

Wave Functions for the Excited States of Neutral Helium*†

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Wave functions have been found for the excited states of neutral helium for the 1^1S , 3^1S , 1^1P , 3^1P , 1^1D , and 3^1D series up through terms for which the principal quantum number of the running electron is 9 for the S series and 8 for the others. The wave functions are obtained from the minimum principle by a configuration-interaction procedure. At the final stage of the calculation, the wave functions are found by the solution of a secular equation of order 9×9 or less. If one excludes the energy of the 1^1S term, the average agreement between computed and observed energies for the 42 remaining terms is better than 1 part in 300 000. The energies gotten for the more highly excited states appear to be more than an order of magnitude, better than any which have been previously obtained. The values of the parameters in the various wave functions are made available.

INTRODUCTION

THE far-ultraviolet spectra of the light atoms, highly ionized ions, and simple molecules play an important role in the recent observations of the sun and stars from above the earth's atmosphere.¹ These spectra are also much to the fore in the study of controlled thermonuclear reactions and in plasma physics in general.² For any relatively complete quantitative interpretation of these spectra, it is essential to have available the relevant transition probabilities. To obtain dependable transition probabilities theoretically, it is necessary to employ wave functions of considerable accuracy. This requirement follows from the sensitivity of the transition probabilities to the form of the wave functions particularly to the positions of the zeros.³ The present work presents results of an attempt to obtain wave functions of satisfactory accuracy for the excited states of neutral He. He I was chosen because of its importance in both terrestrial and astrophysical sources, because the extent of the experimental information available, especially the number of known term values, allowed numerous tests of the validity and effectiveness

of the method employed, and because the number and variety of the existing theoretical investigations allowed one to gain some perspective in judging the value of the method used here.

The wave functions which are reported here have been surprisingly effective in reproducing the observed energies. If this effectiveness is maintained for the highly ionized ions, the possibility is open of computing the wavelengths of lines in the far ultraviolet which have not been observed in the laboratory but may appear in the rocket spectra. It appears that the accuracy of the predicted wavelengths may well be greater than that of the measurements on the plates and therefore more than adequate for identification.

The wave functions which result from the present work are being used to find transition probabilities. These transition probabilities, together with a discussion of their accuracy and possible procedures for further improvement, will form a second paper to be published elsewhere. The emphasis in the work reported here is rather on the wave functions themselves, the procedures employed for determining them and the regularities which appear in the results.

GENERAL CONSIDERATIONS

For He I and the various ions of the same isoelectronic sequence, certain coordinate systems have proved to lead to rapid convergence of the expansions employed. Thus it was shown very early, and it has often been demonstrated since, that $s=r_1+r_2$, $t=r_1-r_2$ and r_{12} give very excellent values of the energies of the two-electron systems.⁴⁻¹² The form usually assumed for the wave function is that of a product of an exponential and a series of positive integral powers of s , t , and r_{12} .

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‡ A part of this work was done while on appointment as Visiting Professor at the Max Planck Institut für Physik und Astrophysik in Munich, Germany, and a later part while in residence as a member of the Institute for Advanced Study in Princeton, New Jersey.

¹ R. Tousey, *Quart. J. Roy. Astron. Soc.* **5**, 123 (1964). This paper contains numerous references to earlier work.

² K. Bockasten, R. Hallin, K. B. Johansson, and P. Tsui, *Phys. Rev. Letters* **8**, 181 (1964); K. Bockasten, R. Hallin, and T. P. Hughes, *Proc. Phys. Soc. (London)* **81**, 522 (1963). B. C. Fawcett, A. H. Gabriel, B. B. Jones, N. J. Peacock, *ibid.* **84**, 257 (1964). B. C. Fawcett, A. H. Gabriel, W. G. Griffin, B. B. Jones, and R. Wilson, *Nature* **200**, 1303 (1963); A. J. Bearden, F. L. Ribe, G. A. Sawyer, and T. F. Stratton, *Phys. Rev. Letters* **6**, 257 (1961).

