

more generally as follows: The approximate first-order wave functions obtained via Eq. (3) automatically satisfy the same orthogonality conditions as the exact first-order wave functions. In order to present a proof, define

$$(\psi, \Omega\phi) = \int d\tau \psi^* \Omega\phi,$$

$$(\psi, \phi) = \int d\tau \psi^* \phi,$$

and let the total wave function for a state p have the following perturbation expansion

$$\psi^p = \sum_n \lambda^n \psi_n^p.$$

(For the particular case of an N -electron atomic system, $\lambda = Z^{-1}$, of course.) The orthogonality condition that two states, p and q , must satisfy is given by

$$(\psi_1^p, \psi_0^q) + (\psi_0^p, \psi_1^q) = 0. \quad (\text{AII.1})$$

Let $\psi_1'^p$ be an approximation to ψ_1^p , and let

$$\psi_1'^p = \sum_\alpha a_{1,\alpha}^p \psi_0^\alpha = a_{1,p}^p \psi_0^p + \phi_1^p, \quad (\text{AII.2})$$

so that

$$(\psi_0^q, \phi_1^p) = 0,$$

and likewise

$$\psi_1'^q = \sum_\alpha a_{1,\alpha}^q \psi_0^\alpha = a_{1,q}^q \psi_0^q + \phi_1^q$$

$$(\psi_0^p, \phi_1^q) = 0. \quad (\text{AII.3})$$

Insertion of Eqs. (AII.2) and (AII.3) into Eq. (AII.1) yields that

$$(\psi_1'^p, \psi_0^q) + (\psi_0^p, \psi_1'^q) = a_{1,q}^p + a_{1,p}^q = 0 \quad (\text{AII.4})$$

must hold if the theorem is to be true. Set $\psi_1'^p$, say, into the variational equation, Eq. (3), and form the variance with respect to $a_{1,p}^p$. It follows that

$$a_{1,q}^p = (\psi_0^p, H' \psi_0^q) (\epsilon_0^p - \epsilon_0^q)^{-1},$$

and likewise, by starting with ψ_1^q ,

$$a_{1,p}^q = (\psi_0^q, H' \psi_0^p) (\epsilon_0^q - \epsilon_0^p)^{-1}.$$

A comparison of these last two equations shows that Eq. (AII.4) is valid, and hence that the theorem is established.

It is interesting to note to what extent the present 1^1S and 2^1S approximate first-order wave functions fulfill Eq. (AII.1). For the choice $p = 1^1S$, $q = 2^1S$, the computed values are

$$(\psi_0^2, \psi_1'^1) = -0.336939,$$

$$(\psi_1'^2, \psi_0^1) = +0.336968,$$

which sum to 2.9×10^{-5} . The exact magnitude of these integrals may be computed from elementary perturbation theory, and is 0.3369789... Since the ϵ_2 values are regarded as converged to only six or seven decimal places, the extent of agreement obtained is satisfactory.

Two-Electron Atoms

III. A Sixth-Order Perturbation Study of the 1^1S Ground State*

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I. INTRODUCTION

IN the two earlier papers of this series^{1,2} the variational perturbation procedure of Hylleraas has been applied in first order to the ground state and to some of the lower lying excited states of the helium atom isoelectronic series. The straight (i.e., nonperturbational) variational treatment of these systems

has been carried out to astonishing lengths by Pekeris³ and others,⁴ furnishing estimates of energy eigenvalues which are in some cases converged to as much as nine or more significant figures, and furnishing expectation values for other operators than the Hamiltonian with corresponding precision. With this background in mind it seems clear that for a perturbation treatment of N -electron atoms to be more than

* This work was supported by a grant from The National Aeronautics and Space Administration.

¹ R. E. Knight and C. W. Scherr, Phys. Rev. **128**, 2675 (1962).

² R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 431 (1963), preceding paper.

³ (a) C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); (b) **115**, 1216 (1959); (c) **126**, 143 (1962); (d) **126**, 1470 (1962).

