

# Analysis of the Three Parameter Wave Function of Hylleraas for the He I Ground State in Terms of Central Field Wave Functions\*

LOUIS C. GREEN, MARJORIE M. MULDER,† PAUL C. MILNER,‡ MARGARET N. LEWIS,§ AND JOHN W. WOLL, JR.†  
*Strawbridge Observatory, Haverford College, Haverford, Pennsylvania*

AND

ELEANOR K. KOLCHIN AND DAVID MACE, *Watson Scientific Computing Laboratory, Columbia University, New York, New York*  
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A study of configuration interaction in the ground state of He I has been carried through by expanding the various angular components of the three parameter wave function of Hylleraas in orthonormal sets of functions. The different sets have been constructed from symmetrized products of hydrogenic wave functions with different values of the parameter  $Z$ . The importance of the various configurations for  $Z=2$  is commented upon at some length. Configurations involving a free electron are shown to make surprisingly large contributions. The changing importance of the various components with changing  $Z$  is illustrated. In particular, the minimum with respect to  $Z$  of the contribution of configurations containing a free electron is pointed out. The implications of the results of these expansions for attempts to obtain wave functions for both normal and excited states of two-electron systems by the minimum principle from linear combinations of products of hydrogenic functions of the proper symmetry are discussed.

EXCELLENT approximate solutions of the Schrödinger equation can be obtained variationally for two-electron systems by using as one coordinate  $r_{12}$ , the interelectron distance. It has been pointed out<sup>1-3</sup> that a study of configuration interaction in these simple structures can be carried out by expanding such excellent solutions in central field wave functions.<sup>4</sup> In earlier work<sup>1</sup> an expansion of this type in symmetrized numerical self-consistent field functions was undertaken for the three- and the six-parameter wave functions given by Hylleraas<sup>5</sup> for the ground state of He I. For the three-parameter function a second expansion was also obtained using analytic variationally determined wave functions for the  $1s^2$  and  $1s2s$  configurations. However, the coefficient of the  $1s2s$  configuration was distinctly different in the numerical and the analytic expansions. It seemed probable that the same would be true of other configurations as well. This would mean that, unless one made relatively complete expansions in sets of orthonormal functions, one would find differing importance for the various angular components of the ground-state wave function depending on which type of radial functions was employed in the expansion.

Furthermore, the size of the various expansion coefficients suggested that for the purpose in hand one would not obtain a satisfactory approximation to a complete set unless one considered a large number of configurations. The effort required to find the necessary numerical radial functions appeared to be prohibitive.

To avoid these difficulties, an expansion of the form<sup>6</sup>

$$\Psi_H^N(r_1, r_2, r_{12}) = \sum_i c_i \Phi_i^N(r_1, r_2) P_i^N(\cos\theta) \quad (1)$$

was employed.<sup>2</sup> Here  $\Psi_H^N$  is the normalized Hylleraas wave function of  $r_1$  and  $r_2$ , the nuclear distances of the two electrons, and  $r_{12}$ , the interelectron distance. The  $\Phi_i^N$ 's are normalized functions of  $r_1$  and  $r_2$  whose form is determined by Eq. (1).<sup>2</sup> The  $P_i^N$ 's are the normalized Legendre polynomials of order  $i$  of the cosine of the angle between the two radius vectors.  $\Psi_H^N$  was normalized with respect to integration over  $r_1$ ,  $\theta_1$ , and  $\varphi_1$ , the coordinates of the first electron,  $r_2$  for the second electron,  $r_{12}$ , and  $\varphi$ , the Euler angle, which together with  $r_{12}$  specifies the direction of  $\mathbf{r}_2$  with respect to  $\mathbf{r}_1$ . The  $\Phi_i^N$ 's were normalized with respect to integration over  $r_1$ ,  $\theta_1$ ,  $\varphi_1$ ,  $r_2$ , and  $\varphi$ . The expressions for the  $\Phi_i^N$ 's and the values of the  $c_i$ 's have been presented in an earlier paper for both the three- and the six-parameter Hylleraas functions.<sup>2</sup> This earlier work also gives the values of the  $E_{ij}$ 's, the interaction energies between the  $i$ th and  $j$ th angular components, that is,

$$E = \sum_{ij} E_{ij} = \int \sum_i (c_i \Phi_i^N P_i^N)^* H \sum_j (c_j \Phi_j^N P_j^N) d\tau. \quad (2)$$

The results obtained in this way, as to the importance of the various angular components of  $\Psi_H^N$ , are, of course, not dependent on the choice of the radial

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† Now with Remington Rand Inc., Philadelphia, Pennsylvania.

‡ Now at Princeton University, Princeton, New Jersey.

§ Now at Brown University, Providence, Rhode Island.

<sup>1</sup> Green, Mulder, Ufford, Slaymaker, Krawitz, and Mertz, *Phys. Rev.* **85**, 65 (1952).

<sup>2</sup> Green, Mulder, and Milner, *Phys. Rev.* **91**, 35 (1953).

<sup>3</sup> Green, Lewis, Mulder, Wyeth, and Woll, *Phys. Rev.* **93**, 273 (1954).