³ D. R. Bates, *Proc. Roy. Soc. (London)*, **A188**, 350 (1947); L. C. Green and N. E. Weber, *Astrophys. J.* **111**, 582 (1950); A. Delgarno and N. Lynn, *Proc. Phys. Soc. (London)* **A70**, 802 (1957); A. Delgarno and A. E. Kingston, *ibid.* **72**, 1053 (1958).

⁴ E. A. Hylleraas, *Z. Physik*, **54**, 347 (1929).

⁵ S. Chandrasekhar, D. Elbert and G. Herzberg, *Phys. Rev.* **91**, 1172 (1953).

⁶ S. Chandrasekhar and G. Herzberg, *Phys. Rev.* **98**, 1050 (1955).

⁷ E. A. Hylleraas and J. Midtdal, *Phys. Rev.* **103**, 829 (1956).

⁸ J. F. Hart and G. Herzberg, *Phys. Rev.* **106**, 79 (1957).

⁹ T. Kinoshita, *Phys. Rev.* **105**, 1490 (1957); **115**, 366 (1959).

¹⁰ J. Traub and H. M. Foley, *Phys. Rev.* **111**, 1098 (1958).

¹¹ J. Traub and H. M. Foley, *Phys. Rev.* **116**, 914 (1959).

¹² J. F. Hart and G. Herzberg, *Z. Physik* **171**, 83 (1963).

Hylleraas and Midtdal⁷ and Kinoshita⁹ have included in the series some terms with negative integral powers. The former authors have also made use of a logarithmic term. Terms employing half-integer powers of s , t , and r_{12} have been shown to yield substantial improvement in the energies obtained for a given number of parameters.¹³⁻¹⁷ Schwartz¹⁵ has given some consideration to more general fractional powers. Pekeris and his co-workers have shown that the product of an exponential and three Laguerre polynomials in each of the three perimetric coordinates $u = \epsilon(r_2 + r_{12} - r_1)$, $v = \epsilon(r_1 + r_{12} - r_2)$, and $w = 2\epsilon(r_1 + r_2 - r_{12})$ can yield excellent results both for the ground and for the excited states of He I and the isoelectronic ions.¹⁸⁻²¹ Unfortunately, in problems involving three or more electrons, it is rather involved to use coordinates similar to those just described. This situation results in large part because of the number of r_{ij} 's which occur and because of the repeated divisions of space which are necessary to deal with integrals involving them. In particular, as far as the present authors are aware, there is no known way of extending the method of perimetric coordinates to deal with three or more electrons. In contrast, the atomic spectroscopists have had remarkable success in analyzing the experimental data, at least in the first approximation, in terms of central-field wave functions, even in the case of very complicated structures such as the rare earths. It was therefore decided to employ central-field wave functions but at the higher approximation in which configuration interaction was included. The reasons for this decision were the methodological interest in comparison with the methods mentioned above, as well as the possibilities it allowed for the treatment of three or more electrons, although at a lower level of accuracy, and finally the fact that with this method experimental information could serve as a guide to the reasonable choice of at least some of the parameters in the wave functions.

The approach to the two-electron problem through configuration interaction has been applied primarily to the ground state.²²⁻²⁴ Although conclusive proof is not yet available, it seems highly probable that the convergence of the configuration-interaction approach is very much slower^{25,26}; certainly in all calculations for

the ground state so far reported, the configuration-interaction results have been far surpassed for an equal number of parameters by the results obtained by the Hylleraas method. However, it is not clear *a priori* that for excited states the discrepancy will be so large, and it was one of the purposes of the present work to explore the situation. The results proved to be more favorable to the configuration-interaction approach than was expected.