⁴ (a) T. Kinoshita, Phys. Rev. **105**, 1490 (1957); (b) **115**, 366 (1959).

of didactic interest, the perturbation must be quite small, or the process must be carried through to fairly high orders. It may be possible to make some limited progress in the direction of making the perturbation small, but the direction of attack which seems most promising and most capable of indefinite extension is the extension to higher orders, assuming the perturbation process itself converges.

In this report a sixth-order perturbation wave function is presented for the 1^1S ground state of the helium atom isoelectronic series. A sixth-order wave function furnishes energy estimates through 13th order. The energy estimates to 13th order are better, i.e., more nearly converged to the true values, than any previously reported energy values obtained by any procedure including Pekeris' extrapolated values for Be^{2+} and higher members of the series, and are also better than Pekeris' n^* values^{3(a)} for helium and Li^+ .

Improved estimates of energy eigenvalues, however, are not the only reason for extending the perturbation theory calculations to higher orders. It has long been recognized that wave functions constructed by an energy criterion are often inadequate for the satisfactory calculation of expectation values of other operators of interest. It is entirely possible that the higher-order correction functions for the wave function are actively concerned with regions of configuration space that are not at all important energetically. Some discussion of this point is presented in Sec. VII.

The above-mentioned point is particularly apparent in calculations of transition moment probabilities where there are at least three available procedures for calculating the same expectation value. All three procedures would, of course, be in numerical agreement if exact wave functions were used in the calculations, but with the available variational wave functions wide disparities are the rule. Since the perturbation results should be in close agreement—nearly to the order of the calculation—it is particularly desirable to obtain transition moments via higher-order perturbation theory. Paper V in this series presents some excited states to higher order so that these calculations become feasible.

The authors have previously presented a preliminary report of the calculation of a fifth-order wave function.⁵ This paper extends that work both from fifth to sixth order, and from 70- to 100-term basis sets.

II. METHOD

Let the Hamiltonian H be written as⁶

$$H = H_0 + H', \quad (\text{II.1})$$

where H_0 is called the zero-order Hamiltonian, and H' is called the perturbation. For the N -electron atom, the conventional choice for H' is $(Zr_{12})^{-1}$, the electron interaction terms in H . By this choice the atomic wave functions for a given state of the system are obtained as an expansion in inverse powers of the nuclear charge Z :

$$\psi = \sum_n Z^{-n} \psi_n, \quad (\text{II.2})$$

where the sum to a particular m is called the m th-order wave function. Similarly the energy is given by

$$E = \sum_n \epsilon_n Z^{-n}, \quad (\text{II.3})$$

where ϵ_n is referred to as the n th-order perturbation energy coefficient.⁷

Define

$$G_0 = H_0 - \epsilon_0, \quad (\text{II.4})$$

$$G_1 = H' - \epsilon_1. \quad (\text{II.5})$$

The familiar equations for Schrödinger perturbation theory then read⁷

$$G_0 \psi_0 = 0, \quad (\text{II.6.0})$$

$$G_0 \psi_1 + G_1 \psi_0 = 0, \quad (\text{II.6.1})$$

$$G_0 \psi_2 + G_1 \psi_1 - \epsilon_2 \psi_0 = 0, \quad (\text{II.6.2})$$

and in general for all n

$$G_0 \psi_n + G_1 \psi_{n-1} - \sum_{k=2}^n \epsilon_k \psi_{n-k} = 0. \quad (\text{II.7})$$

It is possible⁷ to arrive at the correct perturbation variational integral equations by requiring that the variance with respect to the unknown ψ_n lead to an Euler equation identical with one of the Eqs. (7). It is necessary only to take care that for exact ψ_n the equations indeed furnish a correct expression for ϵ_{2n} . Alternately, it is possible to start from the variational theorem. The variational theorem states that for any ψ meeting well-known, easily satisfied restrictions

$$\int d\tau \psi^* H \psi - E \int d\tau \psi^* \psi \geq 0. \quad (\text{II.8})$$

⁶ Note added in proof. Units of length, Za_0 ; units of energy $2RhcZ^2$ are used unless it is explicitly indicated that atomic units are being used. These latter are units of length a_0 , units of energy $2Rhc$, where a_0 is the Bohr radius.