<sup>4</sup> The possibility of investigating configuration interaction in He I in this manner was suggested to one of us (L. C. G.) by Dr. G. Breit.

<sup>5</sup> E. A. Hylleraas, *Z. Physik* **54**, 347 (1929).

<sup>6</sup> The value of an expansion in terms of Legendre functions was pointed out to two of us (L. C. G. and M. M. M.) by Dr. E. U. Condon.

eigenfunctions of any particular central-field problem. One of the most interesting results of this work was the large size found for the nonspherically symmetric components of the ground state wave function.

In the present paper we extend this earlier work by expanding the  $\Phi_i^N$ 's for the three-parameter Hylleraas function in terms of symmetrized products of the eigenfunctions of hydrogenic central fields for several different  $Z$ 's.

The expansion has the form

$$2\sqrt{2}\pi\Phi_i^N = \sum_{nm} c_{nlm} [2 + 2\delta(n, m)]^{-\frac{1}{2}} \\ \times \{R^N(nl|1)R^N(ml|2) + R^N(ml|1)R^N(nl|2)\} \\ + \sum_n \int c_{nl\epsilon} \frac{1}{\sqrt{2}} \{R^N(nl|1)R^N(\epsilon l|2) \\ + R^N(\epsilon l|1)R^N(nl|2)\} d\epsilon + \int c_{nl\eta} [2 + 2\delta(\epsilon, \eta)]^{-\frac{1}{2}} \\ \times \{R^N(\epsilon l|1)R^N(\eta l|2) + R^N(\eta l|1)R^N(\epsilon l|2)\} d\epsilon d\eta. \quad (3)$$

Here  $\Phi_i^N$  is the particular normalized angular component of the ground-state wave function that is to be expanded. The  $c$ 's are the various expansion coefficients. The  $\delta$ 's are Kronecker deltas.  $R^N(nl)$  and  $R^N(ml)$  are normalized radial eigenfunctions for discrete states of the central field, and  $R^N(\epsilon l)$  and  $R^N(\eta l)$  are normalized radial eigenfunctions for states lying in the continuum. These continuum eigenfunctions are normalized, so that for sufficiently large  $\rho$  the amplitude will approach<sup>7</sup>

$$\frac{1}{\sqrt{\pi}} \left[ \epsilon + \frac{2Z}{\rho} - \frac{l(l+1)}{\rho^2} \right]^{-\frac{1}{2}}.$$

Here  $\epsilon$  is the energy measured in units of  $R_{\text{He}}hc$ , where  $R_{\text{He}}$  is the Rydberg constant for He expressed in  $\text{cm}^{-1}$ , and  $\rho$  is the nuclear distance expressed in atomic units. The factor  $2\sqrt{2}\pi$  on the left side of Eq. (3) arises from the difference in the normalization of the  $\Phi_i^N$ 's and the  $R^N$ 's. The complexity which might accompany an expansion in central field wave functions has been greatly reduced in Eq. (3) by several considerations. In the first place, superposition of configurations can only occur between configurations of the same parity.<sup>8</sup> Thus, among the configurations of even parity which involve electrons with smaller  $l$  values, we need only consider  $ss$ ,  $pp$ ,  $sd$ , and  $dd$ . Second, the intervals in the  $1s2p\ ^3P$  term of He I are roughly two thousand times smaller than the separation of the  $^3P$  and  $^1P$ . The coupling is therefore closely Russell-Saunders. If the assumption is made that it is precisely so, it is only necessary to include on the right-hand side of Eq. (3) terms with the same  $L$  and  $S$  as the He I ground state

since these are the only ones which interact in pure Russell-Saunders coupling.<sup>8</sup> The  $sd$  configurations can therefore be dropped since they do not yield a  $^1S$  term, and in the  $ss$ ,  $pp$ , and  $dd$  configurations, only those combinations of single electron wave functions which yield  $^1S$  terms need to be considered. In the third place, the only configurations which can contribute to the spherically symmetric component of the ground state are the  $ss$  configurations, since these are the only ones for which the spherical harmonics in  $\theta_1$ ,  $\varphi_1$ , and  $\theta_2$ ,  $\varphi_2$  can combine to yield  $P_0^N(\cos\theta)$ . Similarly the only ones which can contribute to the expansion of  $\Phi_1^N$  are  $pp$  configurations. The justification for the notation in Eq. (3) is now clear: the only nonvanishing coefficients in the expansion of  $\Phi_i^N$  are those of the symmetrized products of the radial components of the  $ll$  configuration.

The choice still remains as to what type of radial wave functions to employ in the expansions. Earlier work<sup>1</sup> suggested that to obtain a relatively complete expansion, it would be necessary to employ a large number of configurations. Although a rapid convergence in the first few terms could be had by using numerical Hartree functions, it was not clear that the convergence would be more rapid in the later terms than with other simpler orthogonal sets. Among the possible sets of analytic functions, the hydrogenic functions offered the advantages of relative simplicity and of reasonably rapid convergence. It was decided to use two different sets of hydrogenic functions. In the first set, the emphasis in the expansion was to be on ease of determining the coefficients. It was expected that this expansion would require a large number of configurations to obtain a satisfactory approximation to completeness. In the second set, the emphasis was to be on the rapidity of the convergence. It was thought that the physical interpretation of the results would be about equally easy in the two cases. For the first set, hydrogenic functions with  $Z=2$  were employed, that is, the solutions of the radial part of the Schrödinger equation for  $\text{He}^+$ . For the second set, certain expansion coefficients were evaluated for hydrogenic functions for a series of values of  $Z$ , and then that  $Z$  was chosen which made the sum of the squares of those coefficients a maximum.