It is perhaps well to say a word about what is meant by the term "configuration interaction" in the present work. Here, as in all similar work, the configurations to be superposed must have the proper angular and spin dependence. However, the radial dependence of the configuration is not necessarily that associated with the same configuration in the central field approximation. To make the matter clear, let us define the "dominant configuration" contributing to a term to be that to which the term is assigned by the experimental spectroscopists where such assignment is unambiguous. Then in the present meaning of "configuration interaction" it is only the dominant configuration which is required to have sufficient radial terms to be able to have the proper number of radial zeros. The radial dependence of the other configurations is chosen solely on the basis of the effectiveness of the particular radial factor in lowering the energy of the spectroscopic term which is being considered. It has also been known for a number of years that a specific choice of the nonlinear parameters in a wave function, in particular in the coefficient of the exponents in the exponential factors, is helpful in lowering the energy.^{27,28} Thus, the use of configurations which may not be immediately recognizable in the central field approximation leads to more rapid convergence. In contrast to the present usage of the term "configuration interaction," it is sometimes taken to mean that more or less good, orthogonal solutions of the Schrödinger equation are found for each configuration and that then the interactions of these configurations are considered.

CHOICE OF THE TRIAL VARIATIONAL FUNCTION

In choosing the form of the trial variational function, one may begin by establishing the type of coupling. The ratio of the total width of each triplet term to the corresponding singlet-triplet interval may be taken as a conservative estimate of the relative importance of the magnetic and the electrostatic interaction. The necessary term values are given by Martin.²⁹ The ratios found are roughly 0.0005 for the $1s2p$ and $1s3p$ configurations and 0.0015 for $1s3d$ and $1s4d$. Furthermore, all of the series of singly excited states in He I have as a limit the single level, $1s^2S_{1/2}$, of He II. It is therefore

¹³ L. Levitt, G. E. Tauber, and T. Y. Wu, Abstract, Phys. Rev. **99**, 1659 (1955).

¹⁴ H. M. Schwartz, Phys. Rev. **103**, 110 (1956).

¹⁵ H. M. Schwartz, Phys. Rev. **128**, 483 (1960).

¹⁶ C. Schwartz, Phys. Rev. **128**, 1146 (1962).

¹⁷ C. Schwartz, Phys. Rev. **134**, 1181 (1964).

¹⁸ C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959); **126**, 1470 (1962).

¹⁹ C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

²⁰ C. L. Pekeris, Phys. Rev. **127**, 509 (1962).

²¹ C. L. Pekeris, B. Schiff and H. Lifson, Phys. Rev. **126**, 1057 (1962).

²² D. H. Tycko, L. H. Thomas and K. M. King, Phys. Rev. **109**, 369 (1958).

²³ R. K. Nesbet and R. E. Watson, Phys. Rev. **110**, 1073 (1958).

²⁴ H. Shull and P. O. Löwdin, J. Chem. Phys. **30**, 617 (1959).

²⁵ C. Schwartz, Phys. Rev. **126**, 1015 (1962).

²⁶ C. W. Scherr and R. E. Knight, J. Chem. Phys. **40**, 1777 (1964).

²⁷ G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U. S. **38**, 154 (1952).

²⁸ L. C. Green, M. M. Mulder, P. C. Milner, M. N. Lewis, J. W. Woll Jr., E. K. Kolchin, and D. Mace, Phys. Rev. **96**, 319 (1954).

²⁹ W. C. Martin, J. Res. Natl. Bur. of Std. **64A**, 19 (1960).

reasonable in discussing the term scheme for He I to consider only LS coupling.

Since we wish to minimize the energy integral and at the same time to satisfy the normalization condition, we introduce a Lagrangian multiplier λ and write the expression to be varied in the form

$$E = \int \Psi_n^* H \Psi_n d\tau - \lambda \left\{ \int \Psi_n^* \Psi_n d\tau - 1 \right\}, \quad (1)$$

where

$$\Psi_n = \sum_{k=L+1}^n c_k \Phi_k \quad (2)$$

$$\psi_i = \sum_{m_s} \left\{ C\left(\frac{1}{2}, \frac{1}{2}, S, m_s\right) \sum_{m_i=-l_i}^{l_i} [C(l_i, \lambda_i, L, m_i) \cdot N \cdot \mathcal{Q} \{ r_1^{a_i} \exp(-Z(\alpha_i/n_{\alpha_i})r_1) Y(l_i, m_i; \theta_1, \varphi_1) \delta(m_s; \sigma_1) \right. \\ \left. \times r_2^{b_i} \exp(-Z(\beta_i/n_{\beta_i})r_2) Y(\lambda_i, -m_i; \theta_2, \varphi_2) \delta(-m_s; \sigma_2) \} \right\}, \quad (4)$$

