Lecture 8

Approximation methods

1. **Time-Independent Perturbation Theory**
2. **Variation method**

Time Independent Perturbation Theory

Introduction

One often finds in QM that the Hamiltonian for a particular problem can be written as:

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

$$H = \boxed{-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2} + \boxed{\gamma x^3 + \delta x^4 + \ldots}$$

$\qquad\qquad$ **H$^{(0)}$** $\qquad\qquad\qquad$ **H$^{(1)}$**

Exactly Solvable $\quad$ **Correction Term**

$$\boxed{\Delta E = \int \psi^{(0)} * H^{(1)} \psi^{(0)} d\tau}$$ is the first order perturbation theory correction to the energy.

Brief Introduction to Second Order Perturbation Theory

As noted above, one also can obtain additional corrections to the energy using higher orders of Perturbation Theory; i.e.

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$

$E_n^{(0)}$ is the energy of the nth level for the unperturbed Hamiltonian

$E_n^{(1)}$ is the first order correction to the energy, which we have called ΔE

$E_n^{(2)}$ is the second order correction to the energy, etc.

The second order correction to the energy of the nth level is given by:

$$E_n^{(2)} = \sum_{k=1}^{\infty} \frac{\left| \left\langle \psi_k^{(0)} \left| H^{(1)} \right| \psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} \quad for \; k \neq n$$

where $\left\langle \psi_k^{(0)} \left| H^{(1)} \right| \psi_n^{(0)} \right\rangle = \int \psi_k^{(0)} \ast H^{(1)} \psi_n^{(0)} d\tau$

If the correction is to the ground state (for which we'll assume n=1), then:

$$E_1^{(2)} = \sum_{k=2}^{\infty} \frac{\left| \left\langle \psi_k^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle \right|^2}{E_1^{(0)} - E_k^{(0)}}$$

$$E_1^{(2)} = \frac{\left| \left\langle \psi_2^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle \right|^2}{E_1^{(0)} - E_2^{(0)}} + \frac{\left| \left\langle \psi_3^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle \right|^2}{E_1^{(0)} - E_3^{(0)}} + \frac{\left| \left\langle \psi_4^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle \right|^2}{E_1^{(0)} - E_4^{(0)}} + \cdots$$

Note that the second order Perturbation Theory correction is actually an infinite sum of terms.

However, the successive terms contribute less and less to the overall correction as the energy, $E_k^{(0)}$, increases.

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

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

if the function φ is not normalized then

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

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 mininmize the variational integral W
III. The lowest one is the best
$$\frac{\partial W}{\partial c} = 0$$

$$< E >= E_{trial} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} = \frac{\int \varphi * H \varphi d\tau}{\int \varphi * \varphi d\tau} \geq E_0$$

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 $\phi = c_1 f_1 + c_2 f_2 + c_3 f_3 + \quad ...... + c_n f_n$

A **linear variation function** is a linear combination of n linearly independent functions f_1, f_2,c, f_n:

So $\Phi = c_1 f_1 + c_2 f_2 + c_3 f_3 + \ldots + c_n f_n$ 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 $\quad S_{jk} = \int f_j f_k \partial t \quad$ *called* overlap integral

$$\int \phi^* \phi \partial t = \sum_{j=1}^{n} c_j \sum_{k=1}^{n} c_k S_{jk}$$

the variational integral $W = \dfrac{\int \phi^* H \phi \partial t}{\int \phi^* \phi \partial t}$

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

$$f_j \text{ called Basis set (they must stasfy the boundary condition)}$$

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 $\qquad W = \dfrac{\int \phi^* H \phi \partial t}{\int \phi^* \phi \partial t} \qquad for$ the numenator

$$\int \phi^* H \phi \partial t = \int \sum_{j=1}^{n} c_j f_j H \sum_{k=1}^{n} c_k f_k = \sum_{j=1}^{n} c_j \sum_{k=1}^{n} c_k \int f_j H f_k \partial t$$

assume $\qquad H_{jk} = \int f_j H f_k \partial t$

$$\int \phi^* \phi \partial t = \sum_{j=1}^{n} c_j \sum_{k=1}^{n} c_k H_{jk} \qquad\qquad \int \phi^* \phi \partial t = \sum_{j=1}^{n} c_j \sum_{k=1}^{n} c_k S_{jk}$$

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

So lets evaluate it……..

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

we can minimize W in a way to approach a position of $E_1 [W \geq E_1]$.

