Variational Method for the Helium Ground State

The Hamiltonian for Helium is given by

$$H = \frac{1}{2m}\left(P_1^2 + P_2^2\right) - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}, \tag{1}$$

where $r_{12} = |\vec{r}_1 - \vec{r}_2|$. To obtain an estimate function for the ground state consider neglecting the r_{12}. The remaing contribution to the Hamiltonian is then given by, using spherical coordinates,

$$H = \sum_{i=1}^{2}\left[-\frac{\hbar^2}{2m}\frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2\frac{\partial}{\partial r_i}\right) - \frac{Ze^2}{r_i}\right]. \tag{2}$$

Since the Hamiltonian is symmetric with respect to particle one and two in this form it can be seen that the ground state functions will be of the same form (assuming that the two electrons couple their spins to total spin = 0, which means that their *spatial* wave function will be symmetric). In this respect, the ground state (lowest energy) solution of the two particle wave function can be found in the form

$$|\psi_0(r_1, r_2)>= \prod_{i=1}^{2} u(r_i). \tag{3}$$

With this functional form of the ground state the Schrodinger equation,

$$H|\psi_0(r_1, r_2)>= E|\psi_0(r_1, r_2)>,$$

leads to the equation

$$\frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2\frac{\partial u}{\partial r_i}\right) + \frac{2m}{\hbar^2}\left(E_i + \frac{Ze^2}{r_i}\right)u = 0, \tag{4}$$

for $u_(r_i)$ for $i = 1, 2$ and $E = E_1 + E_2 = 2E_1$. The solution of the differential equation is of the form

$$u(r) = Ae^{-ar}. \tag{5}$$

It is easily seen that $a = Z/a_0$, where $a_0 = \hbar^2/me^2$, and $E_i = -(Ze)^2/(2a_0)$. From this it is readily clear that

$$|\psi_0(r_1, r_2)>= A^2 e^{-\frac{Z}{a_0}(r_1+r_2)}. \tag{6}$$

The normalization will invoke the use of a symmetry argument during the calculation. With this in mind the normalization follows.

$$\begin{aligned}
1 &= < \psi_0(r_1, r_2)|\psi_0(r_1, r_2) > \\
&= A^4 \int_{r_1} \int_{r_2} e^{-\frac{2Z}{a_0}(r_1+r_2)} d^3r_1 d^3r_2 \\
&= A^4 \left[\int_0^\infty \int_\Omega e^{-\frac{2Zr}{a_0}} r^2 dr d\Omega \right]^2 \\
&= A^4 (4\pi)^2 \left[\int_0^\infty e^{-\frac{2Zr}{a_0}} r^2 dr \right]^2 \\
1 &= A^4 \left(\frac{\pi a_0^3}{Z^3} \right)^2 . \qquad (7)
\end{aligned}$$

From this result the value of A is given by

$$A = \sqrt{\frac{Z^3}{\pi a_0^3}}. \qquad (8)$$

The normalized ground state wave function to be used is now provided by

$$|\psi_0(r_1, r_2) >= \frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0}(r_1+r_2)} \qquad (9)$$

while the energy is given by $E = -(Ze)^2/a_0 = 8E_H = -108.8$ eV. This is considerably more negative than the experimentally known binding energy of He, -78.6 eV.

Since the ground state function for non-interactions has been found it can now be used to estimate the general state with interaction terms. In general the variational method is given by the form

$$< E >= \frac{< \psi|H|\psi >}{< \psi|\psi >}. \qquad (10)$$

Since the wave functions being used have been normalized the form of $< E >$ is then reduced to $< E >=< \psi|H|\psi >$.

Consider the argument that in the presence of another electron, each of the electrons are influenced by a decreased charge from the nucleus. With this in mind let $Z \to Z - \sigma$, where σ is the screening charge. Under this change the ground state wave function becomes

$$|\psi_0(r_1, r_2) >= \frac{(Z-\sigma)^3}{\pi a_0^3} e^{-\frac{Z-\sigma}{a_0}(r_1+r_2)}. \qquad (11)$$

The Hamiltonian, equation (1), can be seen in the following form.

$$\begin{aligned}
H &= \frac{1}{2m}\left(P_1^2 + P_2^2\right) - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}} \\
H &= \sum_{i=1}^{2} \left[\frac{P_i^2}{2m} - \frac{(Z-\sigma)e^2}{r_i} \right] - \sigma e^2 \left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}. \qquad (12)
\end{aligned}$$