where $l_i \leq \lambda_i$. In Eq. (4), the C 's are Clebsch-Gordan coefficients, N is the normalization constant for the antisymmetrized product which follows, \mathcal{Q} is the antisymmetrizer operator, the Y 's are surface spherical harmonics and the δ 's are the usual Kroeneker deltas, employed here as spin functions. The a_i 's and b_i 's are integers. The three constants in the coefficients of the exponent in the exponential factor could be considered as somewhat redundant, but two of them, Z and n_{α_i} or n_{β_i} are usually, but not always, fixed. Z is customarily set equal to the nuclear charge but can be varied to ascertain the extent to which the virial theorem is satisfied. The quantities n_{α_i} and n_{β_i} are the principal quantum numbers of the two electrons in that configuration which is thought to be the dominant configuration contributing to the term in question. Since only terms which are singly excited are considered in this paper, the dominant configuration is always of the form $1snl$ so that $n_{\alpha_i}=1$ and $n_{\beta_i}=n$.

Since in LS coupling, there are no nonvanishing matrix elements of the electrostatic interaction between terms of differing L , S , or parity,³⁰ the number of configurations which need to be included in any computation which involves configuration interaction is considerably reduced. Thus, for the well-known 1S and 3S series of He I, the series of singly excited states which converge to the $1s^2S$ ground state of He II, the only types of configurations which need to be considered are $nsn's$, $n\bar{p}n'p$, $ndn'd$, etc. For the 1S series, the n and n' are not necessarily different, but there are no 3S terms from these configurations if n equals n' . For the corresponding $^1P^0$ and $^3P^0$ series, the configurations to be considered are of the types $nsn'p$, $n\bar{p}n'd$, $ndn'f$, etc. For the 1D and 3D series, the types of configuration are $nsn'd$, $n\bar{p}n'p$, $n\bar{p}n'f$, $ndn'd$, $ndn'g$, etc.

³⁰ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 366.

and

$$\Phi_k = \sum_i c_{ki} \psi_i. \quad (3)$$

Here L gives the total orbital angular momentum of the terms of the series being considered and n is the principal quantum number of the running electron. The ψ_i 's are taken to be linear combinations of normalized antisymmetrized products of Slater orbitals. The orbitals are chosen so that $M_S=0$ and $M_L=0$ for each product. Weights are assigned to these products so that their linear combinations have the correct spin and angular dependence for eigenfunctions in LS coupling. The ψ_i 's therefore have the form

Since the parameters which occur in the radial parts of the antisymmetrized product of two Slater orbitals do not in general allow sufficient flexibility for the radial behavior of the wave function to show the proper number of zeros, a sum of terms of the type given by Eq. (4) and differing only in the values of the a_i 's and b_i 's are employed for each configuration. The number of terms in such a sum is taken systematically equal to, or larger than, the minimum necessary to yield the correct number of zeros for the dominant configuration contributing to the term.

For any term our total wave function Ψ may be considered as consisting of three mutually orthogonal parts, the Hartree-Fock component, the radial correlation component and the angular correlation component. The dominant configuration, together with all others which contain Slater orbitals which do not differ in l or λ from it, gives both the Hartree-Fock part of the wave function and the radial correlation. If the Hartree-Fock wave function for the dominant configuration is known, or can be well approximated, one may expand this sum of configurations of the same l and λ in terms of the Hartree-Fock function and a second function orthogonal to it. The difference between the sum and its Hartree-Fock part is this second function or the radial correlation.³¹ Those configurations which contain Slater orbitals whose l or λ do differ from those of the dominant configuration yield the angular correlation in the wave function.