#### EXPANSION COEFFICIENTS FOR $Z=2$

The results of the expansion of  $\Phi_0^N$ , the spherically symmetric component of the ground-state wave function, in terms of hydrogenic functions with  $Z=2$  are given in Table I. In the first section the values of the expansion coefficients and their squares are given for each of the configurations listed in the first column. The integrals necessary to determine these quantities were first computed directly and were then checked by the factorization method.<sup>9</sup> In the second section is given

<sup>7</sup> E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), p. 178.

<sup>8</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 366.

<sup>9</sup> L. Infeld and T. E. Hull, *Revs. Modern Phys.* **23**, 21 (1951).

the value for the sum of the squares of the coefficients for all the configurations from  $1s6s$  to  $1s\infty s$ , estimated as described below, and the integral from  $\epsilon=0$  to  $\epsilon=\infty$  of the square of the coefficient for configurations involving a  $1s$  function and an  $s$  continuum function. The final line of Table I gives the sum of the squares of the coefficients for all configurations which were considered. If the expansion represented  $\Phi_0^N$  exactly, this sum would be one since both the wave functions for the different configurations and  $\Phi_0^N$  are normalized.

The estimated value, which appears in Table I, for the sum of the squares of the coefficients for the configurations from  $1s6s$  to  $1s\infty s$  was arrived at in the following manner. The series of discrete states from  $6s$  to  $\infty s$  was replaced by a continuum of states. The wave functions for these states were taken to be the series expansion for the hydrogenic continuum function in terms of powers of the energy,  $\epsilon$ , and Bessel functions of the nuclear distance,  $r$ .<sup>10</sup> This expansion converges rapidly for small  $\epsilon$ . Symmetrized products of this wave function and a  $1s$  wave function were constructed in the usual manner. The accuracy with which this symmetrized function gives the square of the expansion coefficients for the discrete states was determined by computing the integral of the square of the expansion coefficient between negative values of  $\epsilon$  corresponding to the quantum numbers  $n=3.5$  and  $n=4.5$  and between values corresponding to  $n=4.5$  and  $n=5.5$ . The values of these integrals were then compared with the values found for  $(c_{1s4s})^2$  and  $(c_{1s5s})^2$  by the usual methods. The differences proved to be 4.8 percent and 2.6 percent, respectively. It therefore seemed probable, that if the sum of the squares of the expansion coefficients for the configurations from  $1s6s$  to  $1s\infty s$  was taken to be the value of the above integral from an  $\epsilon$  corresponding to  $n=5.5$  to  $\epsilon=0$ , the resulting error would be less than 2.0 percent.

The values of the expansion coefficients for configurations involving a free electron were computed using the hydrogenic  $s$  continuum function. For small values of  $\epsilon$  the results were checked by the use of the Bessel function expansion for the continuum function.<sup>10</sup> The

TABLE I. Coefficients for the expansion of  $\Phi_0^N$  in the form of Eq. (3) where the  $R^N$ 's are hydrogenic functions with  $Z=2$ .

Configuration	$c_{nsm}$	$(c_{nsm})^2$
$1s^2$	0.96430	0.92988
$1s2s$	-0.21637	0.04682
$1s3s$	-0.07586	0.00576
$1s4s$	-0.04316	0.00186
$1s5s$	-0.02913	0.00085
$2s^2$	-0.01437	0.00021
$\sum_{n=6}^{\infty} (c_{1sns})^2$		0.00156
$\int_{\epsilon=0}^{\epsilon=\infty} (c_{1s\epsilon s})^2 d\epsilon$		0.01199
Sum		0.99893

<sup>10</sup> Yost, Wheeler, and Breit, Phys. Rev. 49, 174 (1936).

TABLE II. Coefficients for the expansion of  $\Phi_1^N$  in the form of Eq. (3) where the  $R^N$ 's are hydrogenic functions with  $Z=2$ .

Configuration	$c_{npmp}$	$(c_{npmp})^2$
$2p^2$	-0.47010	0.22100
$2p3p$	-0.27863	0.07763
$2p4p$	-0.16661	0.02776
$3p^2$	-0.08401	0.00706
$\sum_{n=5}^{\infty} (c_{2pmp})^2$		0.0387
$\int_{\epsilon=0}^{\epsilon=\infty} (c_{2p\epsilon p})^2 d\epsilon$		0.290
Sum		0.662

results were further checked over a wider range of  $\epsilon$  by using numerical hydrogenic wave functions computed at the Watson Scientific Computing Laboratory of IBM at Columbia University. Among other values of  $\epsilon$ , the values of  $c_{1s\epsilon s}$  were found at  $\epsilon=0.0$ , 2.0, 4.0, 10.4, and 21.6 to be -0.1043, -0.0407, -0.0215, -0.0059, and -0.0017, respectively. When the values of  $c_{1s\epsilon s}$  had been determined, the integral of the square of these coefficients from  $\epsilon=0$  to  $\epsilon=21.6$  was computed numerically. Beyond  $\epsilon=21.6$  the integrand was estimated to be too small to contribute in the fifth decimal place to the value of the integral. The integral is therefore listed in the next to last line of Table I as extending from  $\epsilon=0$  to  $\epsilon=\infty$ .