The variational integral W is a function of of the n independent variable

W=W($c_1, c_2, c_3 .... c_n$)

minimize W mean $\dfrac{\partial W}{\partial c_i} = 0$

the proof is not important lets go to the results

$$\sum\limits_{k=1}^{n} \left(H_{ik} - S_{ik} W \right) c_k = 0 \qquad\qquad i = 1, 2, 3, 4, 5 ...., n$$

It is a set of simultaneous Linear homogeneous equations in the unknown $c_1, c_2, c_3, … c_n f_n$

$$\phi = c_1 f_1 + c_2 f_2 + c_3 f_3 + c_4 f_4 + ... + c_n f_n = \sum\limits_{j=1}^{n} c_j f_j$$

The solution of the equation is:

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

$$\left(H_{11} - S_{11}W \right)c_1 + \left(H_{12} - S_{12}W \right)c_2 + \left(H_{13} - S_{13}W \right)c_1 + \ldots\ldots\ldots\ldots + \left(H_{1n} - S_{1n}W \right)c_n = 0$$

$$\left(H_{21} - S_{21}W \right)c_1 + \left(H_{22} - S_{22}W \right)c_2 + \left(H_{23} - S_{23}W \right)c_1 + \ldots\ldots\ldots\ldots + \left(H_{2n} - S_{2n}W \right)c_n = 0$$

$$\left(H_{31} - S_{31}W \right)c_1 + \left(H_{32} - S_{32}W \right)c_2 + \left(H_{33} - S_{33}W \right)c_1 + \ldots\ldots\ldots\ldots + \left(H_{3n} - S_{3n}W \right)c_n = 0$$

.

.

$$\left(H_{11} - S_{11}W \right)c_1 + \left(H_{12} - S_{12}W \right)c_2 + \left(H_{13} - S_{13}W \right)c_1 + \ldots\ldots\ldots\ldots + \left(H_{1n} - S_{1n}W \right)c_n = 0$$

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

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

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

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

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

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

$f_2 = x^2(l-x)^2$ 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 $f2, f3,$ and $f4$. 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 l – x)

$$f_1 = x(l-x) \quad \textit{multiply by } (\frac{1}{2}l-x) \textit{ to get } f_3$$

$$f_2 = x^2(l-x)^2 \quad \textit{multiply by } (\frac{1}{2}l-x) \textit{ to get } f_4$$

$$f_3 = x(l-x)\left(\frac{1}{2}l-x\right)$$

$$f_4 = x^2(l-x)^2\left(\frac{1}{2}l-x\right)$$

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

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

The secular equation become: since

$$\begin{vmatrix} H_{11}-S_{11}W & H_{12}-S_{12}W & H_{13}-S_{13}W & H_{14}-S_{14}W \\ H_{21}-S_{21}W & H_{22}-S_{22}W & H_{23}-S_{23}W & H_{24}-S_{24}W \\ H_{31}-S_{31}W & H_{32}-S_{32}W & H_{33}-S_{33}W & H_{34}-S_{34}W \\ H_{41}-S_{41}W & H_{42}-S_{42}W & H_{43}-S_{43}W & H_{44}-S_{44}W \end{vmatrix}$$

$$\left(\begin{array}{l} S_{13}=S_{31}=0 \quad S_{14}=S_{41}=0 \\ S_{23}=S_{32}=0 \quad\;\; S_{24}=S_{42}=0 \\ \text{and} \\ H_{13}=H_{31}=0 \quad H_{14}=H_{41}=0 \\ H_{23}=H_{32}=0 \quad\;\; H_{24}=H_{42}=0 \end{array} \right)$$

so

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

$$\begin{pmatrix} H_{11}-S_{11}W & H_{12}-S_{12}W \\ H_{21}-S_{21}W & H_{22}-S_{22}W \end{pmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

$$\begin{pmatrix} H_{33}-S_{33}W & H_{34}-S_{34}W \\ H_{43}-S_{43}W & H_{44}-S_{44}W \end{pmatrix} \begin{bmatrix} c_3 \\ c_4 \end{bmatrix} = 0$$

$$(H_{11}-S_{11}W)c_1 + (H_{12}-S_{12}W)c_2 = 0$$

$$(H_{33}-S_{33}W)c_3 + (H_{34}-S_{34}W)c_3 = 0$$

$$(H_{21}-S_{21}W)c_1 + (H_{22}-S_{22}W)c_2 = 0$$

$$(H_{43}-S_{43}W)c_4 + (H_{44}-S_{44}W)c_4 = 0$$

Evaluate H₁₁   S₁₁….etc

$$H_{11} = <f_1 \vdots H \vdots f_1> = \int_0^l x(l-x)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\left[x(l-x)\right]\partial x = \frac{\hbar^2 l^3}{6m}$$