METHOD OF COMPUTATION

For the lowest term in any series, a trial set of ψ_i 's is selected. For a given choice of the parameters in each of the ψ_i 's, the problem of finding the minimum E

³¹ L. C. Green, M. N. Lewis, M. M. Mulder, C. W. Wyeth, and J. W. Woll, Jr., *Phys. Rev.* **93**, 273 (1954).

reduces to that of determining the lowest eigenvalue of λ in the secular determinant,

$$|H_{ij} - N_{ij}\lambda| = 0. \quad (5)$$

Programs which evaluate the matrix elements in Eq. (5),

$$H_{ij} = \int \psi_i^* H \psi_j d\tau \quad \text{and} \quad N_{ij} = \int \psi_i^* \psi_j d\tau, \quad (6)$$

and solve the secular determinant have been written in both single and double precision and run on various of the IBM 7000-series machines. When the eigenvalue has been found for one choice of parameters, a new choice is made, either automatically by the program or at will by the user, and a new eigenvalue is determined. Examination of the eigenvalues which result from various choices of the parameters may also lead to the decision to either increase or decrease the number of ψ_i 's employed. When an eigenvalue which is considered to be sufficiently accurate has been found, the values of the weighting constants, the c_{1i} 's, the linear parameters of the variational function, can be determined. With the values of both the linear and nonlinear parameters established for the lowest eigenvalue, the normalized function, $\Phi_1 = \sum c_{1i} \psi_i$, is fixed, and from this point on, it enters the calculations as a known function but with its own weighting constant c_1 , chosen by the minimum principle, which varies from case to case as described below.

For the second term of a series, the trial function has the form

$$\Psi_2 = c_1 \Phi_1 + \sum c_{2i} \psi_i. \quad (7)$$

Here Φ_1 is known but the number of ψ_i 's and the choice of c_1 and the c_{2i} 's as well as the nonlinear parameters which occur in the ψ_i 's is still to be made. For a specific choice of the parameters in each of the ψ_i 's, the problem becomes that of determining the second lowest eigenvalue of λ in a secular determinant much like that of Eq. (5) except that a row and column have been added. The form of the elements in the new row is

$$H_{k=1,j} = \int \Phi_1^* H \psi_j d\tau \quad \text{and} \quad N_{k=1,j} = \int \Phi_1^* \psi_j d\tau, \quad (8)$$

and since the secular determinant is symmetric, the elements in the new column are the same. When a sufficiently accurate wave function has been found for the second term, all the c_{2i} 's and all the parameters in the ψ_i 's making up this function, except those in Φ_1 are frozen into a second function, Φ_2 .

The trial wave function for the third term of the series then contains two known, normalized functions, Φ_1 and Φ_2 , each of which is multiplied by a weighting constant, and a number of ψ_i 's, also with weighting constants,

$$\Psi_3 = c_1 \Phi_1 + c_2 \Phi_2 + \sum c_{3i} \psi_i. \quad (9)$$

In this case the secular determinant will contain, in addition to the types of terms already described, some

of the form

$$H_{kl} = \int \Phi_k^* H \Phi_l d\tau \quad \text{and} \quad N_{kl} = \int \Phi_k^* \Phi_l d\tau. \quad (10)$$

The process of constructing Φ_k 's in this manner is continued up the series through as many terms as desired.

As a final step one may find all of the eigenvalues of the secular determinant whose elements are all of the form given by Eq. (10), that is, we replace the upper limit, n , of the summation in Eq. (2) by N , where in each series, N is the value of k for the highest series member which was computed:

$$\Psi_n = \sum_{k=L+1}^N c_k \Phi_k. \quad (11)$$

In view of the ordered manner in which the Φ_k 's were found, it is to be expected that the weighting constants for the n th eigenfunction will be small for all Φ_k 's for which $k > n$ in Eq. (11). Thus at this final state of the calculation, the wave functions are found by the solution of a secular equation of order $(N-L-1) \times (N-L-1)$.

The initial search for the best values of the nonlinear parameters for a wave function was conducted with the set of single-precision programs. The results were then refined, using double precision. Since the calculations led to matrices which were as large as 50×50 and since the individual ψ_i 's were far from orthogonal to one another or to the Φ_k 's, it was particularly important to establish the dependability of the numerical procedures. To do so, once all the linear and nonlinear parameters in a particular Ψ were known, the energy was computed directly *de novo* from the energy integral in double precision. The energy so computed was then compared with the eigenvalue of the secular determinant as found from a double-precision calculation. In all cases which are reported here, the agreement was to at least nine figures.