The last line of Table I shows that the expansion of  $\Phi_0^N$  is relatively complete in spite of the fact that only one configuration not involving a  $1s$  electron has been considered. This is true even though  $Z$  has been set equal to 2, a value which must be rather far from that which best describes the average field acting on each electron. With  $Z=2$  one might expect that configurations including two excited electrons would play an important role. In fact, configurations involving  $1s$  electrons account for at least 99.82 percent of the sum of the squares of the expansion coefficients. Perhaps the most interesting result in Table I is the large contribution of those configurations in which one electron is in a continuum state. In fact the  $1s\epsilon s$  configurations taken together account for more than any other configuration except  $1s^2$  and  $1s2s$ . The continuum configurations which are considered here account for 49 percent of what remains after the contribution of the  $1s^2$  and  $1s2s$  configurations have been removed from the sum of the squares of expansion coefficients. Without a complete expansion of  $\Phi_0^N$ , it is, of course, impossible to say what the absolute importance of the higher configurations is in the wave function, but it is clear that the relative importance of  $1s2s$  and the continuum configurations to the  $1s^2$  is large.

The results of the expansion of  $\Phi_1^N$  in terms of hydrogenic functions with  $Z=2$  are given in Table II. The arrangement of Table II is the same as that of Table I. The computations for the various quantities were carried out in the same way as described above, except that in the case of  $c_{2p\epsilon p}$ , only numerical con-

TABLE III. Coefficients for the expansion of  $\Phi_1^N$  using symmetrized products of hydrogenic  $s$  wave functions with  $Z=2$ .

Wave functions	$c_{nms}$	$(c_{nms})^2$
$1s^2$	-0.84620	0.71605
$1s2s$	0.24799	0.06150
$1s3s$	0.12162	0.01479
$1s4s$	0.07130	0.00508
$2s^2$	-0.09154	0.00838
$3s^2$	-0.04515	0.00204
$4s^2$	-0.02696	0.00073
$\sum_{n=5}^{\infty} (c_{1sns})^2$		0.0075
$\int_{\epsilon=0}^{\epsilon=\infty} (c_{1se\epsilon})^2 d\epsilon$		0.113
Sum		0.929

tinuum functions and the Bessel function expansion for the continuum function were employed. The values of  $c_{2pep}$  were estimated for  $\epsilon$  greater than 4.0.

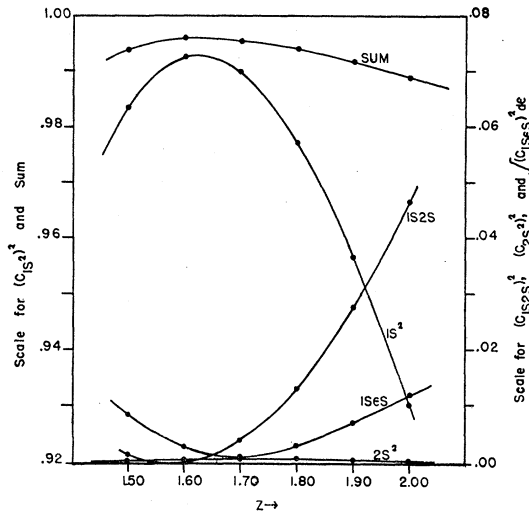
The most interesting result which appears in Table II is the small size of the contribution to  $\Phi_1^N$  of  $2p^2$ , the lowest configuration considered. The higher discrete configurations contribute more to the expansion relative to the lower than in the case of  $\Phi_0^N$ . This is clearly shown by the importance of the continuum configurations, which contribute more to the expansion than any one of the discrete configurations considered. The sum of the squares of the  $c$ 's in the final line of Table II is rather far from 1.0, that is, the expansion is rather far from complete. This result is somewhat surprising in view of the considerable number of configurations which are included in the expansion. One notes that  $(c_{1s})^2$  for the expansion of  $\Phi_0^N$  is 0.92988 but that  $(c_{2p})^2$  for the expansion of  $\Phi_1^N$  is only 0.22100. Furthermore  $(c_{3d})^2$  for the expansion of  $\Phi_2^N$  is still smaller, 0.00140. It is therefore clear that any relatively complete expansion of the  $\Phi_i^N$ 's for  $i > 0$  in terms of hydrogenic functions with  $Z=2$  will be a laborious undertaking. One reason for this situation is that the exponential factor is the same in all  $\Phi_i^N$ 's, but increasingly different from the exponential factors in the  $(nl)^2$  wave functions as  $l$  increases. It therefore seemed worthwhile to attempt the expansion of the higher  $\Phi_i^N$ 's in terms of  $s$  electron wave functions even though  $s$  wave functions used in this way cannot be considered as belonging strictly to the class of central field wave functions. The results of this expansion are given in Table III. The arrangement of Table III is similar to that of Table II and the computations for the various quantities have

TABLE IV. Squares of the coefficients in the expansion of  $\Phi_0^N$  in hydrogenic  $s$  wave functions for different values of  $Z$ .

