Orbital Model for Helium like atoms

The Schrodinger equation for He like atoms is

$$\hat{H}\Psi(1,2) = E\Psi(1,2)$$

where 1&2 are the spatial and spin coordinates of the two electrons.
The Hamiltonian in atomic units is

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}} = \hat{f}(1) + \hat{f}(2) + \frac{1}{r_{12}} = \hat{H}^0 + \frac{1}{r_{12}}$$

where

$$\hat{f} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$ is a hydrogenic Hamiltonian and the inter-electron separation

is

$$r_{12} = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}$$

The exact wave-function for a two electron atom is separable into a product of functions of space and spin coordinates

$$\Psi(1,2) = \psi(\vec{r}_1, \vec{r}_2)\chi(1,2)$$

where the spin function is either a singlet

$$\chi_1(1,2) = \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$$

or a triplet

$$\chi_3(1,2) = \begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) + \alpha(2)\beta(1)\right) \\ \beta(1)\beta(2) \end{cases}$$

These are all eigenfunctions of $\hat{S}^2$ & $\hat{S}_z$

	function	S	M_s

singlet	$\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)-\alpha(2)\beta(1)\right)$	0	0
triplet	$\alpha(1)\alpha(2)$	+1	+1
triplet	$\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)+\alpha(2)\beta(1)\right)$	+1	0
triplet	$\beta(1)\beta(2)$	+1	-1

Since the total electronic wavefunction must be antisymmetric WRT electron interchange the parity of the spatial function is determined by the spin function. The singlet spin function is antisymetric so the singlet space function must be symmetric while the triplet spin functions are symmetric so the triplet space function must be antisymmetric.

Note that because the exact wave function is a product of spin and space functions and the Schrodinger Hamiltonian doesn't contain spin, matrix elements of the Hamiltonian have the form

$$\left\langle \psi\chi \left| \hat{H} \right| \psi\chi \right\rangle = \left\langle \psi \left| \hat{H} \right| \psi \right\rangle \left\langle \chi \left| \chi \right\rangle = \left\langle \psi \left| \hat{H} \right| \psi \right\rangle$$

so we can ignore the spin function and a singlet or triple state is determined by weather the spatial function is symmetric or antisymmetric.

The Schrodinger equation for the spatial function is

$$\hat{H}\psi(\vec{r_1},\vec{r_2}) = E\psi(\vec{r_1},\vec{r_2})$$

and to date has not been solved analytically so we must seek an approximate solution. There are two ways to obtain an approximation to the energy and wave-function, the Variation Principle and Perturbation theory. Lets begin with the Variation principle.

As we have seen earlier the first order of business when using the Variation Principle is to select a trial function that satisfies the same boundary conditions as the function we are approximating and since the ground state of the two-electron atom is a singlet our approximate wave-function must be symmetric WRT electron interchange. The simplest choice is a function of the form $\varphi(\vec{r_1})\varphi(\vec{r_2})$. If we could

neglect $\dfrac{1}{r_{12}}$ in the Hamiltonian the exact ground state function would be a product of

two $1s$ functions $1s(r_1)1s(r_2)$ where $1s(r) = \sqrt{\dfrac{Z^3}{\pi}}e^{-Zr}$ is a hydrogenic 1s orbital for an atom with nuclear charge Z so its reasonable to take this as a trial function.
Using this function the energy is given by

$$E = \left\langle 1s(r_1)1s(r_2)\left|\hat{H}\right|1s(r_1)1s(r_2)\right\rangle = \dfrac{\left\langle 1s(r_1)1s(r_2)\left|\hat{H}\right|1s(r_1)1s(r_2)\right\rangle}{} = 2\left\langle 1s(r)\left|\hat{f}\right|1s(r)\right\rangle + \left\langle 1s(r_1)1s(r_2)\left|\dfrac{1}{r_{12}}\right|1s(r_1)1s(r_2)\right\rangle$$

where we use

$$\left\langle 1s(r_1)\left|\hat{f}(1)\right|1s(r_1)\right\rangle = \left\langle 1s(r_2)\left|\hat{f}(2)\right|1s(r_2)\right\rangle$$

The one electron term is simply the energy of a one-electron hydrogenic atom

$$\left\langle 1s(r)\left|\hat{f}\right|1s(r)\right\rangle = -\dfrac{Z^2}{2} \quad \text{while the two electron term}$$

$$\left\langle 1s(r_1)1s(r_2)\left|\dfrac{1}{r_{12}}\right|1s(r_1)1s(r_2)\right\rangle = \int 1s^2(r_1)\,dV_1 \int 1s^2(r_2)\dfrac{1}{r_{12}}\,dV_2$$

and to evaluate this integral we make use of the identity

$$\dfrac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \dfrac{r_<^\ell}{r_>^{\ell+1}}P_\ell(\omega_{12}) \quad \text{where } r_< \ \& \ r_> \text{ are the lesser and greater of } r_{12} \text{ (this will become}$$

clear subsequently) and ω_{12} is the angle between $\vec{r}_1 \ \& \ \vec{r}_2$. If we take the polar axis along $\vec{r}_1$, ω_{12} becomes θ and the integral involving $\dfrac{1}{r_{12}}$ becomes

$$\int 1s^2(r_2)\dfrac{1}{r_{12}}\,dV_2 = \sum_{\ell=0}^{\infty}\int 1s^2(r_2)\dfrac{r_<^\ell}{r_>^{\ell+1}}P_\ell(\cos\theta)r_2^2\,dr_2\sin^2\theta\,d\theta\,d\phi = 4Z^3\int_0^\infty e^{-2Zr_2}\dfrac{1}{r_>}r_2^2\,dr_2$$

