

HYLLERAASIAN WAVE FUNCTION OF $2s^2\ ^1S$ OF HELIUM

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ABSTRACT

A variational calculation of the energy of the $2s^2\ ^1S$ state of helium has been carried out with the use of a wave function of the Hylleraasian type. The wave function is

$$\psi = e^{-0.2278s} \left\{ 1 - 0.17079s - 0.063155u - 0.013869t^2 \right. \\ \left. + 0.010044u^2 + 0.0064785s^2 \right\}$$

where s, t, u are in units of 4 times the first Bohr radius of hydrogen. The energy is

$$E(2s^2\ ^1S) = -1.5412 \text{ Rh.}$$

compared with the value -1.4403 Rh obtained by the method of self-consistent field.

There has been considerable interest in the theoretical energy values of the doubly excited states of helium since the suggestion, now abandoned, that the corona lines may be due to transitions between these doubly excited states. Variational calculations of the energy states have been carried out by a number of authors using single-electron wave function products ^(1), a), b), d) and the method of self-consistent field. ^(1), c) The energy values so obtained, while

(1) a) F. G. Fender and J. P. Vinti, *Phys. Rev.* 46, 78 (1934); b) Ta-You Wu, *ibid* 46, 239, (1934); c) Wm. S. Wilson *ibid* 43, 533 (1933); d) Wu and Ma, *ibid* 48, 917 (1935); *J. Chin. Chem. Soc.* 4, 344 (1935).

plausible, are expected to be subject to the same inaccuracy that similar calculations for the ground state of helium reveal. There is further the disturbing question concerning the orthogonality of the wave functions of the doubly excited states to the normal and those singly excited states of the same symmetry character. However, the problem of more accurate determination of these doubly excited states is of considerable interest in connection with the identification of the extreme ultraviolet lines $\lambda\lambda$ 329 and 357 \AA .⁽²⁾ The purpose of the present work is to carry out a calculation for the $2s^2\ ^1S$ state with a trial wave function of the type that Hylleraas has shown to be eminently suitable for the normal state of helium.

For the trial wave function of the state $2s^2\ ^1S$, we choose the following

$$\begin{aligned}\psi(r_1, r_2) &= \sum C_i \psi_i \\ &= e^{-ks} \{ C_1 + C_2(ks) + C_3(ks)^2 + C_4(kt)^2 + C_5(ku) + C_6(ku)^2 \} \quad (1)\end{aligned}$$

where $s=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$, and k is a scale factor to be determined by the variational calculation. The considerations that lead to this choice of the trial wave function are as follows: (i) The wave function (1) has been shown by Hylleraas to give for $1s^2\ ^1S$ an energy -5.80648 Rh , compared with the observed -5.8070 Rh .⁽³⁾ Now the $2s^2\ ^1S$ state has the same symmetry property as the normal state $1s^2\ ^1S$ and it is reasonable to assume that one of the six eigenvalues resulting from the application of the variational principle to the function (1) may be identified with the energy of $2s^2\ ^1S$. It is true that there are infinitely many states, namely, $1s\ ns\ ^1S$, that have the same symmetry as $1s^2\ ^1S$ and $2s^2\ ^1S$, i.e., symmetrical in the space coordinates of the two electrons. As the work of Hylleraas has shown⁽⁴⁾, however, the wave functions of such states as $1s\ 2s\ ^1S$ have to be approximated by functions of a different type than (1), namely, functions containing hyperbolic sines and hyperbolic cosines in s and t , corresponding to the presence of two effective charge parameters for the $1s$ and ns electrons in the approximation in which the wave

(2) Ta-You Wu, *Phys. Rev.* **66**, Dec. 1-15, (1944).

(3) E. A. Hylleraas, *Z. f. Phys.* **54**, 247 (1929).

(4) E. A. Hylleraas, *Ibid.*, **63**, 759 (1939).

function is constructed from single-electron wave functions. The form of (1) corresponding to only one effective charge parameter may hence be expected to be best suited for such states as $ns^2\ ^1S$. These considerations, it will be seen, seem to be borne out by the present calculation.

