

### Hylleraas wavefunction for He

The reason why the Hartree method cannot reproduce the exact solution is due to the inability of the Hartree wave-function to account for electron correlation. We know that the two electrons in He repel one another and absent any other factor they would stay as far apart as possible so that the probability of finding them close to one another would be small. Given the wave-function  $\psi$  the probability of finding electron 1 at the terminus of  $\vec{r}_1$  and in the volume element  $dV_1$  while electron 2 is at  $\vec{r}_2$  in the volume element  $dV_2$  is  $\psi^2(\vec{r}_1, \vec{r}_2)dV_1dV_2$  which for the Hartree function is  $\phi^2(\vec{r}_1)\phi^2(\vec{r}_2)dV_1dV_2$  and the probability is uncorrelated in that the location of electron 1 is independent of the location of electron 2. Another way of looking at this is to realize that the wave-function for the ground (spherically symmetric) state is a function of three variables:  $r_1$  &  $r_2$  the distances of the two electrons from the nucleus and  $r_{12}$  the distance between the electrons and the Hartree or orbital model doesn't include  $r_{12}$  in the trial function. A simple trial function that does include  $r_{12}$  is  $\phi(r_1)\phi(r_2)f(r_{12})$  and if we expand  $f(r_{12})$  around  $r_{12} = 0$ , the region of interest, our trial function becomes  $\phi(r_1)\phi(r_2)f(r_{12}) = \phi(r_1)\phi(r_2)(f(0) + f^{(1)}(0)r_{12} + f^{(2)}(0)r_{12}^2/2 + \dots)$  and if we factor out  $f(0)$  we have an un-normalized trial function  $\phi(r_1)\phi(r_2)(1 + br_{12} + cr_{12}^2 + \dots)$  where  $b, c, \dots$  are variational parameters. The first to propose a trial function of this form was Hylleraas and using the function

$$\psi = e^{-\alpha r_1} e^{-\alpha r_2} (1 + br_{12}) = e^{-\alpha(r_1+r_2)} (1 + br_{12})$$

he determined the optimum values  $\alpha = 1.849$  &  $b = 0.364$  resulting in an energy -2.8913 au that is greater than the exact energy -2.90372 by 0.42%, a significant improvement over the simple product result. Since this calculation is somewhat tedious we reserve the details to the appendix. Hylleraas explored several trial functions containing what are called the Hylleraas coordinates

$s = r_1 + r_2, t = r_2 - r_1$  &  $u = r_{12}$  and laid the groundwork for subsequent calculations using trial functions of the form  $\psi = e^{-\alpha s} \sum_{ijk} c_{ijk} s^i t^j u^k$

Pekeris (*vide supra*) used this functional form with 1078 terms and found  $E = -2.903724375$  and after correcting for the size of the nucleus and relativistic effects predicts the ionization energy 198,310.69 cm<sup>-1</sup> compared to the experimental energy 198,310.82 cm<sup>-1</sup>. While trial functions involving  $r_{12}$  can give excellent results they are not easily interpreted whereas a function consisting of optimized orbitals gives a reasonable energy and is more in keeping with qualitative

chemical ideas. Also wavefunctions consisting of orbital products are almost always the starting point for more accurate calculations.

### ***Appendix . He like atoms and a Hylleraas wavefunction.***

#### Preliminaries

Our goal is to use the variation principle to calculate the energy of a two-electron atom in an S state using the simplest Hylleraas wavefunction

$$\psi = e^{-\alpha(r_1+r_2)}(1+br_{12})$$

where  $\alpha$  &  $b$  are variational parameters and  $r_{12}$  is the separation between electrons. The energy is given by

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$$

with the Hamiltonian in atomic units

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

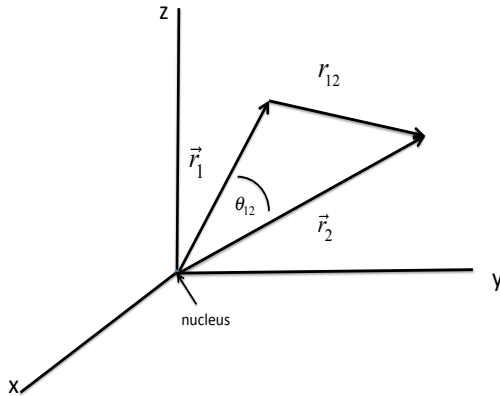
Because of  $r_{12}$  in the wavefunction it's convenient to use what are called Hylleraas coordinates  $(s, t, u)$  instead of  $r_1, \theta_1, \phi_1$  and  $r_2, \theta_2, \phi_2$ . These are defined as

$$s = r_1 + r_2, t = r_2 - r_1 \text{ \& } u = r_{12}.$$

We need to have the integrand  $\psi^* \hat{H} \psi$  and the volume element  $d\tau$  in these coordinates so let's begin with the volume element.