⁷ H. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35, Pt. 1, pp. 208 ff.

⁵ R. E. Knight and C. W. Scherr, J. Chem. Phys. **37**, 2503 (1962).

The derivation in this latter case is presented in the following paragraph.

Define

$$\langle n|\Omega|m\rangle = \int d\tau \phi_n^* \Omega \phi_m, \quad (\text{II.9})$$

where the ϕ_n now refer to the approximation functions which will be furnished by the variational procedure to be derived below.

Since ψ_0 is known exactly, it follows immediately that

$$\langle n|G_0|0\rangle = 0, \quad (\text{II.10})$$

$$\langle 0|G_1|0\rangle = 0. \quad (\text{II.11})$$

Insertion of Eqs. (2) and (3) into Eq. (8) yields an infinity of terms that may be viewed as a power series in Z^{-1} . The leading power of Z is Z^0 , whose coefficient, $\langle 0|G_0|0\rangle$, vanishes by Eq. (10). The coefficient of Z^{-1} is

$$2\langle 1|G_0|0\rangle + 2\langle 0|G_1|0\rangle, \quad (\text{II.12})$$

which also vanishes via Eqs. (10) and (11). However, the coefficient of Z^{-2} is

$$\langle 1|G_0|1\rangle + 2\langle 1|G_1|0\rangle - \epsilon_2\langle 0|0\rangle. \quad (\text{II.13})$$

The expression (13) is necessarily positive for it is the dominant term for large enough Z , and would cause Eq. (8) to be violated if it were not positive (or zero). Hence,

$$\epsilon_2\langle 0|0\rangle \leq \langle 1|G_0|1\rangle + 2\langle 1|G_1|0\rangle. \quad (\text{II.14})$$

This equation is the variational perturbation equation originally derived and used by Hylleraas in his great pioneering work.^{7,8} It is this equation which furnishes the variational criterion for determining ϕ_1 via minimizing an estimate of ϵ_2 . The coefficient of Z^{-3} reads

$$2\langle 2|G_0|1\rangle + 2\langle 2|G_1|0\rangle + \langle 1|G_1|1\rangle - 2\epsilon_2\langle 1|0\rangle - \epsilon_3\langle 0|0\rangle. \quad (\text{II.15})$$

To the extent that Eq. (14) has furnished an accurate ϕ_1 , the first two terms in this equation will vanish due to Eq. (6.1). Equation (15) then furnishes an estimate of ϵ_3 , as all the remaining quantities may now be calculated. *With the assumption that ϕ_1 is known exactly*, the coefficients of Z^{-2} and Z^{-3} vanish exactly, and the coefficient of Z^{-4} is now the dominating term, and hence is necessarily positive. After similar simplifications as above, there remains

$$\langle 2|G_0|2\rangle + 2\langle 2|G_1|1\rangle - 2\epsilon_2\langle 0|2\rangle - \epsilon_2\langle 1|1\rangle - 2\epsilon_3\langle 0|1\rangle - \epsilon_4\langle 0|0\rangle \geq 0. \quad (\text{II.16})$$

⁸ E. Hylleraas, Z. Physik **65**, 209 (1930).

Similarly, the coefficient of Z^{-5} will furnish an accurate estimate of ϵ_5 to the extent that Eq. (16) has furnished an accurate ϕ_2 . After similar simplifications as above, this coefficient is

$$\langle 2|G_1|2\rangle - 2\epsilon_2\langle 2|1\rangle - \epsilon_3\langle 1|1\rangle - 2\epsilon_3\langle 2|0\rangle - 2\epsilon_4\langle 1|0\rangle - \epsilon_5\langle 0|0\rangle. \quad (\text{II.17})$$