	1.5	1.6	1.7	1.8	1.9	2.0
$(c_{1s})^2$	0.98338	0.99247	0.98967	0.97704	0.95653	0.92988
$(c_{1s2s})^2$	0.00145	0.00015	0.00406	0.01332	0.02772	0.04682
$(c_{2s})^2$	0.00026	0.00043	0.00053	0.00051	0.00039	0.00021
$\int (c_{1se\epsilon})^2 d\epsilon$	0.010	0.0030	0.0012	0.00303	0.00722	0.01199
Sum	0.995	0.9961	0.9955	0.99390	0.99186	0.98890

been carried out in the same way. It is clear that for low  $n,s$  wave functions are much more effective in representing  $\Phi_1^N$  than are the  $p$  wave functions. Similarly the expansions of  $\Phi_2^N$  and  $\Phi_3^N$  in terms of  $1s^2$  yield 0.60635 and 0.50747 for  $(c_{1s})^2$ . The former value is more than 400 times as large as  $(c_{3d})^2$  found for the expansion of  $\Phi_2^N$  in  $3d^2$ . These results, and those given in Table III, suggest the desirability of using values of  $Z$  other than 2 in the expansions.

The same suggestion also follows from the work of Taylor and Parr on He I.<sup>11</sup> These authors constructed various linear combinations of  $1s^2$ ,  $2p^2$ ,  $3d^2$ , and  $4f^2$  hydrogenic wave functions. The  $1s^2$  configuration was assigned one or two values of the parameter  $Z$ . To each of the other configurations, a single value of  $Z$  was assigned. The particular combination which gave the lowest energy was then chosen. They obtained a wave

FIG. 1. Squares of the coefficients for the expansion of  $\Phi_0^N$  in symmetrized products of hydrogenic  $s$  wave functions for different values of  $Z$ .

function giving the ground-state energy correct to 0.2 percent by the choice of  $Z=4.95$  for the  $2p$  function,  $Z=11.3$  for the  $3d$ , and  $Z=19.0$  for the  $4f$ . The exponents in the exponential factors in these wave functions were therefore 2.5, 3.8, and 4.8 whereas for the choice of  $Z=2$  they would have been 1.0, 0.67, and 0.50, respectively.

#### EXPANSION COEFFICIENTS FOR $Z$ VARIABLE

In view of the above results, the  $\Phi_i^N$ 's were also expanded in hydrogenic functions with variable  $Z$  with the purpose of choosing that  $Z$  which would give the best representation of the  $\Phi_i^N$ 's in a few terms.

The results of the expansion of  $\Phi_0^N$  in terms of various configurations of  $s$  electrons for different  $Z$ 's are presented in Table IV and Fig. 1. Values of  $c_{1se\epsilon}$

<sup>11</sup> G. R. Taylor and R. G. Parr, Proc. Nat. Acad. Sci. U. S. 38, 154 (1952).

were found using the analytic hydrogenic  $\epsilon s$  continuum function in all cases except for  $Z=2$ , which has been discussed previously. The computations were made for a series of values of  $\epsilon$  up to at least  $\epsilon=16.8$ . Beyond this point the values of  $c_{1s\epsilon s}$  were estimated. It is thought that any error resulting from these estimates will not be large enough to change the values of the integrals of  $(c_{1s\epsilon s})^2$  in Table IV by more than 1 in the last decimal place given.

By summing the squares of the coefficients for various groups of the configurations given in Table IV, and interpolating for the value of  $Z$  which makes the sum a maximum, one finds the results in Table V.

The corresponding information on the expansion of  $\Phi_1^N$  in terms of configurations of  $p$  electrons is given in Tables VI and VII and Fig. 2. Values of  $c_{2p\epsilon p}$  were found using the hydrogenic  $2p$  continuum function for

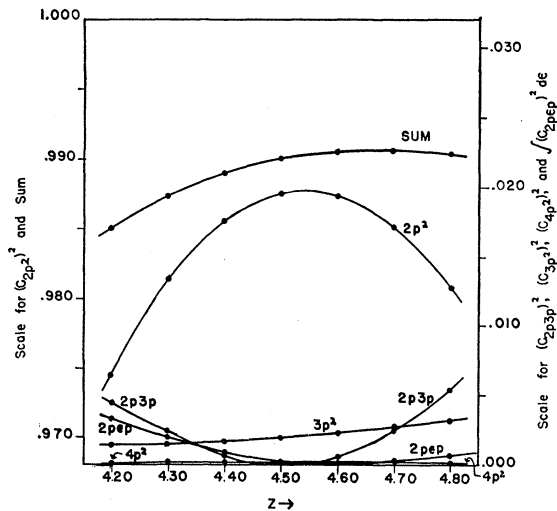


FIG. 2. Squares of the coefficients for the expansion of  $\Phi_1^N$  in symmetrized products of hydrogenic  $p$  wave functions for different values of  $Z$ .