$$S_{11} = <f_1 f_1> = \int_0^l x(l-x)\left[x(l-x)\right]\partial x = \frac{l^5}{30}$$

$$H_{12} = H_{21} = \frac{\hbar^2 l^5}{30m} \qquad S_{12} = S_{21} = \frac{l^7}{140} \qquad H_{22} = \frac{\hbar^2 l^7}{105m} \qquad S_{22} = \frac{l^9}{630}$$

$$H_{33} = \frac{\hbar^2 l^5}{40m} \qquad S_{33} = \frac{l^7}{840} \qquad H_{44} = \frac{\hbar^2 l^9}{1260m} \qquad S_{44} = \frac{l^{11}}{27720}$$

$$H_{34} = H_{43} = \frac{\hbar^2 l^7}{280m} \qquad S_{43} = S_{34} = \frac{l^9}{5040}$$

So

Energy states

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

$$W = \left(\dfrac{\hbar^2}{ml^2}\right)\left(28 \pm \sqrt{532}\right) = \begin{pmatrix} 0.1250018 \; h^2/ml^2 \\[1em] 1.293495 \; h^2/ml^2 \end{pmatrix} \text{ and from } c_3 \text{ and } c_4 \text{ matrix}$$

$$W = \left(\dfrac{\hbar^2}{ml^2}\right)\left(60 \pm \sqrt{1620}\right) = \begin{pmatrix} 0.500293 \, h^2/ml^2 \\[1em] 2.5393425 \, h^2/ml^2 \end{pmatrix}$$

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*

$$\left(H_{11} - S_{11}W\right)c_1 + \left(H_{12} - S_{12}W\right)c_2 = 0 \qquad\qquad \left(H_{21} - S_{21}W\right)c_1 + \left(H_{22} - S_{22}W\right)c_2 = 0$$

give

$$0.023095c_1 - 0.02038\ c_2l^2 \qquad = 0 \quad ....(1)$$

$$-0.061144c_1 + 0.053960c_2l^2 = 0 \ ....(2)$$

assume c_1=k so for eqn 1 $0.023095c_1 - 0.02038\ c_2l^2 \qquad = 0$ *will be*

$$0.023095k = 0.02038\ c_2l^2 \Rightarrow c_2 = 1.132\text{k}/l^2$$

to find k $<\phi_1/\phi_1>=1$ and so $<\left(c_1f_1 + c_2f_2\right)/\left(c_1f_1 + c_2f_2\right)>$

$$= <\left(kf_1 + 1.132k/l^2\right)/\left(kf_1 + 1.132k/l^2\right) = 1$$

$$k = 4.404/l^{5/2}$$

$$\phi_1 = c_1f_1 + c_2f_2 = 4.404\, f_1l^{5/2} + 4.990\, f_1l^{9/2}$$

$$\phi_1 = l^{-1/2}\left[4.404\left(x/l\right)\left(1-\left(x/l\right)\right) + 4.990\left(x/l\right)^2\left(1-\left(x/l\right)\right)^2\right]$$

using W2,W3 and W4 we will get the follwing normailzed function in which X=$\dfrac{x}{l}$

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

1. Time-Independent Perturbation Theory
2. Variation method

The Helium Atom Schrödinger Equation

The Hamiltonian

$$H = \frac{p_1^2(\vec{r}_1)}{2m} + \frac{p_2^2(\vec{r}_2)}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

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

$$H = -\frac{\hbar^2}{2m}\nabla_1^2(\vec{r}_1) - \frac{\hbar^2}{2m}\nabla_2^2(\vec{r}_2) - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

