SEPARABLE WAVE FUNCTION OF THE GROUND STATE OF HELIUM CONSTRUCTED FROM HYLLERAAS' WAVE FUNCTION

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ABSTRACT

The single-electron wave function of the ground state of the helium atom is obtained from Hylleraas' well-known wave function by integrating the latter over the coordinates of one electron. The energy of the ground state calculated with this one-electron wave function is -5.717Rh, compared with the value -5.755 given by the self-consistant field solution.

The energy of the normal state of helium has been calculated by various methods. The variational calculation with the use of one-parameter hydrogenic wave function yields the value −5.695Rh compared with the observed value −5.810 Rh.[1] The method of self-consistant field yields the value −5.755 Rh.[2] It is shown by Hylleraas that considerable improvement can be achieved by employing wave functions containing the distance r_{12} between the two electrons. Thus the comparatively simple wave function[1]

$$\Phi(r_1, r_2) = e^{-\frac{1}{2}(r_1 + r_2)} \left\{ 1 + 0.08\, r_{12} + 0.01(r_1 - r_2)^2 \right\} \qquad (1)$$

yields the considerably better value −5.8048S. Now theory requires that energy value obtained by the method of self-consistant field is the best obtainable on the assumption of the separability of the wave function into one-electron functions. It is possible to obtain the one-electron function by integrating over the coordinates of one of the two electrons in (1) and it is of some interest to calculate the energy of the normal state of helium with the one-electron wave function so obtained and to compare it with those obtained by the use of (1), and by the

(1) Hylleraas; *Z. f. Phy.* *54*. 347 (1929), *65*. 209 (1930).
(2) Hartree, *Proc. Camb. Phil. Soc.* *24*. 89, 111, 426 (1928).

self-consistent field method.   The object of the present note is to carry out this calculation.

The probability of finding the electron 1 within the volume element $d\tau_1$ is given by squaring $\Phi(r_1, r_2)$ in (1) and integrating over $d\tau_2$, thus

$$\sigma(r_1)d\tau_1 = d\tau_1 N^2 \iiint |\Phi(r_1, r_2)|^2 d\tau_2 \qquad (2)$$

where the normalization factor is given by

$$N^2 \iint |\Phi(r_1, r_2)|^2 d\tau_1 d\tau_2 = 1$$

or

$$\int \sigma(r_1)d\tau_1 = 1 \qquad (3)$$

Following Hylleraas, we shall employ for the scale factor of length the value $3.6310\,\text{Å}$.   Putting (1) into (2) and expressing r_{12}^2 in terms of $r_1 r_2 \cos\theta_{12}$, we find

$$\sigma(r_1) = N^2\left\{ 4\pi \cdot \frac{1}{(3.6310)^3}\int_0^\infty r_2^2\, e^{-(r_1+r_2)}\left[1+0.02(r_1-r_2)^2\right.\right.$$

$$+0.0064(r_1^2+r_2^2)+0.0001(r_1-r_2)^4\Big] dr_2$$

$$+ \iiint e^{-(r_1+r_2)}\left[0.16r_{12}+0.0064(-2r_1 r_2 \cos\theta_{12})\right.$$

$$+0.0016\, r_{12}(r_1-r_2)^2\Big] d\tau_2 \bigg\}$$

The first integral may be integrated directly.   For the second integral, it is obvious that the term with $\cos\theta_{12}$ factor gives no contribution because it has opposite signs and equal magnitudes on the two sides of $\theta_{12} = \pi/2$.   To evaluate

$$.0016 \iiint e^{-(r_1+r_2)}\left[100+(r_1-r_2)^2\right] r_{12}\, d\tau_2$$

it is convenient to use the bipolar coordinates r_2, r_{12} and the angle φ about the radius vector r_1 as axis as the coordinates.   The volume element is

$$\frac{1}{(3.6310)^3}\, r_2^2 \sin\theta_{12}\, dr_2\, d\theta_{12}\, d\varphi,$$

or, in terms of the bipolar coordinates,

$$\frac{1}{(3.6310)^3}\frac{r_2}{r_1}\, r_{12}\, dr_{12}\, dr_2\, d\varphi.$$

On integrating over φ, the above integral becomes

$$\frac{1}{(3.6310)^3}\frac{0.0032\pi}{r_1}\, e^{-r_1}\int_0^\infty r_2\, e^{-r_2}\, dr_2 \int_{r_1-r_2}^{r_1+r_2} r_{12}^2\left[100+(r_1-r_2)^2\right]dr_{12}$$

