right]$
$-2.892+0.4 \%$

$$
\begin{array}{rcc}
A\left[\left(e^{-Z r_{i} r^{-Z r_{2}}}+e^{-Z \eta_{r_{2}}} e^{-Z_{2}^{\prime} r_{2}}\right) \cdot\left(1+b \cdot r_{12}\right)\right] & -2.9014 & +0.08 \% \\
\varphi=A\left[e^{-Z\left(r_{1}+r_{2}\right)}\left(1+g\left(r_{1}, r_{2}, r_{12}\right)\right]\right. & -2.9037 & \sim 0 \%
\end{array}
$$

Notes: 1. The computed energy is always higher than experiment.
2. One can compute an "approximate" energy to whatever degree of accuracy desired.