He: Z=2

Atomic Units: $\hbar = m = e = 4\pi\varepsilon_0 = 1$

$$H = -\frac{1}{2}\nabla_1^2(\vec{r}_1) - \frac{1}{2}\nabla_2^2(\vec{r}_2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$
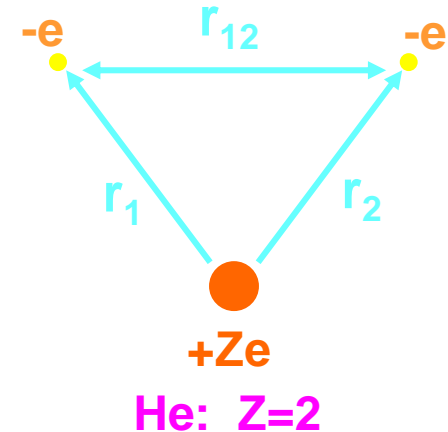
$$\nabla_1^2(\vec{r}_1) = \frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_1^2\sin^2\theta_1}\frac{\partial}{\partial\theta_1}\left(\sin\theta_1\frac{\partial}{\partial\theta_1}\right) + \frac{1}{r_1^2\sin^2\theta_1}\frac{\partial^2}{\partial\varphi_1^2}$$

$$\nabla_2^2(\vec{r}_2) = \frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) + \frac{1}{r_2^2\sin^2\theta_2}\frac{\partial}{\partial\theta_2}\left(\sin\theta_2\frac{\partial}{\partial\theta_2}\right) + \frac{1}{r_2^2\sin^2\theta_2}\frac{\partial^2}{\partial\varphi_2^2}$$

The Schrödinger Equation

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

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

Ψ depends upon the coordinates of both electrons

$$H = \left[-\frac{1}{2}\nabla_1^2(\vec{r}_1) - \frac{Z}{r_1}\right] + \left[-\frac{1}{2}\nabla_2^2(\vec{r}_2) - \frac{Z}{r_2}\right] + \frac{1}{r_{12}}$$
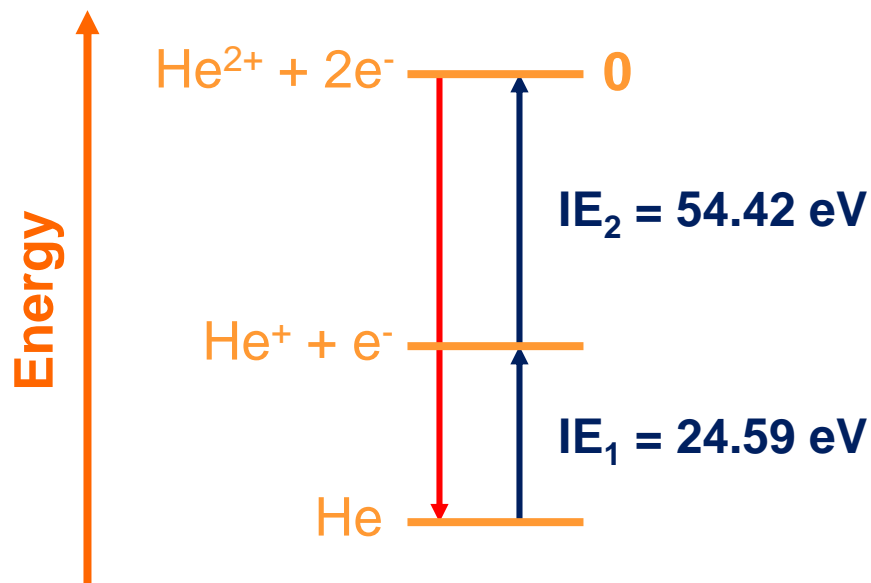
$$H = H_1(\vec{r}_1) + H_2(\vec{r}_2) + \frac{1}{r_{12}}$$

Can we separate variables?

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

Electron Repulsion

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

The Experimental Electronic Energy of He

Energy

$He^{2+} + 2e^-$ ——— 0

$IE_2 = 54.42$ eV

$He^+ + e^-$ ———

$IE_1 = 24.59$ eV

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.

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

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

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

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

The Independent Particle Model

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

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

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

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

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

$$H_1(\vec{r_1})\psi_1(\vec{r_1}) = E_1\psi_1(\vec{r_1}) \qquad \text{and} \qquad H_2(\vec{r_2})\psi_2(\vec{r_2}) = E_2\psi_2(\vec{r_2})$$

$$\left[-\frac{1}{2}\nabla_1^2(\vec{r_1}) - \frac{Z}{r_1}\right]\psi_1(\vec{r_1}) = E_1\psi_1(\vec{r_1}) \qquad \left[-\frac{1}{2}\nabla_2^2(\vec{r_2}) - \frac{Z}{r_2}\right]\psi_2(\vec{r_2}) = E_2\psi_2(\vec{r_2})$$