Now, with the assumption that ϕ_1 and ϕ_2 are known exactly, the coefficients of Z^{-4} and Z^{-5} vanish exactly, and the coefficient of Z^{-6} becomes the dominant and hence necessarily positive term, and will furnish estimates of ϕ_3 and ϵ_6 . The coefficient of Z^{-7} will correspondingly furnish an estimate of ϵ_7 . The process may be continued to as high an order as is desired. In general,

$$\langle 0|0\rangle_{\epsilon_{2n}} = \langle n|G_0|n\rangle + 2\langle n|G_1|n-1\rangle - \sum_{p=2}^{2n-1} \epsilon_p \sum_{i=n-p}^n \langle i|2n-p-i\rangle, \quad (\text{II.18})$$

$$\langle 0|0\rangle_{\epsilon_{2n+1}} = \langle n|G_1|n\rangle - \sum_{p=2}^{2n} \epsilon_p \sum_{i=n+1-p}^n \langle i|2n+1-p-i\rangle, \quad (\text{II.19})$$

where terms with negative indices are ignored.

III. NORMALIZATION

There are two further requirements on the functions that are furnished by the variational perturbation procedure. The first is that the functions formally satisfy the perturbation equations, Eqs. (II.6). The second is that they correspond to a normalized total wave function.

Let the functions furnished by the variational procedure be represented by ϕ_n . Then it will be sufficient to write

$$\psi_n = a_0\phi_n + \sum_{i=0}^{n-1} b_{n,i}\psi_i. \quad (\text{III.1})$$

When the successive ψ_n are inserted in the successive perturbation equations there results, by a sequence of steps that is much simpler to perform than to describe, a necessary and sufficient requirement for the satisfaction of the perturbation equations. This requirement is that the $b_{n,i}$ not be a two-index function, but rather a singly indexed function, indexed in fact by $n-i$, so that actually Eq. (1) may be rewritten as

$$\psi_n = a_0\phi_n + \sum_{i=0}^{n-1} a_{n-i}\psi_i. \quad (\text{III.2})$$

The normalization condition

$$\int d\tau \psi^* \psi = 1 \quad (\text{III.3})$$

becomes, by insertion of Eq. (II.2),

$$\sum_{n=0}^{\infty} Z^{-n} \sum_{i+j=n} \langle i|j \rangle = 1, \quad (\text{III.4})$$

where $\langle i|j \rangle$ is explicitly an integral between the ψ_n , rather than between the ϕ_n which was its actual meaning in the previous section. Since Z is completely arbitrary, Eq. (4) will be satisfied if and only if

$$\sum_{i+j=n} \langle i|j \rangle = \delta_{n,0}, \quad (\text{III.5})$$

where $\delta_{n,0}$ is the Kronecker delta function. The validity of Eq. (5) is further discussed below. Equation (5) is the final condition needed to fix the a_{n-i} . Let

$$\langle i|j \rangle = \int d\tau \phi_i^* \phi_j. \quad (\text{III.6})$$

Then

$$\begin{aligned} a_0 &= 1, \\ a_1 &= -(1|0) \end{aligned} \quad (\text{III.7})$$

(i.e., ψ_0 is normalized and orthogonal to ψ_1), and

$$\begin{aligned} 2a_2 &= -[2(2|0) + (1|1)] + a_1^2, \\ 2a_3 &= -[2(3|0) + 2(2|1)] + a_1(2a_2), \\ 2a_4 &= -[2(4|0) + 2(3|1) + (2|2)] + a_1(2a_3) + a_2^2, \\ 2a_5 &= -[2(5|0) + 2(4|1) + 2(3|2)] + a_1(2a_4) \\ &\quad + a_2(2a_3), \quad (\text{III.8}) \\ 2a_6 &= -[2(6|0) + 2(5|1) + 2(4|2) + (3|3)] \\ &\quad + a_1(2a_5) + a_2(2a_4) + a_3^2. \end{aligned}$$

The a_i are characteristic of the basis set employed and not of the perturbation wave function, and hence are not listed.