(ii). Another justification for the assumption of the form (1) for the wave function for $2s^2\ ^1S$ is based on the following consideration: In the approximation in which the wave function is a product of one-electron wave functions, the wave function is

$$\begin{aligned}\psi &= \psi(r_1) \psi(r_2) = e^{-\alpha(r_1+r_2)} (1-\beta r_1)(1-\beta r_2) \\ &= e^{-ks} \left\{ 1 - \beta s + \frac{\beta^2}{4} (s^2 - t^2) \right\},\end{aligned}$$

a better approximation is obtained by allowing the coefficients of the various terms to vary independently. By introducing terms containing $r_{12}=u$ which are found to achieve an essential improvement in the case of the normal state of helium, considerable improvement may be expected also in this case. This is also borne out by the result that the calculated energy comes out to be lower than that obtained by the method of self-consistent field.

The problem is now to find the stationary values of the variational problem⁽⁴⁾

$$\frac{M - (L - L')}{N} = \lambda$$

or
$$\sum_{i,j} \left[\lambda N_{ij} + (L_{ij} - L'_{ij}) - M_{ij} \right] C_i C_j = 0 \quad (2)$$

where

$$\begin{aligned}M &= \sum_{i,j} C_i C_j M_{ij}, & L &= \sum_{i,j} C_i C_j L_{ij}, \\ L' &= \sum_{i,j} C_i C_j L'_{ij}, & N &= \sum_{i,j} C_i C_j N_{ij},\end{aligned}$$

$$M_{ji} = M_{ij} = \int_0^\infty ds \int_0^s du \int_0^u dt \left\{ u(s^2 - t^2) \left[\frac{\partial \psi_i}{\partial s} \cdot \frac{\partial \psi_j}{\partial s} + \frac{\partial \psi_i}{\partial t} \cdot \frac{\partial \psi_j}{\partial t} \right. \right. \\ \left. \left. + \frac{\partial \psi_i}{\partial u} \cdot \frac{\partial \psi_j}{\partial u} \right] + s(u^2 - t^2) \left[\frac{\partial \psi_i}{\partial s} \cdot \frac{\partial \psi_j}{\partial u} + \frac{\partial \psi_i}{\partial u} \cdot \frac{\partial \psi_j}{\partial s} \right] \right. \\ \left. + t(s^2 - t^2) \left[\frac{\partial \psi_i}{\partial t} \cdot \frac{\partial \psi_j}{\partial u} + \frac{\partial \psi_i}{\partial u} \cdot \frac{\partial \psi_j}{\partial t} \right] \right\}$$

$$L_{ji} = L_{ij} = 2 \int_0^\infty ds \int_0^s du \int_0^u dt \cdot s u \psi_i \psi_j$$

$$L'_{ji} = L'_{ij} = \frac{1}{2} \int_0^\infty ds \int_0^s du \int_0^u dt \cdot (s^2 - t^2) \psi_i \psi_j$$

$$N_{ji} = N_{ij} = \frac{1}{2} \int_0^\infty ds \int_0^s du \int_0^u dt \cdot u(s^2 - t^2) \psi_i \psi_j$$

The energy λ is here in units of 4 Rh, and the distances s, t, u are in units of $\frac{1}{2}$ the Bohr radius. Application of the variational principle, $\frac{\partial \lambda}{\partial C_i} = 0$, gives

$$\sum_j \left[\lambda N_{ij} + L_{ij} - L'_{ij} - M_{ij} \right] C_j = 0, \quad (3)$$

and consequently the determinantal equation for the eigenvalues λ

$$|\lambda N_{ij} + L_{ij} - L'_{ij} - M_{ij}| = 0. \quad (4)$$

The various integrals $M_{ij}, L_{ij}, L'_{ij}, N_{ij}$ can be readily evaluated. They are given in the following tables

TABLE I.

$512 M_{ij} / k^2$	1	2	3	4	5	6
1	256	512	1,152	384	400	768
2		1,408	4,224	1,152	1,080	2,688
3			16,128	3,840	3,200	9,984
4				3,840	1,168	3,840
5					1,024	2,800
6						9,984

TABLE II.

$512(L_{ij}-L'_{ij})/k$	1	2	3	4	5	6
1	216	540	1,620	348	416	1,012
2		1,620	5,670	1,218	1,248	3,542
3			22,680	4,872	4,368	14,168
4				2,148	1,924	3,532
5					1,012	2,976
6						19,260

TABLE III.