RESULTS

With the exception of the 1^1S , experience showed that satisfactory agreement with the experimental value of the energy of any term could be obtained using the same α_i and β_i for all ψ_i 's of a given angular dependence which contributed substantially to the wave function. The number of ψ_i 's employed in the various wave functions varied from 50 for 1^1S and 42 each for 2^1P and 2^3P to 7 for 5^3S , 8 for 6^3S and 9 for 7^3S , 4^1P and 4^3P . Values for the α_i 's, β_i 's, c_{ki} 's, and c_k 's were determined for the 1^1S , 3^1S , 1^1P , 3^1P , 1^1D , and 3^1D series up through terms for which the principal quantum number of the running electron is 9 for the S series and 8 for the others.³²

³² Complete tables of the values of a_i , α_i , l_i , b_i , β_i , λ_i , c_{ki} , and c_k as determined both from Eq. (2) and from Eq. (11) have been deposited as Document No. 8396 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$3.75 for photoprints or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I. Energies of He I in rydbergs.

| <i>n</i> | <i>n</i> ¹ <i>S</i> | | | <i>n</i> ³ <i>S</i> | | | <i>n</i> ¹ <i>P</i> | | |
|----------|--------------------------------|--------------|------------------|--------------------------------|------------|----------------|--------------------------------|------------|----------------|
| | <i>E</i> | ΔE^a | $(\Delta E)_p^b$ | <i>E</i> | ΔE | $(\Delta E)_p$ | <i>E</i> | ΔE | $(\Delta E)^c$ |
| 1 | -5.806765 | -684 | -0 | | | | | | |
| 2 | -4.291875 | -74 | -13 | -4.350427 | -32 | 0 | -4.247563 | -116 | +4 |
| 3 | -4.122520 | -25 | -33 | -4.137365 | -13 | 0 | -4.110250 | -41 | -16 |
| 4 | -4.067164 | -10 | -48 | -4.073016 | -10 | -2 | -4.062118 | -21 | |
| 5 | -4.042348 | -6 | -53 | -4.045233 | -6 | -2 | -4.039800 | -11 | |
| 6 | -4.029122 | -4 | -55 | -4.030752 | -4 | -5 | -4.027661 | -7 | |
| 7 | -4.021249 | -3 | -52 | -4.022258 | -2 | -12 | -4.020334 | -5 | |
| 8 | -4.016186 | 0 | -50 | -4.016853 | -2 | -27 | -4.015575 | -4 | |
| 9 | -4.012738 | -2 | -53 | -4.013202 | -2 | -52 | | | |

| <i>n</i> | <i>n</i> ³ <i>P</i> | | | <i>n</i> ¹ <i>D</i> | | <i>n</i> ³ <i>D</i> | |
|----------|--------------------------------|------------|----------------|--------------------------------|------------|--------------------------------|------------|
| | <i>E</i> | ΔE | $(\Delta E)_p$ | <i>E</i> | ΔE | <i>E</i> | ΔE |
| 1 | | | | | | | |
| 2 | -4.266256 | -86 | -15 | | | | |
| 3 | -4.116135 | -31 | -23 | -4.111229 | -14 | -4.111260 | -13 |
| 4 | -4.064633 | -18 | | -4.062554 | -7 | -4.062571 | -7 |
| 5 | -4.041092 | -11 | | -4.040028 | -5 | -4.040038 | -4 |
| 6 | -4.028411 | -4 | | -4.027794 | -3 | -4.027801 | -2 |
| 7 | -4.020806 | -4 | | -4.020419 | -3 | -4.020423 | -1 |
| 8 | -4.015892 | -2 | | -4.015632 | -1 | -4.015635 | -1 |
| 9 | | | | | | | |

^a ΔE gives the value of the "uncorrected nonrelativistic energy" minus the value calculated here in units of 10^{-6} Ry. The "uncorrected nonrelativistic energies" are taken to be the same as the experimental energies except for the 1¹S, 2¹S, 2³S, and 3³S terms. In the case of these terms, the relativistic, radiative, and mass polarization corrections given by Pekeris (Ref. 18) have been applied to the experimental values.