This expression can be directely integrated. Combining the result with the first integral, we obtain the expression for $\sigma(r_1)$:

$$\sigma(r_1) = \frac{4\pi N^2 e^{-r_1}}{r_1}\left\{1.6640+2.5576\, r_1+0.0832\, r_1^2+0.0480\, r_1^3+0.0008 r_1^4\right.$$

$$\left.+0.0002\, r_1^2-e^{-r_1}(1.6640+0.384\, r_1)\right\}.$$

The condition of normalization gives

$$1 = \int \sigma(r_1)d\tau_1 = \frac{4\pi}{(3.6310)^3}\int_0^\infty \sigma(r_1)r_1^2\, dr_1 = \frac{16\pi^2\times 8.1984\, N^2}{(3.6310)^3\times 10^3}.$$

whence
$$N^2 = \frac{(3.6310)^3\times 10^3}{16\pi^2+8.1984}.$$

Then the separated wave function which gives the correct probability is clearly given by the simple product

$$\psi_{1s}(1)\,\psi_{1s}(2) = \sqrt{\sigma(r_1)\cdot\sigma(r_2)}.$$

We shall proceed to compute the energy of the system as described by this wace function. The Hamiltonian operator may be written in atomic units in the form

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

which may be regarded as consisting of the three parts

$$T = -\nabla_1^2 - \nabla_2^2,$$

$$V_{12} = \frac{2}{r_{12}},$$

$$V = -2\left(\frac{2}{r_1} + \frac{2}{r_2}\right).$$

Take first V. Since coordinates 1 and 2 enter symmetrically, we may write

$$V = -8\left\{ 4\pi \int_0^\infty \frac{\sigma(r_1)}{r_1} r_1^2\, dr_1 \right\} = 13.5038.$$

Next we take V_{12}.

$$V_{12} = 2 \iint \sigma(r_1)\, \sigma(r_2)\, \frac{1}{r_{12}}\, d\tau_1\, d\tau_2\,.$$

We may expand $1/r_{12}$ according to

$$\frac{1}{r_{12}} = \sum_{k=0}^\infty \left(\frac{r_<^k}{r_>^{k+1}} \right) P_k(\cos\theta_{12}).$$

where $r_<$ is the smaller of r_1, r_2 and $r_>$ the greater of them. For fixed coordinates 1, we may use the polar coordinates $(r_2, \theta_{12}, \varphi)$ for coordinates 2 with r_1 as polar axis.

Since the integrand does not depend on φ, the integration over φ gives a factor 2π. The integration over θ_{12} gives a factor 2, and the only surviving term in the series of $1/r_{12}$ is the first term $(k=0)$. After performing the integration over r_2 and some quite lengthy numerical simplifications, we find

$$\overline{V}_{12} = \frac{4\times(3.6310)^3}{(8.1984)^2} \int_0^\infty \left\{ e^{-2r_1} \left[7.866\, r_1 + 17.333\, r_1^2 + 8.7349\, r_1^3 \right.\right.$$

$$+1.2165\, r_1^4 + .31376\, r_1^5 + .0249155\, r_1^6 + .00412696\, r_1^7$$

$$+1.9696\times10^{-4}\, r_1^8 + 2.208\times10^{-5}\, r_1^9 + 5.2\times10^{-7}\, r_1^{10} + 4\times10^{-8}\, r_1^{11}$$

$$- e^{-3r_1} \left[9.4302\, r_1 + 9.64585\, r_1^2 + 2.1609\, r_1^3 + .247910\, r_1^4 \right.$$

$$+ .034150\, r_1^5 + 1.9632\times10^{-3}\, r_1^6 + 1.152\times10^{-4}\, r_1^7$$

$$+ e^{-4r_1} \left[1.5442\, r_1 + .67684\, r_1^2 + .073728\, r_1^3 \right) \right] \right\} dr_1\,.$$

which may be readily evaluated and gives

$$\overline{V}_{12} = 2.0528.$$

Now we go on to compute the value of $\overline{T}$. Due to the symmetry between coordinates 1 and 2, it may be written as

$$\overline{T} = -8\pi \int_0^\infty \sqrt{\sigma}\, \frac{d}{dr}\left(r^2 \frac{d}{dr} \sqrt{\sigma} \right) dr\,.$$