IV. PROCEDURE AND RESULTS

The form of ψ_0 is of course fixed. Each of the other ϕ_i is of the form

$$\phi_i = \exp\left(-\frac{1}{2} k_i s\right) \sum_{l,m,n} A_{l,m,n} \frac{k_i^{l+3}}{l+2!} s^l p^m q^n, \quad (\text{IV.1})$$

where s , p , and q are the Kinoshita variables.⁴ The k_i are scale factors that are individually varied for each ϕ_i .⁹ The summation was extended to include all the terms considered by Kinoshita in his 80-term calculation^{4(b)} (exclusive of $l = m = n = 0$ which is not in-

⁹ Selection of the k_i to be 2.0 (the hydrogenic value) results in a loss of two orders of magnitude of accuracy.

cluded in the summation) plus enough additional terms to make up a 100-term expansion. The calculations were performed in "double precision" (22 decimal figure arithmetic) on a CDC 1604 located on this campus. The original formulation of Hylleraas was followed down to the details of the arithmetic. The calculations were carried through sixth order, thus furnishing the ϵ_n through thirteenth order. The ϵ_n are tabulated in Table I. The total energies computed from these coefficients for the first ten members of the helium isoelectronic sequence are tabulated in Table II. The choice of the number of significant figures reported in these tables is discussed below.

TABLE I. The ϵ_n in atomic units.

n	ϵ_n	r_n
2	-0.15766	6405-
3	0.00869	8991
4	-0.00088	8587
5	-0.00103	6372
6	-0.00061	2917
7	-0.00037	2187
8	-0.00024	2872
9	-0.00016	5651
10	-0.00011	6157
11	-0.00008	3281
12	-0.00006	0866
13	-0.00004	5213

TABLE II. The energies in atomic units.

Z	E to 13th order
1	-0.5275 9152
2	-2.9037 2433
3	-7.2799 1339
4	-13.6555 6622
5	-22.0309 7156
6	-32.4062 4658
7	-44.7814 4513
8	-59.1565 9510
9	-75.5317 1234
10	-93.9068 0649

V. TWO IMPORTANT THEOREMS

Two useful sets of relations are as follows:

$$\langle r_{12}^{-1} \rangle_p = (p+1) \epsilon_{p+1} \quad (\text{V.1})$$

and

$$\langle r_1^{-1} + r_2^{-1} \rangle_p = (p-2) \epsilon_p, \quad (\text{V.2})$$

where the symbols on the left are defined by

$$\langle \Omega \rangle_p = \sum_{i+j=p} \langle i|\Omega|j \rangle = \sum_{i+j=p} \int d\tau \psi_i^* \Omega \psi_j. \quad (\text{V.3})$$

$\langle \Omega \rangle_p$ is referred to as the coefficient of the p th-order contribution to the expectation value of the operator Ω . A special case of Eq. (2) has already been presented

in an Appendix to the second paper of this series.

Equation (1) is readily established by forming

$$\sum_{i=0}^p (p+1-2i) \int d\tau \psi_i^* \epsilon_{p+1-i} = 0, \quad (\text{V.4})$$

where ϵ_{p+1-i} is the terms in the $(p+1-i)$ th-order perturbation equation, i.e., the terms on the left of Eq. (II.7) when n is set equal to $p+1-i$. In addition to terms that directly cancel, a number of terms are also eliminated in the summation in Eq. (4) via the normalization condition, Eq. (III.5). What remains is exactly Eq. (1).

For particles interacting through a Coulomb law of force, the virial theorem states that

$$E = \frac{1}{2} \langle V \rangle, \quad (\text{V.5})$$

where V is the potential energy part of the complete Hamiltonian. When the quantities in Eqs. (II.2) and (II.3) are inserted into Eq. (5), a power series in Z arises whose coefficients may be equated indently to zero. This procedure leads directly to

$$\epsilon_p = -\frac{1}{2} \langle r_1^{-1} + r_2^{-1} \rangle_p + \frac{1}{2} \langle r_{12}^{-1} \rangle_{p-1}. \quad (\text{V.6})$$

Insertion of Eq. (1) into Eq. (6) yields Eq. (2).