Using this shifted form of the Hamiltonian it is evident that $H|\psi_0>$ becomes

$$
\begin{aligned}
H|\psi_0(r_1, r_2)> &= \left[E(Z-\sigma) - \sigma e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{r_{12}}\right]|\psi_0(r_1, r_2)> \\
&= \left[-\frac{(Z-\sigma)^2 e^2}{a_0} - \sigma e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{r_{12}}\right]|\psi_0(r_1, r_2)> . \quad (13)
\end{aligned}
$$

Since $<E> = <E(\sigma)>$ is being sought in the form $<\psi|H|\psi>$ it is evident that

$$
\begin{aligned}
<E> = &-\frac{(Z-\sigma)^2 e^2}{a_0} <\psi_0|\psi_0> - \sigma e^2 <\psi_0|\left(\frac{1}{r_1}+\frac{1}{r_2}\right)|\psi_0> \\
&+ <\psi_0|\frac{e^2}{r_{12}}|\psi_0> \\
= &-\frac{(Z-\sigma)^2 e^2}{a_0} - \sigma e^2 <\psi_0|\left(\frac{1}{r_1}+\frac{1}{r_2}\right)|\psi_0> + <\psi_0|\frac{e^2}{r_{12}}|\psi_0> . \quad (14)
\end{aligned}
$$

The expected energy value can be seen as

$$<E> = -\frac{(Z-\sigma)^2 e^2}{a_0} - \sigma e^2 I_1 + e^2 I_2, \quad (15)$$

where

$$I_1 = <\psi_0|\left(\frac{1}{r_1}+\frac{1}{r_2}\right)|\psi_0> \quad (16)$$

and

$$I_2 = <\psi_0|\frac{1}{r_{12}}|\psi_0> . \quad (17)$$

The caculations of I_1 and I_2 are to follow. For I_1 it proceeds as follows, where A_σ^2 is the normalization constant of (11).

$$
\begin{aligned}
I_1 &= <\psi_0|\left(\frac{1}{r_1}+\frac{1}{r_2}\right)|\psi_0> \\
&= A_\sigma^4 \int_{r_1}\int_{r_2}\left(\frac{1}{r_1}+\frac{1}{r_2}\right) e^{-\frac{2(Z-\sigma)}{a_0}(r_1+r_2)} d^3r_1 d^3r_2 \\
&= A_\sigma^4 (4\pi)^2 \left[\int_0^\infty e^{-\frac{2(Z-\sigma)}{a_0}r_1} r_1 dr_1 \cdot \int_0^\infty e^{-\frac{2(Z-\sigma)}{a_0}r_2} r_2^2 dr_2 \right. \\
&\quad \left. + \int_0^\infty e^{-\frac{2(Z-\sigma)}{a_0}r_2} r_2 dr_2 \cdot \int_0^\infty e^{-\frac{2(Z-\sigma)}{a_0}r_1} r_1^2 dr_1 \right] \\
&= 2^5 \pi^2 A_\sigma^4 \int_0^\infty e^{-\frac{2(Z-\sigma)t}{a_0}} t dt \cdot \int_0^\infty e^{-\frac{2(Z-\sigma)u}{a_0}} u^2 du \\
&= 2^5 \pi^2 A_\sigma^4 \cdot \frac{a_0^2}{4(Z-\sigma)^2} \cdot \frac{a_0^3}{4(Z-\sigma)^3} \\
&= \frac{2a_0^5 \pi^2 A_\sigma^4}{(Z-\sigma)^5} . \quad (18)
\end{aligned}
$$

Using the normalization constant A_σ^2 from equation (11) the desired value becomes

$$I_1 = \frac{2(Z-\sigma)}{a_0}. \tag{19}$$

The calculation of I_2 is a little more difficult as will be seen. The method of calculation is to use the multipole expansion

$$\frac{1}{r_{12}} = \begin{cases} \frac{1}{r_2}\sum_{n=0}^{\infty}\left(\frac{r_1}{r_2}\right)^n P_n(\cos\theta) & 0 \le r_1 \le r_2 \\ \\ \frac{1}{r_1}\sum_{n=0}^{\infty}\left(\frac{r_2}{r_1}\right)^n P_n(\cos\theta) & r_2 \le r_1 \le \infty \end{cases}. \tag{20}$$

It is seen that the only contribution comes from the $n = 0$ terms in the case being considered in this example, since $\int P_n(\cos\theta)d\Omega = 0$ for all $n > 0$.