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

$$\psi_1^{n_1 l_1 m_1}(\vec{r_1}) = A \cdot R_{n_1 l_1}(r_1) \cdot Y_{l_1 m_1}(\theta_1, \varphi_1) \qquad \psi_2^{n_2 l_2 m_2}(\vec{r_2}) = A \cdot R_{n_2 l_2}(r_2) \cdot Y_{l_2 m_2}(\theta_2, \varphi_2)$$

Ground State Wavefunctions
(1s: n=1,l=0,m=0)

$$\psi_1^{100}(\vec{r_1}) = A \cdot e^{-Zr_1} \qquad \psi_2^{100}(\vec{r_2}) = A \cdot e^{-Zr_2}$$

Remember that in atomic units, a_0 = 1 bohr

Energies

$$E_1 = -\frac{Z^2}{2n_1^2} \qquad\qquad E_2 = -\frac{Z^2}{2n_2^2}$$

$$E = E_1 + E_2 = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2}$$

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

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

Z = 2 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:

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

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

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: $\quad H^{(1)} = + \dfrac{1}{r_{12}} \quad$ and $\quad \psi^{(0)} = \dfrac{Z^3}{\pi} e^{-Z(r_1 + r_2)} = A e^{-Z(r_1 + r_2)}$

Therefore: $\quad \Delta E = A^2 \int d\vec{r}_1 \int d\vec{r}_2 e^{-2Zr_1} e^{-2Zr_2} \dfrac{1}{r_{12}} \quad$ where $\quad d\vec{r}_1 \equiv r_1^2 \sin(\theta_1) dr_1 d\theta_1 d\varphi_1$

$$d\vec{r}_2 \equiv r_2^2 \sin(\theta_2) dr_2 d\theta_2 d\varphi_2$$

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

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

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!!

$$< E > = E_{trial} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} = \frac{\int \varphi * H \varphi d\tau}{\int \varphi * \varphi d\tau} \geq E_0$$

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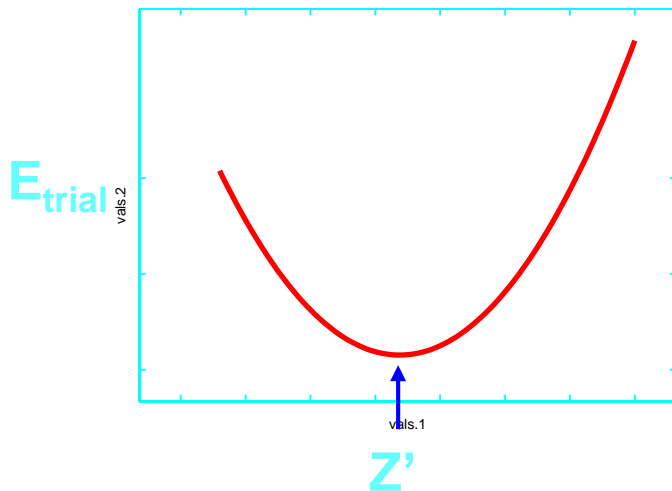
By using methods similar to those above (Independent Particle Model + First Order Perturbation Theory Integral), it can be shown that

for $\quad H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$ $\qquad$ Z = 2 for He

and $\quad \varphi = \left(\frac{Z'^3}{\pi}\right)^{1/2} e^{-Z'(r_1+r_2)}$

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

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

E$_{\textbf{trial}}$ vals.2

vals.1

Z'

(Z E)

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.
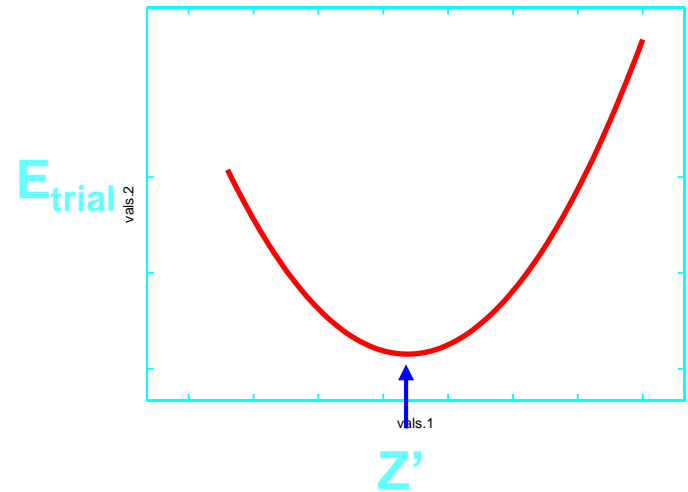
$$E_{trial} = Z'^2 - \frac{27}{8}Z'$$