First write  $d\tau$  as (figure 1)

Figure 1



$$d\tau = 8\pi^2 r_1^2 dr_1 r_2^2 dr_2 \sin\theta_{12} d\theta_{12}$$

The factor  $8\pi^2$  comes about because the orientation of the triangle defined by  $r_1, r_2$  &  $\theta_{12}$  is arbitrary and we have integrated over  $\phi_1$  &  $\phi_2$  each contributing a factor of  $2\pi$  and then one  $\theta$  contributing a factor of 2.

Using

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}$$

we have  $r_{12} dr_{12} = r_1 r_2 \sin\theta_{12} d\theta_{12} = u du$  giving

$$d\tau = 8\pi^2 r_1 r_2 u dr_1 dr_2 du$$

from the definition of  $s$  &  $t$  we have  $r_1 r_2 = \frac{s^2 - t^2}{4}$  and using the Jacobian  $\frac{\partial(r_1, r_2)}{\partial(s, t)} = \frac{1}{2}$

we have  $dr_1 dr_2 = \frac{1}{2} ds dt$  with the final result

$$d\tau = \pi^2 u (s^2 - t^2) ds du dt$$

with the limits  $0 \leq s < \infty$ ,  $0 \leq u \leq s$ , &  $-u \leq t \leq u$

Now for the integrand. When we use Hylleraas coordinates it will be simpler to rewrite the kinetic energy terms as follows. Let's consider the integral

$$\int f \nabla^2 f dV = \int f \left( \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right) dx dy dz$$

and consider the term

$$\int f \frac{\partial^2 f}{\partial x^2} dx dy dz = \int dy dz \left( f \frac{\partial f}{\partial x} \Big|_{-\infty}^{\infty} - \left( \frac{\partial f}{\partial x} \right) \left( \frac{\partial f}{\partial x} \right) dx \right) = - \int dy dz \left( \frac{\partial f}{\partial x} \right)^2 dx$$

where the term  $f \frac{\partial f}{\partial x} \Big|_{-\infty}^{\infty} = 0$  because we assume  $f(\pm\infty) = 0$

Extending this to the remaining coordinates results in

$$\int f \nabla^2 f dx dy dz = - \int \left( \left( \frac{\partial f}{\partial x} \right)^2 + \left( \frac{\partial f}{\partial y} \right)^2 + \left( \frac{\partial f}{\partial z} \right)^2 \right) dx dy dz = - \int \nabla f \cdot \nabla f dx dy dz$$

and so

$$\int \psi \hat{H} \psi d\tau = \frac{1}{2} \int \left( \nabla_1 \psi \cdot \nabla_1 \psi + \nabla_2 \psi \cdot \nabla_2 \psi - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) d\tau$$

Our goal is to express the integrand in terms of the Hylleraas coordinates. Lets first consider  $\nabla_1 \psi$ .

$$\nabla_1 \psi = \frac{\partial \psi}{\partial x_1} \hat{i} + \frac{\partial \psi}{\partial y_1} \hat{j} + \frac{\partial \psi}{\partial z_1} \hat{k}$$

using the chain rule

$$\frac{\partial \psi}{\partial x_1} = \frac{\partial \psi}{\partial s} \frac{\partial s}{\partial x_1} + \frac{\partial \psi}{\partial t} \frac{\partial t}{\partial x_1} + \frac{\partial \psi}{\partial u} \frac{\partial u}{\partial x_1} = \frac{x_1}{r_1} \frac{\partial \psi}{\partial s} - \frac{x_1}{r_1} \frac{\partial \psi}{\partial t} - \frac{(x_2 - x_1)}{u} \frac{\partial \psi}{\partial u}$$

and by symmetry

$$\frac{\partial \psi}{\partial y_1} = \frac{y_1}{r_1} \frac{\partial \psi}{\partial s} - \frac{y_1}{r_1} \frac{\partial \psi}{\partial t} - \frac{(y_2 - y_1)}{u} \frac{\partial \psi}{\partial u}$$

and

$$\frac{\partial \psi}{\partial z_1} = \frac{z_1}{r_1} \frac{\partial \psi}{\partial s} - \frac{z_1}{r_1} \frac{\partial \psi}{\partial t} - \frac{(z_2 - z_1)}{u} \frac{\partial \psi}{\partial u}$$