$512N_{ij}$	1	2	3	4	5	6
1	32	86	336	46	70	192
2		326	1,344	192	245	768
3			6,048	864	980	3,456
4				288	154	576
5					192	620
6						2,400

To solve the determinantal equation (4) for the eigenvalues λ , the procedure suggested by James and Coolidge is found very convenient⁽⁵⁾. It consists in reducing the equation (4), now written in the form

$$D = |d_{ij}| = 0, \quad (4)$$

$$\text{to } D = D_{11}D_{22} \cdots D_{nn} = 0 \quad (5)$$

$$\text{where } D_{ij} = d_{ij} - \sum_{k=1}^{i-1} \frac{D_{ki} D_{kj}}{D_{kk}} \quad (6)$$

(5) H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933)

with $D_{1j} = d_{1j}$ and $D_{ij} = 0$ for $i > j$. In the actual calculation, an appropriate value for the scale factor k is first chosen on the basis of the earlier calculations using single-electron wave function product for ψ . (1d) A value for λ also based on the earlier calculations is then substituted into (4) and D is calculated according to (5) and (6). If D comes out to be positive, another value for λ is tried to make $D < 0$. The eigenvalue is then obtained by interpolation between these two values of λ . Finally the scale factor k is varied in its neighbourhood to locate the minimum for the particular root in question.

In this way, the values of k and λ corresponding to $2s^2$ 1S obtained with the wave function

$$\psi = e^{-k\ell} [C_1 + C_2(k\ell) + C_3(k\ell)^2 + C_4(k\ell)^3]$$

are $k = 0.223$, $\lambda = -0.35722$ (4 Rh)

corresponding to an effective charge parameter 0.892 and energy -1.4285 Rh. With the 6-term wave function (1), it is found

$$k = 0.2278, \quad \lambda = -0.3853 \text{ (4 Rh)}$$

corresponding to effective charge parameter = 0.9112.

$$E = -1.5412 \text{ Rh}$$

and

$$\psi = e^{-0.2278 s} \left\{ 1 - 0.17079 s - 0.063155 u - 0.013869 t^2 + 0.010044 u^2 + 0.0064785 s^2 \right\} \quad (7)$$

The value $E = -1.5412$ Rh is lower than the self-consistent field value -1.4400 Rh by an amount which is somewhat greater than the corresponding difference in the case of the normal state ($E = -5.897$ vs. -5.750). This is rather unexpected since for the $2s^2$ 1S state the relative importance of terms containing r_{12} may be expected to be smaller because the mutual interaction between the two electrons is smaller. This calls for a closer examination of the assumptions for the wave function (1) for the state $2s^2$ 1S .

TABLE IV.

eigenvalues	1st appro.	2nd appro.	3rd appro.	4th appro.	5th appro.	6th appro.
λ_6						0.01 ($K=0.2$)
λ_5					-0.266 ($K=0.22$)	-0.268 ($K=0.22$)
λ_4				-0.86 ($K=0.23$)	-0.879 ($K=0.23$)	-0.885 ($K=0.23$)
λ_3			-0.70 ($K=0.28$)	-0.89 ($K=0.28$)	-0.896 ($K=0.28$)	-0.90 ($K=0.28$)
λ_2		-0.73 ($K=0.3$)	-0.91 ($K=0.3$)	-1.003 ($K=0.3$)	-1.008 ($K=0.3$)	-1.01 ($K=0.3$)
λ_1	-1.35 ($K=0.42$)	-1.41 ($K=0.43$)	-1.43 ($K=0.44$)	-1.44 ($K=0.45$)	-1.45 ($K=0.45$)	-1.451 ($K=0.45$)