At minimum: $\dfrac{dE_{trial}}{dZ'} = 0 = 2Z' - \dfrac{27}{8}$

For lowest E_{trial}: $Z' = \dfrac{27}{16} = 1.6875$

$$E_{trial} = \left(\frac{27}{16}\right)^2 - \frac{27}{8} \cdot \frac{27}{16}$$

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

vs. $E_{\exp t} = -2.9037 \ au$

E_{trial}

$(Z\ E)$

Z'

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:

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

$g(r_1, r_2, r_{12})$ 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

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

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

Application to Multi electron Atoms

The Hamiltonian for Multielectron Atoms

Helium

SI Units:

$$H = -\frac{\hbar^2}{2m}\nabla_1^2(\vec{r}_1) - \frac{\hbar^2}{2m}\nabla_2^2(\vec{r}_2) - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

Atomic Units:

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

Multielectron Atoms

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 \; - \; \sum_{i=1}^{N}\frac{Z}{r_i} \; + \; \sum_{i=1}^{N-1}\sum_{j>i}\frac{1}{r_{ij}}$$

Elect KE   **Elect-Nuc PE**   **Elect-Elect PE**

$$\sum_{i=1}^{N-1}\sum_{j>i}\frac{1}{r_{ij}} = \frac{1}{r_{12}} + \frac{1}{r_{13}} + \cdots + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \cdots + \frac{1}{r_{34}} + \frac{1}{r_{35}} + \cdots$$

Atomic Orbitals

In performing quantum mechanical calculations on multielectron atoms, it is usually assumed that each electron is in an atomic orbital, ϕ, which can be described as a Linear Combination of Hydrogen-like orbitals, which are called Slater Type Orbitals (STOs).

These STOs are usually denoted as χ_i

$$\text{Thus:} \quad \varphi = \sum c_i \chi_i$$

The goal of quantum mechanical calculations is to find the values of the c_i which minimize the energy (via the Variational Principle).

These STOs are also used to characterize the Molecular Orbitals occupied by electrons in molecules.

The Hartree Method: Helium

Hartree first developed the theory, but did not consider that electron wavefunctions must be antisymmetric with respect to exchange.

Fock then extended the theory to include antisymmetric wavefunctions.

Lets proceed as follows:

1. Outline Hartree method as applied to Helium

2. Show the results for atoms with >2 electrons

3. Discuss antisymmetric wavefunctions for multielectron atoms (Slater determinants)

4. Show how the Hartree equations are modified to get the the "Hartree-Fock" equations.

Basic Assumption

Each electron is in an orbital, ϕ_i (e.g. a sum of STOs).

The total "variational" wavefunction is the product of one electron wavefunctions: $\psi(\vec{r}_1, \vec{r}_2) = \varphi_1(\vec{r}_1) \cdot \varphi_2(\vec{r}_2)$

Procedure

"Guess" initial values the individual atomic orbitals: $\varphi_1^{init}(\vec{r}_1)$ and $\varphi_2^{init}(\vec{r}_2)$
(This would be an initial set of coefficients in the
linear combination of STOs). i.e. $\phi_1 = \sum c_i \chi_i = c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + ...$

Let's first look at electron #1. Assume that its interaction with the second electron (or with electrons #2, #3, #4, ... in multielectron atoms) is with the average "smeared" out electron density of the second electron.

SI Units

$$V_1^{eff}(\vec{r}_1) = e \cdot \int \frac{e\left|\varphi_2^{init}(\vec{r}_2)\right|^2}{4\pi\varepsilon_0 r_{12}} d\vec{r}_2$$

or

Atomic Units

$$V_1^{eff}(\vec{r}_1) = \int \frac{\left|\varphi_2^{init}(\vec{r}_2)\right|^2}{r_{12}} d\vec{r}_2$$

$$= \left\langle \varphi_2^{init}(2)\left|\frac{1}{r_{12}}\right|\varphi_2^{init}(2)\right\rangle$$

It can be shown (using the Variational Principle and a significant amount of algebra) that the "effective" Schrödinger equation for electron #1 is:

$$H_1^{eff} \varphi_1 = \varepsilon_1 \varphi_1 \quad \text{where} \quad H_1^{eff} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{eff} \qquad V_1^{eff} = \left\langle \varphi_2^{init}(2) \left| \frac{1}{r_{12}} \right| \varphi_2^{init}(2) \right\rangle$$

elect KE **elect-Nuc PE** **"Effective" elect-elect PE**

This equation can be solved exactly to get a new estimate for the function, ϕ_1^{new} (e.g. a new set of coefficients of the STOs).