Because of the spherical symmetry of the 1s orbital only the $\ell = 0$ term contributes. When we integrate over r_2 we start at 0 which is less than r_1 so in this interval $r_> = r_1$ then when $r_2 > r_1$, $r_> = r_2$ so we have

$$4Z^3\int_0^\infty e^{-2Zr_2}\dfrac{1}{r_>}r_2^2\,dr_2 = 4Z^3\left(\dfrac{1}{r_1}\int_0^{r_1} e^{-2Zr_2}r_2^2\,dr_2 + \int_{r_1}^\infty e^{-2Zr_2}r_2\,dr_2\right)$$

The first integral equals

$$4Z^3 \frac{1}{r_1} \int_0^{r_1} e^{-2Zr_2} r_2^2 \, dr = \frac{1}{r_1}\left(1 - e^{-2Zr_1}(2Z^2 r_1^2 + 2Zr_1 + 1)\right)$$

and the second

$$4Z^3 \int_{r_1}^{\infty} e^{-2Zr_2} r_2 \, dr = e^{-2Zr_1}(Z + 2Z^2 r_1)$$

and so

$$4Z^3 \int_0^{\infty} e^{-2Zr_2} \frac{1}{r_>} r_2^2 \, dr_2 = \frac{1}{r_1} - e^{-2Zr_1}(Z + \frac{1}{r_1})$$

Inserting this in the integrand of the integral involving $1s^2(r_1)$ gives

$$4Z^3 \int_0^{\infty} e^{-2Zr_1} r_1^2 \left(\frac{1}{r_1} - e^{-2Zr_1}(Z + \frac{1}{r_1})\right) dr_1 = \frac{5}{8}Z$$

and so we have the approximate energy for arbitrary Z

$$E = -Z^2 + \frac{5}{8}Z$$

For Helium in particular $E = -\frac{11}{4} = -2.75au$

Experimentally the energy of the ground state of He is the negative of the sum of its two ionization energies 24.587 and 54.418 eV or -79.005 eV which is -2.90372 au so as required by the variation principle the approximate energy is higher than the exact energy. We can improve our trial function by keeping it as the product of two $1s$ functions but with the atomic number α chosen to minimize the energy.

$$\varphi(r_1)\varphi(r_2) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r_1} \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r_2}$$

Using the complete Hamiltonian, noting that $\varphi(r)$ is normalized we have

$$E = \left\langle \varphi(r_1)\varphi(r_2) \middle| \hat{f}(1) + \hat{f}(2) + \frac{1}{r_{12}} \middle| \varphi(r_1)\varphi(r_2) \right\rangle = 2\left\langle \varphi(r_1) \middle| \hat{f}(1) \middle| \varphi(r_1) \right\rangle + \left\langle \varphi(r_1)\varphi(r_2) \middle| \frac{1}{r_{12}} \middle| \varphi(r_1)\varphi(r_2) \right\rangle$$

From above we have

$$\langle\varphi(r_1)\varphi(r_2)|\frac{1}{r_{12}}|\varphi(r_1)\varphi(r_2)\rangle = \frac{5}{8}\alpha$$

and so

$$\langle\varphi(r)|\hat{f}|\varphi(r)\rangle = \langle\varphi(r)|-\frac{1}{2}\nabla^2 - \frac{Z}{r}|\varphi(r)\rangle = \langle\varphi(r)|-\frac{1}{2}\nabla^2 - \frac{\alpha}{r} - \frac{(Z-\alpha)}{r}|\varphi(r)\rangle$$

and also from above

$$\langle\varphi(r)|-\frac{1}{2}\nabla^2 - \frac{\alpha}{r}|\varphi(r)\rangle = -\frac{\alpha^2}{2}$$

and so we need to evaluate the integral

$$-\langle\varphi(r)|\frac{(Z-\alpha)}{r}|\varphi(r)\rangle = -(Z-\alpha)\langle\varphi(r)|\frac{1}{r}|\varphi(r)\rangle$$

$$\langle\varphi(r)|\frac{1}{r}|\varphi(r)\rangle = \frac{\alpha^3}{\pi}\int_V \frac{e^{-2\alpha r}}{r}dV = 4\alpha^3\int_0^\infty e^{-2\alpha r}rdr = \alpha$$

And so the energy is

$$E = -\alpha^2 + \frac{5}{8}\alpha - 2(Z-\alpha)\alpha = \alpha^2 + \frac{5}{8}\alpha - 2Z\alpha$$

Taking the derivative with respect to α and setting it equal to zero

$$\frac{dE}{d\alpha} = 2\alpha + \frac{5}{8} - 2Z = 0$$

and the energy is a minimum when $\alpha = Z - \frac{5}{16}$ which, for He, is $\frac{27}{16}$. Inserting this

into the formula for E with $Z=2$ results in $E = -\left(\frac{27}{16}\right)^2 = -2.847656 au$ which is 1.92%

higher than the exact He energy. In principle we can continue to modify the trial function until the calculated energy is as low as possible at which point the trial function must be equal to the exact wavefunction. Given how well the function $\varphi(r_1)\varphi(r_2)$ does in approximating the exact energy we can ask if there is a more general trial function that is also the product of two orbitals, $u(r_1)u(r_2)$ that results in

a lower energy? The answer is yes, as we will now see and the very best trial function of this form is called the Hartree or Hartree –Fock wavefunction.