$Z=4.3, 4.5$ , and  $4.7$ . The computations for each  $Z$  were carried out to at least  $\epsilon=100$ . Beyond this point the values of  $c_{2p\epsilon p}$  were estimated. In no case did the estimated values contribute to the integral of  $(c_{2p\epsilon p})^2$  as much as one in the last decimal place in the figures given in Table VI.

The improvement of the representation which can result from allowing  $Z$  to vary is at once obvious from an examination of Tables IV and VI. Whereas, the value of  $(c_{1s})^2$  for  $Z=2$  is 0.92988, its value for  $Z=1.62$  is 0.99279. For the value of  $(c_{1s})^2 + (c_{1s2s})^2$  one obtains 0.97670 when  $Z=2$ , but 0.99396 when  $Z=1.67$ . The results for  $(c_{2p})^2$  are even more improved. For  $Z=2$  one finds  $(c_{2p})^2=0.22100$  but for  $Z=4.54$  one obtains 0.98777. This latter value is also considerably better than the 0.71605 found for  $(c_{1s})^2$  when  $\Phi_1^N$  was expanded in radial  $s$  wave functions. Indeed the  $2p^2$  configuration for  $Z=4.54$  represents  $\Phi_1^N$  more effectively than the entire list of either  $p$  configurations or

TABLE V. Expansion of  $\Phi_0^N$  in hydrogenic  $s$  wave functions with  $Z$  chosen to give the maximum sum for the squares of the coefficients.

Configurations	$Z$	Sum of squares of coefficients
$1s^2$	1.62	0.99279
$1s^2, 1s2s$	1.67	0.99396
$1s^2, 1s2s, 2s^2$	1.67	0.99438
$1s^2, 1s2s, 2s^2, 1s\epsilon s$	1.60	0.996

$s$  configurations for  $Z=2$  which are given in Tables II and III, respectively. Over the ranges of values of  $Z$  shown in Figs. 1 and 2, the contributions of the higher  $p$  configurations to  $\Phi_1^N$  are considerably less than that of the higher  $s$  configurations to  $\Phi_0^N$ .

It is extremely interesting to see in Tables IV and VI or Figs. 1 and 2 how the importance of the various configurations changes with changing  $Z$ . For example, the rapid falling off of  $(c_{1s})^2$  and the accompanying increase in  $(c_{1s2s})^2$  and in the integrated value of  $(c_{1s\epsilon s})^2$  for larger  $Z$  is very obvious from Fig. 1. One also notes that in both Figs. 1 and 2, the plots of the

TABLE VI. Squares of the coefficients in the expansion of  $\Phi_1^N$  in hydrogenic  $p$  wave functions for different values of  $Z$ .

	4.2	4.3	4.4	4.5	4.6	4.7	4.8
$(c_{2p^2})^2$	0.97453	0.98131	0.98562	0.98760	0.98740	0.98517	0.98100
$(c_{2p3p})^2$	0.00550	0.00248	0.00063	0.00000	0.00059	0.00240	0.00540
$(c_{3p^2})^2$	0.00151	0.00161	0.00177	0.00199	0.00230	0.00269	0.00319
$(c_{4p^2})^2$	0.00012	0.00012	0.00012	0.00012	0.00013	0.00013	0.00014
$\int (c_{2p\epsilon p})^2 d\epsilon$	0.00337 <sup>a</sup>	0.00197	0.00096 <sup>a</sup>	0.00033	0.00009 <sup>a</sup>	0.00023	0.00076 <sup>a</sup>
Sum	0.98503	0.98749	0.98910	0.99004	0.99051	0.99062	0.99049

<sup>a</sup> Interpolated or extrapolated from the values of  $\int (c_{2p\epsilon p})^2 d\epsilon$  computed for  $Z=4.3, 4.5$ , and  $4.7$ .

$c^2$ 's for configurations of the nonequivalent electrons are distinctly concave upward in the neighborhood of the maximum of  $(c_{1s})^2$  and  $(c_{2p})^2$ , respectively. This is not true for the plots of the  $c^2$ 's for the remaining equivalent electrons.

One aspect of particular importance in the changing size of the contribution of the different configurations with changing  $Z$ , is the low minimum found for the integrated  $(c_{1s\epsilon s})^2$  and  $(c_{2p\epsilon p})^2$ . The importance of this point arises in connection with any attempt to obtain a good ground-state wave function by the minimum principle, using linear combinations of symmetrized products of hydrogenic wave functions as trial functions. By far the most difficult configurations to include

TABLE VII. Expansion of  $\Phi_1^N$  in hydrogenic  $p$  wave functions with  $Z$  chosen to give the maximum sum for the squares of the coefficients.

Configurations	$Z$	Sum of squares of coefficients
$2p^2$	4.54	0.98777
$2p^2, 2p3p$	4.60	0.98799
$2p^2, 2p3p, 3p^2$	4.65	0.99036
$2p^2, 2p3p, 3p^2, 4p^2, 2p\epsilon p$	4.69	0.99062

TABLE VIII. Energies in units of  $R_{\text{He}}hc$  obtained by the minimum principle from linear combinations of symmetrized products of hydrogenic  $s$  wave functions with  $Z=2$ .