so after some algebra

$$\nabla_1 \psi \cdot \nabla_1 \psi = \left( \frac{\partial \psi}{\partial s} \right)^2 + \left( \frac{\partial \psi}{\partial t} \right)^2 + \left( \frac{\partial \psi}{\partial u} \right)^2 - 2 \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial t} + 2 \left( -\frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial u} + \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial u} \right) \left( \frac{\vec{r}_1 \cdot \vec{r}_2}{r_1 u} - \frac{r_1}{u} \right)$$

in a similar fashion

$$\nabla_2 \psi \cdot \nabla_2 \psi = \left( \frac{\partial \psi}{\partial s} \right)^2 + \left( \frac{\partial \psi}{\partial t} \right)^2 + \left( \frac{\partial \psi}{\partial u} \right)^2 - 2 \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial t} + 2 \left( \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial u} + \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial u} \right) \left( \frac{-\vec{r}_1 \cdot \vec{r}_2}{r_2 u} + \frac{r_2}{u} \right)$$

Adding these and recognizing that

$$\vec{r}_1 \cdot \vec{r}_2 = \frac{s^2 + t^2 - 2u^2}{8} \quad \& \quad \frac{1}{r_1} + \frac{1}{r_2} = \frac{4s}{s^2 - t^2} \quad \& \quad \frac{1}{r_1} - \frac{1}{r_2} = \frac{4t}{s^2 - t^2}$$

we obtain

$$\left( \frac{\partial \psi}{\partial s} \right)^2 + \left( \frac{\partial \psi}{\partial t} \right)^2 + \left( \frac{\partial \psi}{\partial u} \right)^2 - 2 \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial t} + 2 \left( \frac{s(u^2 - t^2)}{u(s^2 - t^2)} \right) \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial u} - 2 \left( \frac{t(u^2 - s^2)}{u(s^2 - t^2)} \right) \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial u} - \frac{4sZ\psi^2}{s^2 - t^2} + \frac{\psi^2}{u}$$

In the text we calculated the energy of Helium using the trial function

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

and found  $\alpha = \frac{27}{8}$  &  $E = -\left(\frac{27}{16}\right)^2$ . Let's redo this calculation using Hylleraas

coordinates to see how the integrations work. Since this trial function depends only on  $s$  and  $\psi$  is normalized the energy is given by

$$E = \pi^2 \int \left( \left( \frac{\partial \psi}{\partial s} \right)^2 - \frac{4sZ\psi^2}{s^2 - t^2} + \frac{\psi^2}{u} \right) u(s^2 - t^2) ds dt$$

There are three terms in the integrand. First the kinetic energy .

$$\int \left( \frac{\partial \psi}{\partial s} \right)^2 u(s^2 - t^2) ds du dt = \frac{\alpha^8}{\pi^2} \int e^{-2\alpha s} u(s^2 - t^2) ds du dt = \frac{\alpha^8}{\pi^2} \int_0^\infty e^{-2\alpha s} ds \int_0^s u du \int_{-u}^u (s^2 - t^2) dt$$

$$\int_0^\infty e^{-2\alpha s} ds \int_0^s u du \int_{-u}^u (s^2 - t^2) dt = 2 \int_0^\infty e^{-2\alpha s} ds \int_0^s u \left( us^2 - \frac{u^3}{3} \right) du = \frac{8}{15} \int_0^\infty e^{-2\alpha s} s^5 ds = \frac{1}{\alpha^6}$$

so

$$\int \left( \frac{\partial \psi}{\partial s} \right)^2 u(s^2 - t^2) ds du dt = \frac{\alpha^2}{\pi^2}$$

now the nuclear attraction..

$$\int -\frac{4sZ\psi^2}{s^2 - t^2} u(s^2 - t^2) ds du dt = -\frac{4Z\alpha^6}{\pi^2} \int_0^\infty s e^{-2\alpha s} ds \int_0^s u du \int_{-u}^u dt = -\frac{2Z\alpha}{\pi^2}$$

and lastly the electron -electron repulsion contribution

$$E = \pi^2 \int \left( \left( \frac{\partial \psi}{\partial s} \right)^2 - \frac{4sZ\psi^2}{s^2 - t^2} + \frac{\psi^2}{u} \right) u(s^2 - t^2) ds du dt$$

$$\int \psi^2 (s^2 - t^2) ds du dt = \frac{\alpha^6}{\pi^2} \int_0^\infty e^{-2\alpha s} ds \int_0^s du \int_{-u}^u (s^2 - t^2) dt = \frac{5\alpha}{8\pi^2}$$

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

and so

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

results in  $\alpha = Z - \frac{5}{16}$  and for He  $\alpha = \frac{27}{16}$  with  $E = -\left(\frac{27}{16}\right)^2$  as required.