The first question that arises is the identification, or correlation, of the eigenvalues of (1) with the actual states of helium. In table IV are shown the eigenvalues for the 1st, 2nd, 3rd, 4th, 5th and 6th approximation corresponding to one, two, . . . , six terms in the wave function in (1). Each eigenvalue is a minimum with respect to its own appropriate value of k . Only the values for the 4th root for the 4th and the 6th approximation have been accurately calculated, the other being only roughly estimated. The trend in the eigenvalues as one proceeds to higher approximations is what one would have expected according to the theory.⁽⁶⁾ The lowest root is shown by Hylleraas to be $1s^2\ ^1S$. The second root λ_2 lies very close to and the third root lies above the ionization limit $1s\ ^1S$. They are probably to be interpreted as very bad approximations to the states $1s\ 2s\ ^1S$ and $1s\ 3s\ ^1S$. That the fourth root lies considerably higher at $E = -1.5412\text{ Rh}$ seems to preclude its interpretation as $1s\ 4s\ ^1S$ and its general position seems to indicate the interpretation as $2s^2\ ^1S$. The fifth root $\lambda_5 = -0.283$ or $E_5 = -1.132\text{ Rh}$ may be interpreted as $2s\ 3s\ ^1S$ since the energy calculated with single-electron wave function is $E_5 = -1.144$.^(1d) The sixth root λ_6 is positive and may be interpreted as a bad approximation for such states as $2s\ 4s\ ^1S$. That there is a gap between the third and the 4th root where there should be infinitely many states $1s\ n s\ ^1S$, $n=4, 5, 6, \dots$ may be understood as follows: The disparity between the effective charge parameters of the $1s$ and the $n s$ electron increases as n increases so that the function ψ with the assumed form (1) cannot even roughly approximate these wave functions when $n > 3$. Even for $n=2, 3$, the function (1) can only be very bad approximations so that the 2nd and the 3rd root differ widely from the true eigenvalues. This consideration, together with a comparison with the eigenvalues and eigenfunctions obtained with single-electron wave function product, namely,^(1, d)

$$2s^2\ ^1S, \quad E = -0.3610\ (4\text{ Rh}).$$

$$\psi = e^{-0.22s} \left[1 - 0.22s - 0.01375(t^2 - s^2) \right] \dots$$

(6) J. K. L. MacDonald, *Phys. Rev.* **43**, 830 (1933)

seems to make the interpretation of the fourth root as the approximate eigenvalue for the state $2s^2\ ^1S$ plausible.

Another question is that of the orthogonality of the eigenfunction now interpreted as belonging to $2s^2\ ^1S$ to those of $1s^2\ ^1S$, $1s n s\ ^3S$. That the approximate eigenfunctions corresponding to the various roots are mutually orthogonal follows directly from the fact that the eigenfunctions are solutions of the equation

$$H\psi = \lambda\psi$$

and the Hermitean character of the Hamiltonian H . Hence the function (7) is orthogonal to that of the normal state. As the eigenfunctions corresponding to the 2nd and the 3rd root are only very rough approximations to the correct eigenfunctions of $1s2s\ ^1S$ and $1s3s\ ^1S$ and as the eigenfunctions of $1s n s\ ^3S$, $n > 3$ are not even roughly represented by the function (1), the wave function (7) is not exactly orthogonal to these eigenfunctions. For this reason, while the interpretation of the fourth eigenvalue as $2s^2\ ^1S$ is very probably correct, there is some uncertainty as to its numerical value. It must be emphasized, however, that all other previous calculations⁽¹⁾ are subject to the same uncertainty since there is no practical rigorous method to insure the orthogonality of the wave function of $2s^2\ ^1S$ to the infinitely many states $1s n s\ ^3S$.

In a recent paper⁽²⁾ it has been pointed out that while the extreme ultraviolet line $\lambda\ 320$ can be satisfactorily accounted as $1s2p\ ^3P - 2p^2\ ^3P$ with respect to both the position and the width of the line, the line $\lambda\ 357$ finds no satisfactory identification. The present calculation lowers the energy of $2s^2\ ^1S$ by about 20.10 R_h. The calculated frequencies of the transition $1s2p\ ^4P - 2s^2\ ^1S$, $1s3p\ ^4P - 2s^2\ ^1S$ are then approximately 276,890 cm^{-1} , 281,800 cm^{-1} compared with the observed value 279,715 cm^{-1} . It is true that a little further lowering of the energy value for $2s^2\ ^1S$ may bring the calculated frequency for the transition $1s3p\ ^4P - 2s^2\ ^1S$ into agreement with the observed value; but then it is not understandable why the transition $1s2p\ ^4P - 2s^2\ ^1S$, which may be expected to be stronger than the other, is not observed. In any case, the observed sharpness of the line $\lambda\ 357$ does not agree with the expected width for these transitions on account of the autoionization of the state $2s^2\ ^1S$.⁽²⁾ Further study of this question is desirable.