There is an analogous equation for ϕ_2:

$$H_2^{eff} \varphi_2 = \varepsilon_2 \varphi_2 \quad \text{where} \quad H_2^{eff} = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + V_2^{eff} \qquad V_2^{eff} = \left\langle \varphi_1^{init}(1) \left| \frac{1}{r_{12}} \right| \varphi_1^{init}(1) \right\rangle$$

This equation can be solved exactly to get a new estimate for the function, ϕ_2^{new} (e.g. a new set of coefficients of the STOs).

A Problem of Consistency

We used initial guesses for the atomic orbitals, $\varphi_1^{init}(\vec{r}_2)$ and $\varphi_2^{init}(\vec{r}_2)$, to compute V_1^{eff} and V_2^{eff} in the Hartree Equations: .

$$H_1^{eff}\varphi_1 = \varepsilon_1\varphi_1 \quad \text{where} \quad H_1^{eff} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{eff} \qquad V_1^{eff} = \left\langle \varphi_2^{init}(2)\left|\frac{1}{r_{12}}\right|\varphi_2^{init}(2)\right\rangle$$ ←

$$H_2^{eff}\varphi_2 = \varepsilon_2\varphi_2 \quad \text{where} \quad H_2^{eff} = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + V_2^{eff} \qquad V_2^{eff} = \left\langle \varphi_1^{init}(1)\left|\frac{1}{r_{12}}\right|\varphi_1^{init}(1)\right\rangle$$ ←

We then solved the equations to get new orbitals, $\varphi_1^{new}(\vec{r}_2)$ and $\varphi_2^{new}(\vec{r}_2)$

If these new orbitals had been used to calculate V_1^{eff} and V_2^{eff} , we would have gotten different effective potentials.

Oy Vey!!! What a mess!!!

What can we do to fix the problem that the orbitals resulting from solving the effective Schrödinger equations are not the same as the orbitals that we used to construct the equations??

The Solution: Iterate to Self-Consistency

Repeat the procedure. This time, use $\varphi_1^{new}(\vec{r}_1)$ and $\varphi_2^{new}(\vec{r}_2)$
to construct V_1^{eff} and V_2^{eff} and solve the equations again.

Now, you'll get an even newer pair of orbitals, $\varphi_1^{newer}(\vec{r}_1)$ and $\varphi_2^{newer}(\vec{r}_2)$

BUT: You have the same problem again. The effective Hamiltonians that were used to compute this newest pair of orbitals were constructed from the older set of orbitals.

Well, I suppose you could repeat the procedure again, and again, and again, and again, until you either: (1) go insane

(2) quit Chemistry and establish
a multibillion dollar international
trucking conglomerate (please
remember me in your will).

Fortunately, the problem is not so dire. Usually, you will find that the new orbitals predicted by solving the equations get closer and closer to the orbitals used to construct the effective Hamiltonians.

When they are sufficiently close, you stop, declare victory, and go out and celebrate with a dozen Krispy Kreme donuts (or pastrami sandwiches on rye, if that's your preference).

When the output orbitals are consistent with the input orbitals, you have achieved a "Self-Consistent Field" (SCF).

Often, you will reach the SCF criterion within 10-20 iterations, although it may take 50-60 iterations or more in difficult cases.

While the procedure appears very tedious and time consuming, it's actually quite fast on modern computers. A single SCF calculation on a moderate sized molecule (with 50-100 electrons) can take well under 1 second.

The Energy

A. The total energy

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

$$H = H_1^{He^+}(1) + H_2^{He^+}(2) + \frac{1}{r_{12}} \quad \text{where} \quad H_1^{He^+} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} \quad \text{and} \quad H_2^{He^+} = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}$$

H_1 and H_2 are just each the Hamiltonian for the electron in a He$^+$ ion.

$$E = \int \psi * H\psi \, d\tau = \langle \varphi_1(1)\varphi_2(2) | H | \varphi_1(1)\varphi_2(2) \rangle$$

$$E = \langle \varphi_1(1)\varphi_2(2) | H_1^{He^+}(1) + H_2^{He^+}(2) + \frac{1}{r_{12}} | \varphi_1(1)\varphi_2(2) \rangle$$