Superposed configurations	Conventional configuration assignments			
	$1s^2$	$1s2s$	$1s3s$	$1s4s$
$1s^2$	-5.50000			
$1s^2, 2s^2$	-5.50189			
$1s^2, 1s2s$	-5.66088	-3.91183		
$1s^2, 1s2s, 1s3s$	-5.67730	-4.27238	-3.64645	
$1s^2, 1s2s, 1s3s, 1s4s$	-5.68278	-4.27380	-4.11489	-3.53477
Experimental	-5.80752	-4.29213	-4.12273	-4.06736

in such treatments are those involving continuum functions. The necessity for their inclusion in the case of hydrogenic functions with  $Z=2$  is indicated in Table VIII, where the best linear combination of the configurations on the left have been chosen by the minimum principle to yield the energies for the conventional configuration assignments along the top. The last line of Table VIII gives the experimental values of the energies of the  $1S_0$  terms in the configurations at the heads of the columns.<sup>12</sup> The successive values of the energy of the ground state, which appear in the second column, make it unlikely that the addition of more configurations of bound  $s$  electrons with  $Z=2$  would give an energy as low as  $-5.76$ , the energy which spherically symmetric functions may be expected to yield.<sup>3</sup> The only remaining spherically symmetric configurations are those involving a free electron. In the expansions above of  $\Phi_0^N$  in hydrogenic functions with  $Z=2$ , configurations involving a free electron have, of course, been shown to be important. On the other hand, both Table IV and Fig. 1 suggest that if in the attempt to obtain a ground-state function one uses a linear combination of symmetrized products of hydrogenic  $s$  functions with  $Z=1.70$ , one may hope to find a very good spherically symmetric component, even though no continuum wave functions are employed.

In comparing the results of expanding  $\Phi_0^N$  with the results of an attempt to obtain the spherically symmetric component of the ground-state wave function by the minimum principle, it is also of interest to compare the values of the squares of the expansion coefficients with the squares of the weighting constants for the various configurations in the linear combination.

TABLE IX. Values of the squares of the weighting constants obtained by the minimum principle in linear combinations of symmetrized products of hydrogenic  $s$  functions with  $Z=2$ .

Superposed configurations	$(c_{1s^2})^2$	$(c_{1s2s})^2$	$(c_{1s3s})^2$	$(c_{1s4s})^2$
$1s^2$	1.00000			
$1s^2, 2s^2$	0.99954			
$1s^2, 1s2s$	0.90802	0.09198		
$1s^2, 1s2s, 1s3s$	0.90874	0.08110	0.01016	
$1s^2, 1s2s, 1s3s, 1s4s$	0.90926	0.07805	0.00937	0.00332

<sup>12</sup> The experimental values of the energies were taken from Charlotte E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467 (U. S. Government Printing Office, Washington, D. C., 1949), p. 5.

The latter quantities are presented in Table IX, where all the functions which are concerned have been normalized. A comparison of Tables I and IX shows that for the configurations considered  $(c_{1s^2})^2$  is somewhat larger and  $(c_{1s2s})^2$ ,  $(c_{1s3s})^2$ , and  $(c_{1s4s})^2$  are considerably smaller for the expansion. However, as more configurations are included in the application of the minimum principle, there is a tendency for a slow increase in  $(c_{1s^2})^2$  and corresponding decrease in the other  $c^2$ 's.

An attractive aspect of the application of the minimum principle to a linear combination of configurations is the fact that by using the different roots of the secular equation to determine the  $c$ 's, one obtains not only a ground-state wave function, but also wave functions for the excited configurations as well. Table VIII lists the various energies found from wave functions obtained in this way. These results illustrate the well-known theorem<sup>13</sup> that the roots of the secular equation of a variational trial solution which is a linear combination of the first  $n$  members of an orthonormal set of functions will separate the roots of the equation of a trial solution made from the first  $n+1$  members of the set. In each case in Table VIII, except for the

TABLE X. Energies in units of  $R_{\text{He}}hc$  obtained by the minimum principle from linear combinations of symmetrized products of hydrogenic functions for  $1s^2$ ,  $1s2s$ , and  $2s^2$  for variable  $Z$ .

Conventional configuration assignment	1.5	1.6	1.7	$Z$	1.8	1.9	2.0
$1s^2$	-5.62821	-5.68175	-5.70725		-5.70920	-5.69250	-5.66199
$1s2s$	-4.05341	-4.10078	-4.11335		-4.08790	-4.02205	-3.91394
$2s^2$	-1.35924	-1.38313	-1.41737		-1.42693	-1.42054	-1.39521

highest root, the energies obtained are at once recognizable as corresponding to certain experimental values. It seemed possible that if, following the suggestion above for avoiding the inclusion of continuum wave functions, one made up trial solutions using hydrogenic functions with  $Z=2$ , one might obtain a better spherically symmetric component for the ground state but poorer components for the excited states. To investigate this point the energies yielded by the superposition of  $1s^2$ ,  $1s2s$ , and  $2s^2$  were computed for six values of  $Z$ . The results appear in Table X. The values in Table X suggest that a choice of  $Z$  in the neighborhood of 1.7 would yield a good spherically symmetrical component, not only for the ground state, but also for at least some of the excited states as well. Therefore, the possibility is strengthened of obtaining moderately good wave functions for both ground and excited states from linear combinations which do not include continuum functions.

