2. Non-Linear Variation Method. For the Be^{+2} ion:
(a) Write down the Hamiltonian.

(b) Assume a trial wavefunction for the two electrons,

$$\Psi(1,2) = 1s(1)1s(2) = \exp(-\alpha r_1)\exp(-\alpha r_2)$$

where α is an adjustable constant (sometimes called an "*effective nuclear charge*"). From information on this type of problem for the He atom, (the kinetic energy, $T = \alpha^2/2$ and potential energy $V = -\alpha Z + 5/8\alpha$ (in a.u.) for each orbital given in Lecture 7 on the website, find the value of α that gives the "best" wavefunction, and the energy given by this wavefunction.

(c) Verify that your answer obeys the virial theorem.

(d) Compare the answer to the exact answer given by that the sum of the *ionization energies of* $\boldsymbol{Be^{+2}}$**.**

$$V = -\alpha Z + 5/8\alpha \text{ (in a.u.)}$$

What is this?

Helium ground state energy:

Hamiltonian: $H = T_1 + T_2 - \frac{2}{r_{1n}} - \frac{2}{r_{2n}} + \frac{1}{r_{12}}$

kinetic E | e-n attraction | e-e repulsion

one-electron operators | **two-electron operator**

The ONLY types we ever have!

$$V = -\alpha Z + 5/8\alpha \text{ (in a.u.)}$$

What is this?

Levine: 9.4 p243

$T = \alpha^2/2$ (why?) $\Psi = e^{-\alpha r}$

because T = -(1/2) 2nd derivative of $\Psi = \alpha^2/2$

$V_{\text{electron-nuclear attraction}} = -\alpha Z$ (why?)

because <1/r> = gets larger as Ψ becomes smaller

$V_{\textbf{Electron repulsion}} = 5/8\ \alpha$ **(why?)**

because $\langle e^2/r_{12} \rangle$ = gets larger as Ψ becomes smaller
(the two electron will be closer on average)

The He Atom

Another interesting example is the He atom. Consider the simple product function, $\psi = N e^{-\alpha r_1} e^{-\alpha r_2}$

The energy obtained with various wavefunctions are as follows:

ψ	E
α = 2 (the right value for He+)	-2.75
α = 1.6875*	-2.848
Hartree SCF (table of numbers)	-2.86
Exact (Experiment)	-2.90

The Hartree SCF wavefunction, whose only restriction is that ψ = product of orbitals $\phi_{1s}(1)$ $\phi_{1s}(2)$ and allows any shape whatsoever for ϕ_{1s}, cannot give the right answer! This proves, to me anyway, that we must think of the electrons in atoms as point charges which do dodge one another because of the repulsion. The motion is correlated; they, to some extent, stay on opposite sides of the atom. By doing so, the energy is lowered by .04 a.u. = ~1ev = 23 kcal/mole.

Helium ground state, and singlet vs triplet excited state

The notation of spin orbital is often used for compactness:

$$\varphi_{1s}(1) = 1s(1)\alpha(1)$$
$$\overline{\varphi}_{1s}(1) = 1s(1)\beta(1)$$

For example the ground state function for He can be written as:

$$\varphi_{1s}(1)\overline{\varphi}_{1s}(2) - \overline{\varphi}_{1s}(1)\varphi_{1s}(2)$$

$$or$$

$$= 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The ***space-spin separated*** form is convenient for understanding the triplet state of a ***2-electron*** system. This factorization, however, cannot be done for 3 or more electrons.

Now consider the lowest excited states of He, 1s2s, an example of an ***open shell*** system.

Here one must consider that electron exchange is also between the spatial orbitals as well as the spin functions.

Because we may factor into space times spin functions, it is obvious that one may achieve an antisymmetric function two general ways:

(1) space = sym, spin= antisymmetric to permutation

2) space = antisym, spin= symmetric to permutation

There is **only 1 way to achieve the (1),** so it is called a **singlet state**:

$$\Psi_{\text{singlet}} = [1s(1)2s(2) + 2s(1)1s(2)]\ [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

There are **3 ways** to have a **symmetric** spin function while having an antisymmetric space function, however:

$$\Psi_{triplet} =$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\alpha(2)], \qquad M_S = 1/2 \quad + \quad 1/2 \quad = 1$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)], \quad M_S = 1/2 \quad - \quad 1/2 \quad = \quad 0$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\beta(1)\beta(2)], \qquad M_S = -1/2 \quad - \quad 1/2 = -1$$

This obeys the universal rule of quantum angular momentum: M_S=-S, -S +1, -S +2 ... +S
i.e., 2S+1 values.

Notice that the antisymmetric space function vanishes whenever the two electron are at the same point in space—ENTIRELY because of the wavefunction, meaning that the two electrons with same m_s avoid each other—
NOT because of Coulombic repulsion, but because of the Pauli exclusion principle

This is qualitatively why TRIPLET STATES have LOWER energy than the corresponding singlet state.