Pekeris has already calculated the expectation values in Eqs. (1) and (2) specifically for the case Z equals two with his 1078-term variational wave function. His values are compared with the present values in Table III.

TABLE III. $\langle r_1^{-1} + r_2^{-1} \rangle$ and $\langle r_{12}^{-1} \rangle$ in atomic units for He.

Integral	Pekeris value ^a	Present values			
		13th order		extrapolated	
$\frac{1}{2} \langle r_1^{-1} + r_2^{-1} \rangle$	1.6883 1680	1.6883	1686	1.6883	1689
$\langle r_{12}^{-1} \rangle$	0.9458 1845	0.9458	1878	0.9458	1895

^a C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

VI. DISCUSSION OF THE ϵ_n AND THE TOTAL ENERGIES

The first important question to be answered is how well converged have the ϵ_n been obtained. In paper I of this series the question was answered by a reference to the extent that the first-order expectation values obtained there agreed with values known exactly from the perturbation theory of Dalgarno and Lewis.¹⁰⁻¹² Exact values for certain $\langle \Omega \rangle_p$ (cf. previous

section) or for certain $\langle i|\Omega|j \rangle_p$ can be obtained¹² from theory, and thus similar comparisons for higher orders than the first can be made, and are made in the next paper in this series. At the moment an estimate of the convergence of ϵ_2 can be made by comparing the total helium energy value computed from the perturbation coefficients with the value found by Pekeris with his 1078-term wave function. It can be concluded that ϵ_2 is most likely converged to within 4 units in the eighth decimal place. Since no energy value can be obtained more precisely than the absolute error in ϵ_2 , the entries in Table II have been rounded to eight decimal places. The entries in Table I, however, are given to nine decimals in order to circumvent a possible loss of accuracy in computing the expectation values of r_1^{-1} and r_{12}^{-1} via Eqs. (V.2) and (V.6).

TABLE IV. Comparison of the ϵ_n with ϵ_n recovered from variational wave functions.

n	Present paper		SS ^a	HM ^b
2	-0.15766	6405 ⁻	-0.1576664	-0.157657 ₅
3	0.00869	8991	0.0086993	0.00853 ₅
4	-0.00088	8587	-0.000894	-0.00034
5	-0.00103	6372	-0.001012	-0.00082
6	-0.00061	2917	-0.000641	-0.00244 ₅

^a C. W. Scherr and J. N. Silverman, J. Chem. Phys. **37**, 1154 (1962).

^b E. Hylleraas and J. Midtdal, Phys. Rev. **109**, 1013 (1958).

Scherr and Silverman¹³ have recovered perturbation energy coefficients through sixth order from the data of Pekeris via a differencing process. A comparison is presented in Table IV where it can be seen that the agreement is good. A similar set of coefficients given by Hylleraas and Midtdal¹⁴ is also tabulated.

An interesting aspect of the calculated perturbation energy coefficients, already noted by Knight and Scherr,⁵ is that the set of r_i defined by $r_i = \epsilon_{i-1}/\epsilon_i$ are approaching a constant ratio r_∞ as the order considered becomes higher. The new set of ratios are given in Table I. They lie on a smooth curve, and probably extrapolate to some value for r_∞ lying between +0.78 and +0.80. Several interesting consequences follow if the ratio is indeed approaching such a constant value. *First*, since r_∞ is less than unity, the absolute convergence of the energy series for $Z > r_\infty$ is established. *Second*, since r_∞ is positive, and since all the ϵ_n from ϵ_4 onwards are negative, it follows that any truncated energy summation past third order is *nec-*

¹⁰ A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **A233**, 70 (1955).

¹¹ A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A247**, 245 (1958).

¹² C. W. Scherr (unpublished material). Scherr finds exact values for operators involving r_{12} . These are useful for estimating the degree of convergence of other similar operators such as the Hamiltonian itself.

¹³ C. W. Scherr and J. N. Silverman, J. Chem. Phys. **37**, 1154 (1962).