On the other hand, there is considerable doubt that

<sup>13</sup> L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 188.

wave functions of high accuracy for the two-electron systems can be found in the form of variationally chosen linear combinations of hydrogenic wave functions of the proper symmetry unless continuum functions are included. This statement follows from the fact that a relatively poor wave function may yield a relatively good energy, or stated in other words, the minor components of a wave function as measured by their contribution to the energy may make up proportionately a much larger part of the wave functions. This result is well-known, and specific examples have been given in earlier papers in the present series.<sup>2,3</sup> As a further illustration, one sees from Table IX that in the superposition of  $1s^2$  and  $1s2s$  the ratio  $c_{1s2s}$  to  $c_{1s^2}$  is 0.32 but the ratio of the contributions to the ground state energy of the  $1s2s$  configuration and the interaction term between the  $1s^2$  and the  $1s2s$  to the contribution of the  $1s^2$  configuration is 0.13.

In summary, the present work has presented expansions of the various angular components of the three-parameter wave function of Hylleraas for the He I ground state in terms of symmetrized products of hydrogenic wave functions for different values of the parameter,  $Z$ . The results of these expansions are interpreted in terms of configuration interaction. The changing importance of the different configurations with changing  $Z$  is illustrated. In particular, the minimum with respect to  $Z$  of the integral over all positive  $\epsilon$  of  $(c_{1s\epsilon s})^2$  is pointed out. The implications of these results are discussed for attempts to obtain wave functions for both ground and excited states of two-electron systems by the minimum principle from linear combinations of products of hydrogen functions of the proper symmetry.

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## Auger Ejection of Electrons from Tungsten by Noble Gas Ions

HOMER D. HAGSTRUM

*Bell Telephone Laboratories, Murray Hill, New Jersey*

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Experimental investigation of electron ejection from atomically clean tungsten by singly and multiply charged ions of the noble gases is reported. Total electron yield,  $\gamma_i$ , and distribution in kinetic energy of the secondary electrons have been measured. Ion energies range from 10 to 1000 ev for singly charged ions.  $\gamma_i$  is found in each case to be roughly constant over this interval although the variations observed are significant and can be accounted for by theory.  $\gamma_i$  values of 0.293, 0.213, 0.094, 0.047, and 0.018 were obtained for 10 ev  $\text{He}^+$ ,  $\text{Ne}^+$ ,  $\text{Ar}^+$ ,  $\text{Kr}^+$ , and  $\text{Xe}^+$  ions, respectively. Comparison with theory makes it quite clear that for 10-ev ions essentially all electrons observed are ejected by a process of Auger neutralization in which the interaction of two conduction electrons causes one electron to neutralize the ion in the ground state and the other to be excited into the continuum above the filled band. The observed  $\gamma_i$  is determined by the probability that these excited electrons escape from the metal. In the case of  $\text{Ne}^+$ , indications are that as ion energy increases toward 100 ev a two-stage electronic transition process occurs in a small fraction of the encounters. In this process the ion is first resonance neutralized to an excited state and the resulting excited atom is subsequently de-excited in an Auger ejection process. Variation of the electron energy distribution with ion energy has been investigated. Careful measurement for  $\text{Ne}^{20}$  and  $\text{Ne}^{22}$  at 200 ev shows  $\gamma_i$  to be independent of nuclear mass. Results of  $\gamma_i$  and energy distribution measurements for electrons from multiply charged ions up to  $\text{Xe}^{6+}$  are also reported. A value of ca 6.3 ev for the energy of the Fermi level above the ground state in the conduction band in tungsten comes out of this work.

### I. INTRODUCTION

A SERIES of studies of electron ejection from atomically clean metals by ions of the noble gases is extended in this work to tungsten. The singly charged ions of He, Ne, Ar, Kr, and Xe, as well as a number of the multiply charged ions ranging up to  $\text{Xe}^{6+}$ , have been used. Evidence presented indicates the tungsten surface to be atomically clean.

The use of singly charged ions of all the noble gases has proved to be particularly fruitful. Comparison with theory shows that for very slow ions (<10 ev) essentially all the electrons are ejected from tungsten by the process of direct Auger neutralization. Here the role of the incoming ion is to provide a low-lying vacant

electronic level (its ground state) for the Auger process. Since the position of this level is determined by the ionization energy of the atom, it is clearly advantageous to study the process for a series of ions.

Of interest is the somewhat anomalous case of  $\text{Ne}^+$  on tungsten. Here it appears that for ions of energies near 100 ev a fraction ( $\sim 10$  percent) of the ions are resonance neutralized, the excited atoms so formed being subsequently de-excited in an Auger process in which a secondary electron may be ejected. The explanation of the restriction of this possibility to  $\text{Ne}^+$  and the means of its detection in that case are thought to be particularly convincing of the essential correctness of the theoretical picture.