The evaluation of I_2 follows.

$$\begin{aligned} I_2 &=< \psi_0|\frac{1}{r_{12}}|\psi_0 > \\ &= A_\sigma^4(4\pi)^2 \int_0^\infty \int_0^\infty e^{-\frac{2(Z-\sigma)}{a_0}(r_1+r_2)} \frac{r_1^2 r_2^2}{r_{12}} dr_1 dr_2 \\ I_2 &= (4\pi)^2 A_\sigma^4 \int_0^\infty e^{-\frac{2(Z-\sigma)}{a_0}r_2} f(r_2) r_2^2 dr_2, \end{aligned} \tag{21}$$

where

$$f(r_2) = \int_0^\infty e^{-\frac{2(Z-\sigma)}{a_0}r_1} \frac{r_1^2}{r_{12}} dr_1. \tag{22}$$

The integral $f(r_2)$ can be evaluated as follows.

$$\begin{aligned} f(r_2) &= \frac{1}{r_2}\int_0^{r_2} e^{-\frac{2(Z-\sigma)}{a_0}r_1} r_1^2 dr_1 + \int_{r_2}^\infty e^{-\frac{2(Z-\sigma)}{a_0}r_1} r_1 dr_1 \\ &= \frac{a_0^3}{8(Z-\sigma)^3 r_2}\int_0^b e^{-t}t^2 dt + \frac{a_0^2}{4(Z-\sigma)^2}\int_b^\infty e^{-t} t dt, \end{aligned} \tag{23}$$

where the substitution $t = 2(Z-\sigma)r_1/a_0$ was used and $b = 2(Z-\sigma)r_2/a_0$.

It is readily seen that

$$\int_0^x e^{-t}t^2 dt = 2 - (x^2 + 2x + 2)e^{-x} \tag{24}$$

and

$$\int_x^\infty e^{-t} t dt = (x+1)e^{-x}. \tag{25}$$

When these relations are used $f(r_2)$ becomes

$$f(r_2) = \frac{a_0^2}{4(Z-\sigma)^2}\left[\frac{a_0}{(Z-\sigma)r_2} - \left(1 + \frac{a_0}{(Z-\sigma)r_2}\right)e^{-\frac{2(Z-\sigma)r_2}{a_0}}\right]. \tag{26}$$

From this result for $f(r_2)$ the value or I_2 from equation (21) becomes

$$\begin{aligned}
I_2 &= \frac{4\pi^2 a_0^2 A_\sigma^4}{(Z-\sigma)^2}\left[\frac{a_0}{Z-\sigma}\int_0^\infty e^{-\frac{2(Z-\sigma)r}{a_0}} r dr - \frac{a_0}{Z-\sigma}\int_0^\infty e^{-\frac{4(Z-\sigma)r}{a_0}} r dr \right. \\
&\qquad \left. - \int_0^\infty e^{-\frac{4(Z-\sigma)r}{a_0}} r^2 dr\right] \\
&= \frac{\pi^2 a_0^5 A_\sigma^4}{(Z-\sigma)^5}\left[\frac{3}{4}\int_0^\infty e^{-t} t dt - \frac{1}{16}\int_0^\infty e^{-t} t^2 dt\right] \\
&= \frac{5\pi^2 a_0^5 A_\sigma^4}{8(Z-\sigma)^5} \\
I_2 &= \frac{5(Z-\sigma)}{8a_0}.
\end{aligned} \tag{27}$$

Now that the elements have been calculated, equations (15), (19), and (27) may be combined to provide the energy form as

$$\begin{aligned}
< E(\sigma) > &= -\frac{e^2}{a_0}(Z-\sigma)^2 - 2\sigma\frac{e^2}{a_0}(Z-\sigma) + \frac{5}{8}\frac{e^2}{a_0}(Z-\sigma) \\
&= -\frac{e^2}{a_0}Z^2 + \frac{e^2}{a_0}\sigma^2 + \frac{5}{8}\frac{e^2}{a_0}(Z-\sigma).
\end{aligned} \tag{28}$$

The maximized value can be found by taking the derivative of $< E >$ with respect to σ and set to zero. This yields

$$0 = \frac{\partial < E >}{\partial \sigma} = 2\frac{e^2}{a_0}\sigma - \frac{5}{8}\frac{e^2}{a_0} \tag{29}$$

from which $\sigma = 5/16$ is obtained.

Using the value of $\sigma = 5/16$ in the energy and wave function lead to

$$|\psi_0(r_1, r_2) >= \frac{1}{\pi a_0^3}\left(Z - \frac{5}{16}\right)^3 e^{-\frac{16Z-5}{16a_0}(r_1+r_2)} \tag{30}$$

and

$$< E >= -\frac{e^2}{a_0}\left(Z - \frac{5}{16}\right)^2. \tag{31}$$

As an example of the resulting analysis let $Z = 2$, as is the case for Helium. The ground state energy is calculated to be $E_0 = -77.456$ eV, which is in fairly good agreement with the known experimental value, $E_0 = -78.975$ eV. The variational method, which overestimates the energy values, differs from the known value by only 1.9%.