^b $(\Delta E)_p$ gives the value of the uncorrected nonrelativistic energy minus the value calculated by Pekeris in units of 10^{-6} Ry.

The values of the α_i 's and β_i 's were recorded to two decimal places. However, the degree of confidence that is to be placed in the specific values assigned to these parameters varies substantially. As a very rough rule, one may say that for the dominant configuration, a variation of 0.01 in α_i or β_i from the value given will raise the energy by one unit or more in the sixth decimal place. For the remainder of the configurations, it may be necessary to make a change of 0.1 or even 0.5 to raise the energy by one unit in the sixth decimal place. The higher value, 0.5, arises for configurations which contribute relatively little to lowering the energy, that is, for example, for configurations in which the individual Slater orbitals have the more complex angular dependencies.

With the exception of the parameter values in the ψ_i 's of the 1¹S term, there tends to be some degree of order and smoothness in the run of the nonlinear parameters both in a single Φ_k and from one Φ_k to the next. A considerable amount of effort and computer time was devoted to the attempt to find a smoother set of nonlinear parameters for 1¹S. In none of the cases tried did a smoother set of parameters give as good an energy with as few as the 50 ψ_i 's employed here.

For the 4¹S, 5¹S, and 6¹S terms, two neighboring values of β for the spherically symmetric ψ_i 's were found to give minima. Of these two values, the one yielding the lower energy, 0.55 in all three cases, was the value employed. A similar phenomenon was suspected several times in 1¹S. Another case in which a relative minimum

has been found close to the neighborhood of an absolute minimum is H₂.³³

Table I gives the energy obtained for each of the terms in the six series. The energies listed are those found using Eq. (11). They are expressed in rydbergs and in no case differ by as much as 0.000001 of a rydberg from those found by the use of Eq. (2). For each series, the column headed ΔE gives the value of the "uncorrected nonrelativistic energy" minus the value calculated here in units of 10^{-6} Ry. The "uncorrected nonrelativistic energies" are taken to be the same as the experimental energies except for the 1¹S, 2¹S, 2³S, and 3³S terms. In the case of these terms, the relativistic, radiative, and mass-polarization corrections given by Pekeris¹⁸ have been applied to the experimental values. The columns headed $(\Delta E)_p$ give the value of the uncorrected nonrelativistic energy minus the value calculated by Pekeris and his coworkers, in units of 10^{-6} Ry.

As a test of the exactness to which the present wave functions satisfied the Virial theorem, the *Z* in Eq. (4) was varied. In those cases in which this test was applied, the optimum *Z* was found to differ very little from 2, by perhaps 0.0001 on the average, and the energy was usually not affected in the last decimal place.

DISCUSSION

It is interesting to note from Table I that, starting with the 3¹S and 6³S terms, all the energies found here

³³ W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960). The authors are indebted to Dr. D. W. Davies for attracting their attention to the relevancy of this paper.

for these series are lower than those of Pekeris. From the 6^1S and 8^3S on, the error in the calculated energy is an order of magnitude or more smaller for the present calculation. One cannot argue that the higher series members in the present case are able to give low energies simply because their wave functions have been required to be orthogonal to a relatively poor ground-state function. This argument implies that a still poorer ground-state function would make it possible to find excited-state functions which would give even lower energies than those obtained here. However, it is well known³⁴ that in the case of a trial variational function which is a sum of linearly independent functions, the eigenvalues of the associated secular determinant are upper limits to the true eigenvalues of the problem; and that if a linearly independent function is added to a trial variational function, the eigenvalues of the new secular determinant will separate those of the old. This theorem shows that the addition of a linearly independent function to our trial variational function will either leave the eigenvalues unchanged, if the added function is orthogonal to the true eigenfunctions, or else will lower them. Numerical illustrations of this effect are very easy to produce in the present case.