Now lets evaluate the energy associated with the Hylleraas function

$$\psi = e^{-\alpha(r_1+r_2)}(1+br_{12}) = e^{-\alpha s}(1+bu)$$

When we evaluate the energy associated with a trial function that depends only on  $s$  &  $u$  such as above we will encounter integrals that have the form

$$I(N, M) = \int_0^\infty s^N e^{-2\alpha s} ds \int_0^s u^M du \int_{-u}^{+u} (s^2 - t^2) dt = \left( \frac{4M + 20}{3(M + 2)(M + 4)} \right) \frac{(M + N + 4)!}{(2\alpha)^{M+N+5}}$$

The first few being

$N$	$M$	$I(N, M)$
0	0	$\frac{5}{8\alpha^5}$
1	0	$\frac{75}{48\alpha^6}$
1	1	$\frac{3}{\alpha^7}$
0	1	$\frac{1}{\alpha^6}$
0	2	$\frac{35}{16\alpha^7}$
0	3	$\frac{6}{\alpha^8}$

First the overlap integral

$$\langle \psi | \psi \rangle = \int e^{-2\alpha s} (1 + bu)^2 u (s^2 - t^2) ds du dt = \int_0^\infty e^{-2\alpha s} ds \int_0^s u (1 + 2bu + b^2 u^2) du \int_{-u}^{+u} (s^2 - t^2) dt$$

$$\langle \psi | \psi \rangle = I(0, 1) + 2bI(0, 2) + b^2 I(0, 3) = \frac{1}{\alpha^6} + b \frac{35}{8\alpha^7} + b^2 \frac{6}{\alpha^8}$$

and now for the expectation value. Note that derivatives wrt  $t$  vanish.

$$\langle \psi | \hat{H} | \psi \rangle = \int \left\{ \left( \frac{\partial \psi}{\partial s} \right)^2 + \left( \frac{\partial \psi}{\partial u} \right)^2 + \frac{2s(u^2 - t^2)}{u(s^2 - t^2)} \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial u} - \psi^2 \left( \frac{4sZ}{s^2 - t^2} \right) + \frac{\psi^2}{u} \right\} u (s^2 - t^2) ds du dt$$

$$\int \left( \frac{\partial \psi}{\partial s} \right)^2 u (s^2 - t^2) ds du dt = \alpha^2 (I(0, 1) + 2bI(0, 2) + b^2 I(0, 3)) = \frac{1}{\alpha^4} + b \frac{35}{8\alpha^5} + b^2 \frac{6}{\alpha^6}$$

$$\int \left( \frac{\partial \psi}{\partial u} \right)^2 u(s^2 - t^2) ds du dt = b^2 I(0,1) = \frac{b^2}{\alpha^6}$$

$$\int 2s(u^2 - t^2) \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial u} ds du dt = -2\alpha b \int_0^\infty s e^{-2\alpha s} \int_0^s (1+bu) du \int_{-u}^{+u} (u^2 - t^2) dt = -b \frac{5}{4\alpha^5} - b^2 \frac{3}{\alpha^6}$$

$$-4Z \int \psi^2 s u ds du dt = -Z \left( \frac{2}{\alpha^5} + b \frac{15}{2\alpha^6} + b^2 \frac{9}{\alpha^7} \right)$$

and lastly

$$\int \psi^2 (s^2 - t^2) ds du dt = I(0,0) + 2bI(0,1) + b^2 I(0,2) = \frac{5}{8\alpha^5} + b \frac{2}{\alpha^6} + b^2 \frac{35}{16\alpha^7}$$

The energy is given by the ratio

$$E = \frac{\alpha^2 - \left(\frac{5}{8} - 2Z\right)\alpha + b \left(\frac{25\alpha}{8} + 2 - \frac{15Z}{2}\right) + b^2 \left(4 + \frac{1}{\alpha} \left(\frac{35}{16} - 9Z\right)\right)}{1 + b \frac{35}{8\alpha} + b^2 \frac{6}{\alpha^2}}$$

and for He

$$E = \frac{\alpha^2 - \frac{27}{8}\alpha + b \left(\frac{25\alpha}{8} - 13\right) + b^2 \left(4 - \frac{253}{16\alpha}\right)}{1 + b \frac{35}{8\alpha} + b^2 \frac{6}{\alpha^2}} = \frac{N}{D}$$

minimizing  $E$  with respect to  $\alpha$  &  $b$  results in

$$\alpha = 1.849 \text{ \& } b = 0.365 \text{ \& } E = -2.8911$$