Helium ground state energy:

Hamiltonian: $H = T_1 + T_2 - \frac{2}{r_{1n}} - \frac{2}{r_{2n}} + \frac{1}{r_{12}}$

kinetic E | e-n attraction | e-e repulsion

one-electron operators | **two-electron operator**

The ONLY types we ever have!

What is left out here?

We are going to assume that *H* has no spin coordinates;

What phenomena will be left out of the picture?
spin-orbit coupling (stronger than e-e repulsion for high Z)
but negligible for H, He
and splitting of angular momentum statesin strong magnetic fields

$$< E > = \langle 1s(1)1s(2) \times [\alpha_{11} \quad \left| H \right| \; 1s(1)1s(2) \times \quad \rangle$$

But we are going to assume that *H* has no spin coordinates

$$< E >= \langle 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \left| H \right| 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \rangle$$

$$= \langle 1s(1)1s(2) \left| H \right| 1s(1)1s(2) \rangle \; \langle \alpha(1)\beta(2) - \beta(1)\alpha(2) \,|\, \alpha(1)\beta(2) - \beta(1)\alpha(2) \rangle$$

$$< T_1 >= \langle 1s(1) \left| T_1 \right| 1s(1) \rangle \times \langle 1s(2) \,|\, 1s(2) \rangle = T_{1s}$$

$$< T_2 >=< T_1 > \text{so} < T \; > = 2\mathrm{T}_{1\mathrm{s}}$$

$$< E >= \langle 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \left| H \right| 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \rangle$$

$$= \langle 1s(1)1s(2) \left| H \right| 1s(1)1s(2) \rangle \langle \alpha(1)\beta(2) - \beta(1)\alpha(2) \,|\, \alpha(1)\beta(2) - \beta(1)\alpha(2) \rangle$$

because H is purely a spatial operator (ignoring spin orbit coupling)

The same will be true for any one-electron operator, so for the e-n attraction

$$< -\frac{2}{r_{1n}} > = < -\frac{2}{r_{2n}} > = 2 < -\frac{2}{r_{1n}} >$$

The 2-electron operator $1/r_{12}$ is different:

$$< \frac{1}{r_{12}} > = \int 1s(1)1s(2)\frac{1}{r_{12}}1s(1)1s(2)d\tau_1 d\tau_2 = J_{1s,1s}$$

J_{ij} repulsion integrals are called "Coulomb integrals";

They are simply the repulsion of two 1s clouds of negative charge, that happen to be superimposed in this case.

Thus, for the He ground state:

$$\mathbf{E_{ground} = 2h_{1s} + J_{1s,1s}}$$

where h_{1s}= is a sum of one-electron operators:

the KE + electron-nuclear attraction for a 1s electron

Next consider the Helium 1s2s configuration

$$\Psi_{\text{singlet}} = [1s(1)2s(2) + 2s(1)1s(2)]\ [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$E_{1s2s}\ \text{singlet} = \left\langle [1s(1)1s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \middle| H \middle| [1s(1)1s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \right\rangle$$

Again, H does not have spin coordinates , ignoring spin-orbit coupling, so:

$$E_{\text{singlet}} = \left\langle s(1)2s(2) + 2s(1)1s(2) \middle| H \middle| s(1)2s(2) + 2s(1)1s(2) \right\rangle$$

Now the 1-electron part has to be $\mathbf{h_{1s} + h_{2s}}$ but appears to be twice that at this point. Must normalize the linear combination,

Normalization

Whenever two orthonormal functions are added $|A\rangle + |B\rangle$, the overlap is no longer 1, but $(\langle A| + \langle B|) \mid (|A\rangle + |B\rangle)$

$= N^2(\langle A|A\rangle + \langle B|B\rangle + \langle A|B\rangle + \langle B|A\rangle$

$= \quad 1 \quad + \quad 1 \quad + \quad 0 \quad + \quad 0 = 2$

So normalization constant square =1/2

N = $\mathbf{2^{-1/2} = 0.707}$

but the 2-electron part has an extra part due **to electron exchange**

$$<1/r_{12}>=\frac{1}{2}\left\langle 1s(1)2s(2)+2s(1)1s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)+2s(1)1s(2)\right\rangle$$

exchanged 1 and 2

$$=\left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)\right\rangle+\left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|2s(1)1s(2)\right\rangle$$

Order does not matter (just multiplying by $1/r_{12}$)

$$=\left\langle 1s(1)1s(1)\left|\frac{1}{r_{12}}\right|2s(2)2s(2)\right\rangle+\left\langle 1s(1)2s(1)\left|\frac{1}{r_{12}}\right|1s(2)2s(2)\right\rangle$$

$$= \quad J_{1s,2s} \quad + \quad K_{1s,2s}$$

where $\mathbf{K_{1s,2s}}$ is called and ***exchange integral*** because it arises only because of the requirement that the electrons must exchange.