It is not surprising that the present method gives substantially lower values for the energies of the higher terms of the series since, at each stage of the calculation, ψ_i 's are added to the variational function which are specifically chosen because their functional form helps in lowering the energy of the term considered. In contrast Pekeris has started with a determinant of rather large order, 220 terms for the third and higher excited S states. He then finds the successive eigenvalues of this single determinant. Experience has generally shown in simple cases that an optimal choice of the values of the nonlinear parameters is more effective in lowering the energy than more uniform procedures, and it seems plausible that a similar improvement may occur in the present case.

The energy found here for the 1^1S term does not compare in accuracy with the best results obtained either by the use of s , t and r_{12} as coordinates⁹ or by the use of perimetric coordinates.¹⁸ On the other hand, it appears satisfactory when compared with other calculations based on configuration interaction. Thus Shull and Löwdin found -5.80246 Ry,²⁴ Nesbet and Watson obtained -5.80552 Ry,²³ and Tycko, Thomas, and King got the best result so far obtained, -5.806886 Ry.²² The last result is lower by 0.000121 Ry than the value

found here but still 0.000563 Ry above the non-relativistic energy.

In the case of the 2^3S , the present computation using configuration interaction surpasses by 0.000021 Ry the 6-parameter value obtained by Traub and Foley¹⁰ using the Hylleraas method. However, the 12-parameter value of Traub and Foley¹⁰ and the 20- and 40-parameter values of Hart and Herzberg¹² give lower results than those found here by 8 , 11 , and 31×10^{-6} Ry, respectively. For the 2^3P , on the other hand, the configuration interaction approach gives a value 0.000053 Ry below that obtained by Traub and Foley with 18 parameters.¹¹

It is clear that as one goes up any one of the six series, there is at first a decrease in the number of ψ_i 's required in a Φ_k to reach some given accuracy in the energy of the terms arising from the $1snl$ configuration. The Φ_k tends to take on the form of one $1s$ hydrogenic electron moving in the field of a nucleus of charge 2 and one nl hydrogenic electron moving in the field of charge 1. This means that the importance of the radial- and angular-correlation components decreases. Even in the case of the $1D$ and $3D$ series, where the pp , pf , and dd configurations have been retained in all terms, the contribution of these ψ_i 's as judged by the c_{ki} 's becomes steadily less as n increases. On the other hand, for the higher n 's the number of radial nodes in Ψ_n is greater, and the number of ψ_i 's is augmented to give Φ_n the necessary flexibility.

It is also clear that for the earlier members of a series, the β_i 's in the ψ_i 's tend to be larger than 0.5 for the dominant configuration contributing to the term and both the α_i 's and β_i 's increase as the complexity of the angular dependency of the individual Slater orbitals in the configuration increases. This behavior is expected since it increases the overlap of the ψ_i 's of higher angular dependence with those of lower.^{27,28} Numerous trials in the course of the present work have suggested that the corresponding effect which is to be expected in the case of the ψ_i 's introduced to represent the radial correlation is avoided, and equally good results obtained by slightly increasing the number of ψ_i 's and keeping the α_i 's and β_i 's the same throughout any group of ψ_i 's having the same angular dependence in their Slater orbitals. The values of 1.00 for α_i and 0.50 for β_i yield minimum energies for all Φ_k 's for $k > 3$ for the $1P$, $3P$, $1D$, and $3D$ series but at a higher k for the $3S$ series and higher still for the $1S$ series.

The energies of the terms of the $3S$ series are given to higher accuracy by fewer ψ_i 's than is the case for $1S$. This more rapid convergence of the $3S$ series has been commented upon by Pekeris²⁰ and by Scherr and Knight.²⁶ The number of ψ_i 's employed for the $1P$ and $3P$ series are the same, and this is also true for the $1D$ and $3D$ series. However, here also Table I shows that the convergence of the triplet series is more rapid.

³⁴L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 188; D. W. Davies, *J. Chem. Phys.* **33**, 781 (1960). The authors are indebted to Dr. Davies for attracting their attention to various articles in the literature to which references are given in his paper.