We're assuming that ϕ_1 and ϕ_2 have both been normalized.

$$E = \left\langle \varphi_1(1)\varphi_2(2) \left| H_1^{He^+}(1) + H_2^{He^+}(2) + \frac{1}{r_{12}} \right| \varphi_1(1)\varphi_2(2) \right\rangle$$

$E = I_1 + I_2 + J_{12}$ Remember, this is the total energy of the two electrons.

$$I_1 = \left\langle \varphi_1(1)\varphi_2(2) \left| H_1^{He^+}(1) \right| \varphi_1(1)\varphi_2(2) \right\rangle = \left\langle \varphi_2(2) \middle| \varphi_2(2) \right\rangle \left\langle \varphi_1(1) \left| H_1^{He^+}(1) \right| \varphi_1(1) \right\rangle = \left\langle \varphi_1(1) \left| H_1^{He^+} \right| \varphi_1(1) \right\rangle$$

I_1 is the energy of an electron in a He$^+$ ion.

$$I_2 = \left\langle \varphi_1(1)\varphi_2(2) \left| H_2^{He^+}(2) \right| \varphi_1(1)\varphi_2(2) \right\rangle = \left\langle \varphi_1(1) \middle| \varphi_1(1) \right\rangle \left\langle \varphi_2(2) \left| H_2^{He^+}(2) \right| \varphi_2(2) \right\rangle = \left\langle \varphi_2(2) \left| H_2^{He^+} \right| \varphi_1(2) \right\rangle$$

I_2 is the energy of an electron in a He$^+$ ion.

$$J_{12} = \left\langle \varphi_1(1)\varphi_2(2) \left| \frac{1}{r_{12}} \right| \varphi_1(1)\varphi_2(2) \right\rangle = \int_{\vec{r}_1} \int_{\vec{r}_2} \frac{\left[\varphi_1^*(\vec{r}_1)\varphi_1(\vec{r}_1) \right]\left[\varphi_2^*(\vec{r}_2)\varphi_2(\vec{r}_2) \right]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

J_{12} is the Coulomb Integral and represents the coulombic repulsion energy of the two electrons

The Energy

B. The Individual Orbital Energies, ε_1 and ε_2

$$\boxed{\varepsilon_1 = I_1 + J_{12}}$$

where $\quad J_{12} = \left\langle \varphi_1(1)\varphi_2(2) \left| \dfrac{1}{r_{12}} \right| \varphi_1(1)\varphi_2(2) \right\rangle = \displaystyle\iint \dfrac{\left[\varphi_1^*\varphi_1\right]\left[\varphi_2^*\varphi_2\right]}{r_{12}} d\vec{r_1} d\vec{r_2}$

$$\boxed{\varepsilon_2 = I_2 + J_{12}}$$

where $\quad J_{12} = \left\langle \varphi_1(1)\varphi_2(2) \left| \dfrac{1}{r_{12}} \right| \varphi_1(1)\varphi_2(2) \right\rangle = \displaystyle\iint \dfrac{\left[\varphi_1^*\varphi_1\right]\left[\varphi_2^*\varphi_2\right]}{r_{12}} d\vec{r_1} d\vec{r_2}$

The sum of orbital energies: $\varepsilon_1 + \varepsilon_2 = \left(I_1 + J_{12}\right) + \left(I_2 + J_{12}\right) = I_1 + I_2 + 2J_{12}$

C. Total Energy versus sum of orbital energies

The sum of orbital energies: $\varepsilon_1 + \varepsilon_2 = I_1 + I_2 + 2J_{12}$

The total energy: $E = I_1 + I_2 + J_{12}$

The sum of the orbital energies has one too many Coulomb integrals, J_{12}.

The reason is that *each* orbital energy has the full electron-electron repulsion – You're counting it one time too many!!!

$$\varepsilon_1 + \varepsilon_2 = I_1 + I_2 + 2J_{12}$$

$$E = I_1 + I_2 + J_{12}$$

Therefore: $E = (I_1 + J_{12}) + (I_2 + J_{12}) - J_{12}$

$$\boxed{E = \varepsilon_1 + \varepsilon_2 - J_{12}}$$

We conclude that one must subtract the Coulomb repulsive energy, J_{12}, from the sum of orbital energies, $\varepsilon_1 + \varepsilon_2$, to correct for the double counting of the repulsion between the two electrons.