¹⁴ E. Hylleraas and J. Midtdal, Phys. Rev. **109**, 1013 (1958)

essarily an upper limit to the true energy.¹⁵ Analogous results follow for $\langle r_1^{-1} \rangle$ and $\langle r_{12}^{-1} \rangle$, cf. Eqs. (V.2) and (V.6). *Third*, an extrapolation to infinite order energies is readily accomplished. Thus, suppose, for all n greater than n' , that r_n is close enough to its limiting value that it is satisfactory to take $r_\infty = r_{n'}$ and to write $\epsilon_{n+1} = r_\infty \epsilon_n$. Then it is easily established that in atomic units

$$E = \sum_{i=0}^{n'} \frac{\epsilon_i}{Z^{i-2}} + \frac{\epsilon_{n'}}{Z^{n'-2}} \frac{r_\infty}{Z - r_\infty}. \quad (\text{VI.1})$$

The 13th-order energies listed in Table II are quite constantly 5 units deeper in the eighth decimal place than Pekeris' n^* energy values in each case except H^- and He . They are also 7 to 8 units deeper in the ninth decimal place than his extrapolated values in each case except H^- , He , and Li^+ . In view of the italicized statement in the previous paragraph, these comparisons are a further indication of the high degree of convergence of the sixth-order wave function.

In order to obtain extrapolated values, it is necessary to determine r_∞ . Since the r_n is only approximately converged, knowledge of r_∞ at this point actually would not give an exact extrapolation even if ϵ_{13} were known exactly. A good estimate is obtainable, however, for it seems clear that r_{13} is within 0.04 or 0.05 units of r_∞ . In view of these uncertainties, r_∞ is here taken as 0.77914, the value which makes the computed H^- energy agree to 8 decimal places with Pekeris' best extrapolated value. To the number of figures reported, the extrapolation only affects $Z = 1$ and 2 as follows (atomic units):

$$\text{H}^- -0.5277\ 5101, \quad \text{He} -2.9037\ 2434.$$

VII. BEHAVIOR NEAR THE NUCLEUS

It is known from theory¹⁶ that the two-electron atom wave functions for the ground states have a behavior near the nucleus in atomic units of

$$\psi = 1 - Zs + \frac{1}{2}u + \cdots, \quad (\text{VII.1})$$

where $s = r_1 + r_2$ and u is r_{12} . It has already been pointed out in the first two papers of this series how poorly first-order perturbation wave functions behave near the nucleus. Thus, specifically for $Z = 2$, for the ground-state 70-term wave function of the "Hylleraas type"¹⁷ considered there,

$$\psi = 1 - 1.9186s + 1.0433u + \cdots, \quad (\text{VII.2})$$

so that the coefficient of u is in error by more than a factor of two. The coefficient of s on the other hand is fairly satisfactory, as is evident if the behavior of Pekeris' 1078-term variational wave function near the nucleus is considered:

$$\psi = 1 - 1.98444s + 0.47391u + \cdots. \quad (\text{VII.3})$$

The behavior of the sixth-order wave function near the nucleus specifically for the case $Z = 2$ is

$$\begin{aligned} \psi = & 1 - 1.98317s + 0.50299u + 0.03163t^2s^{-1} \\ & - 0.04513u^2s^{-1} - 0.01728ut^2s^{-2} + 0.01654u^3s^{-2} \\ & - 0.00023t^2u^{-1} + \cdots, \end{aligned} \quad (\text{VII.4})$$

where $t = r_2 - r_1$. The last five terms arise because the basis set contains Kinoshita variables. Kinoshita has shown that these "extra terms" are properly present, and hence they will contribute to the functional behavior near the nucleus, too. In order to make a qualitative comparison with the theoretical behavior it is sufficient to examine the first three terms in Eq. (4) since the last five terms largely cancel themselves out. In order to make a quantitative comparison with the theoretical values, the actual numerical values of the terms linear in metric variables for given values of r_1 , r_2 , and r_{12} have to be compared to $-Zs + 0.5u$ for those same values. A convenient set of coordinates is defined as