where ∇^2 reduces simply to $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)$. Integrating by parts, we obtain directly the alternative expression

$$T = 8\pi\int_0^\infty\left(\frac{d}{dr}\sqrt{\sigma}\right)^2 r^2 dr = 2\pi\int_0^\infty \frac{\sigma'}{\sigma}\frac{d\sigma'}{dr} \cdot r^2 dr$$

$$= \frac{(3.6510)^2}{2\times8.1984}\int_0^\infty\left\{\left[1.6640+1.6640\,r+2.4944\,r^2+.0125\,r^3+.0456\,r^4\right.\right.$$

$$\left.\left.+.0002\,r^5-e^{-r}(1.6640+3.0323\,r+.768\,r^2)\right]\frac{1}{r}\right\}dr.$$

As this expression cannot be integrated analytically, we have to use the methods of numerical integration. Due to the rather high degree of accuracy required of the result and the lenthy expression of the integrand, a great deal of labor is necessary to carry through the integration. In the first place, every ordinate has to be calculated with great accuracy and a rather large number of ordinates have to be taken. In the second place, we have to be able to estimate the degree of the accuracy attained. For our calculation, in view of the nature of the integrand (varying rapidly and having large magnitude at first), the intervals are taken to be $\frac{1}{4}$ between $r=0$ and $r=3$; $\frac{1}{2}$ between $r=3$ and $r=9$; and 1 between $r=9$ and $r=15$, and all the ordinates are calculated correct to 0.01%

It is found that if we use an expression $0.0039(\frac{1}{2})^{r-15}$ for the integrand for $r<15$, we would introduce no appreciable error. For each of the three regions namely $r=0-3$, $r=3-9$ and $r=9-15$, we may use both of the two most commonly used methods:

A. Simpson's rule

$$S = \frac{d}{3}(a_0+4a_1+2a_2+\ldots\ldots+4a_{2n-1}+a_{2n})$$

B. The three-eights rule [3]

$$S = \frac{3d}{8}(a_0+3a_1+3a_2+2a_3+\ldots\ldots+3a_{3n-1}+a_{3n}),$$

For the three regions, the integral is evaluated by both methods. The results are

$r=3-9$ A. 2.93563   B. 2.93562   difference   .00001

$r=9-15$ A. .097541   B. .0976144   difference   .00007

$r=0-3$ A. 4.08637   B. 4.08717   difference   .00008

For $r>15$

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(3) Whittaker and Robinson, *The Calculus of Observations*, p. 157.

$$\text{yield} \ .00160 \int_{15}^{\infty} (\tfrac{1}{3})^{r-15} \, dr + .00130 \int_{0}^{\infty} (\tfrac{1}{3})^x \, dx = \frac{.00131}{-\ln(\tfrac{1}{3})} = .00189.$$

Summing up the difference,[6] we can say safely that the error should not greatly exceed .001 Combining the contribution from the three regions, we find the integral to have the value

$$7.122 \qquad \text{within} \quad .001$$

Such accuracy is completely satisfactory for our purpose. It then follows that

$$T = 5.734 \qquad \text{within} \quad .001$$

So the total energy is given by

$$E = T + V_{12} + V$$
$$= 5.734 + 2.0528 - 13.5039 = -5.717.$$

which is better than the value −5.695 given by the use of one parameter variation wave function, but is far too high compared with the value −5.755 given by the self-consistent field method. This is in agreement with the theory that the latter method gives the lowest possible energy of a system on the assumption of separation of the wave function into one-electron wave functions.

It is interesting to find how the energy comes out to be much above the value −5.805 of the original Hylleraas function. Using the formulae given in this paper, and converting to the units used in the present paper, the potential energy and kinetic energy are given in his case respectively by

$$V_{12} - V = -11.617, \qquad T = 5.812.$$

A little reflection will show that the value V is the same in our case and in Hylleraas's case. Hence using our value for V, we find for Hylleraas's case

$$V = -13.504, \qquad V_{12} = 1.887, \qquad T = 5.812.$$

We see that T is smaller in our case, but the value for V_{12} is so low in Hylleraas's case that it more than compensates the higher value for T and leads to a lower value for the total energy. The low value for V_{12} is indeed to be more or less expected, for Hylleraas's function containing r_{12} naturally takes better care of the mutual energy between the two electrons than the separable wave function.

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