Triplet State

$$<1/r_{12}>=\frac{1}{2}\left\langle 1s(1)2s(2)-2s(1)1s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)-2s(1)1s(2)\right\rangle$$

$$=\left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)\right\rangle-\left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|2s(1)1s(2)\right\rangle$$

$$=\left\langle 1s(1)1s(1)\left|\frac{1}{r_{12}}\right|2s(2)2s(2)\right\rangle-\left\langle 1s(1)2s(1)\left|\frac{1}{r_{12}}\right|1s(2)2s(2)\right\rangle$$

= $J_{1s,2s}$ minus $K_{1s,2s}$

The triplet state is LOWER than the singlet state!!!

because it can be proved that all J_{ij} and K_{ij} integrals are positive, but $K_{ij} < J_{ij}$.

J_{ij} is classical; It is simply the Coulombic repulsion of two negative clouds of charge described by the squares of the orbitals

K_{ij} is the repulsion of two ij clouds e.g., 1s(1)2s(1)

Generically:

$$\Psi = A(1)B(2)C(3)\ldots - B(1)A(2)C(3)\ldots - C(1)B(2)A(3)\ldots$$

$$\Psi = \begin{vmatrix} A(1) & A(2) & A(3) \\ B(1) & B(2) & B(3) \\ C(1) & C(2) & C(3) \end{vmatrix} \equiv \left|ABC\right|$$

$$\left\langle \left|ABC\right| \middle| \left|ABC\right| \right\rangle$$

Note that it does not matter whether:

columns have same electron number and rows have same orbital,

or vice versa

Normalization (assuming orthonormal orbitals)

There are N! (N factorial) terms for an N-electrons Slater determinant

3! = 6
ABC – ACB + BCA – BAC + CAB – CBA

<ABC – ACB + BCA – BAC + CAB – CBA| ABC – ACB + BCA – BAC + CAB – CBA> =?

= <ABC | ABC> = <A|A><B|B><C|C> = (1)(1)(1)
but, if there is only one mismatch, e.g., <ABC | ACB>
= <A|A><B|C><C|B> =(1)(0)(0) =0

Slater Determinants notation for the same for functions:

$$\Psi_{ground} = \varphi_{1s}(1)\overline{\varphi}_{1s}(2) - \overline{\varphi}_{1s}(1)\varphi_{1s}(2)$$

$$\Psi_{ground} = \begin{vmatrix} \varphi_{1s}(1) & \overline{\varphi}_{1s}(1) \\ \varphi_{1s}(2) & \overline{\varphi}_{1s}(2) \end{vmatrix}$$

Generically:

$$\Psi = A(1)B(2) - B(1)A(2)$$

$$\Psi_{ground} = \begin{vmatrix} A(1) & B(1) \\ A(2) & B(2) \end{vmatrix} = \begin{vmatrix} A(1) & A(2) \\ B(1) & B(2) \end{vmatrix} \equiv |AB|$$

Where |ABCD| means a a slater determinant and the electron numbering in each term is 1,2,3,4

$$\varphi_{1s}(1)\overline{\varphi}_{1s}(2) - \overline{\varphi}_{1s}(1)\varphi_{1s}(2)$$
$$= \begin{vmatrix} \varphi_{1s}(1) & \overline{\varphi}_{1s}(1) \\ \varphi_{1s}(2) & \overline{\varphi}_{1s}(2) \end{vmatrix}$$

$$\Psi_{\text{singlet}} = [1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$= 1s(1)\alpha(1)2s(2)\beta(2) - 1s(1)2s(2)\beta(1)\alpha(2)$$

$$+ 2s(1)\alpha(1)1s(2)\beta(2) - 2s(1)\beta(1)1s(2)\alpha(2)$$

$$= \varphi_{1s}(1)\overline{\varphi}_{2s}(2) - \overline{\varphi}_{1s}(1)\varphi_{2s}(2)$$

$$+ \varphi_{2s}(1)\overline{\varphi}_{1s}(2) - \overline{\varphi}_{2s}(1)\varphi_{1s}(2)$$

$$\begin{vmatrix} \varphi_{1s}(1) & \overline{\varphi}_{1s}(1) \\ \varphi_{2s}(2) & \overline{\varphi}_{2s}(2) \end{vmatrix} + \begin{vmatrix} \varphi_{2s}(1) & \overline{\varphi}_{1s}(1) \\ \varphi_{2s}(2) & \overline{\varphi}_{1s}(2) \end{vmatrix}$$

Hartree SCF method with LCAO

Ab initio Calculations

1. Write down H
2. Select a trial wavefunction *** with variational parameters.
   LCAO generally means vary only the coef.
3.

There are 3 ways to have a symmetric spin function while having an antisymmetric space function, however:

The 2-electron operator $1/r_{12}$ is different:

$$< \frac{1}{r_{12}} >= \int 1s(1)1s(2)\frac{1}{r_{12}}1s(1)1s(2)d\tau_1 d\tau_2 = J_{1s,1s}$$

J_{ij} repulsion integrals are called “Coulomb integrals”;

They are simply the repulsion of two 1s clouds of negative charge,

that happen to be superimposed in this case.