$$\begin{aligned} \lambda &= s_{12}/g_{12}, \\ \cos \theta &= \mathbf{r}_1 \cdot \mathbf{r}_2 / r_1 r_2, \end{aligned} \quad (\text{VII.5})$$

since, fortunately, the problem can be considered as a two-dimensional problem: the *relative* values are the relevant values. The $s_{12}(g_{12})$ is the smaller (larger) of r_1 and r_2 . The λ may be viewed as an "in-out correlation" coordinate, while $\cos \theta$ may be viewed as an "angular correlation" coordinate. Figure 1 abstracts conveniently the important points to be noted in this connection. The curve marked P is the locus of points¹⁸ where Pekeris' wave function, Eq. (3), gives exact agreement with the theoretical values; the curve marked KS is the locus of points where the sixth-order wave function, Eq. (4), gives exact agreement with the theoretical values; and the curve marked P-KS is the locus of points where the sixth-order wave function and the Pekeris' wave function

¹⁵ This statement, of course, requires that the exact ϵ_n be used.

¹⁶ V. Fock, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **18**, 161-172 (1954).

¹⁷ That is, only positive powers of the metric variables are included in the expansion set.

¹⁸ By equating Eq. (3) to Eq. (1) it is possible to obtain $\cos \theta$ as a function of λ , and hence to obtain the equation of the curve P. In fact, the relation is

$$\cos \theta = 0.3221\lambda - 0.3557 + 0.3221\lambda^{-1}.$$

Similar expressions could be found for the other two curves on Fig. 1, though they were actually plotted from a numerical calculation.

have the same relative error, so that everything above that line is the area where the Pekeris wave function does better, and everything below that line is the area where the sixth-order wave function does better. Thus, the Pekeris wave function is superior in the

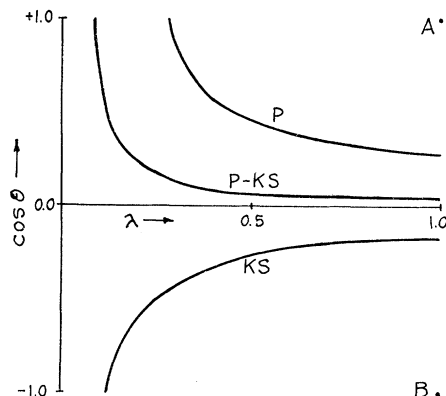


FIG. 1. Comparison of the behavior near the nucleus of the Pekeris 1078-term wave function with the sixth-order wave function for $Z = 2$; lines P and KS are the loci of exact agreement of the Pekeris wave function and the sixth-order wave function, respectively, with theory, and line $P - KS$ is the locus of exact agreement of the two wave functions with each other.

doubly difficult region near the point A where both in-out correlation and angular correlation are most needed ($\lambda = 1$, $\cos \theta = 1$). Fortunately, the superiority of the Pekeris wave function in this region is only marginal. The ratio of values furnished by the

Pekeris wave function to the exact values ranges from a high of 1.0078 at A to a low of 0.9930 in many places¹⁹ including point B. The same ratio for the sixth-order wave function ranges from a high of 1.0084 at A to a low of 0.9942 at B. Thus, in both cases, the linear terms are not in error by more than about 0.8%.

VIII. CONCLUSION

The ability of a sixth-order wave function to hold its own against and even surpass the results of the very best variational calculations extant should lay to rest the objection that it is incapable of highly accurate development. It seems clear that much useful work remains to be done, and in this concluding section the authors would like once more to emphasize the simplicity and ease of the calculations.

The work on expectation values of operators with this sixth-order wave function is nearly completed, and furnishes the subject matter of the next paper of this series. Calculations are also underway to treat various excited states of the two-electron sequence in higher order.

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¹⁹ Thus, the value 0.9930 is obtained all along the $\cos \theta = -1$ axis, and all along the $\lambda = 0$ axis.

Discussion on Atomic and Molecular Calculations

Y. J. P'HAYA, *Chairman*

HYLLERAAS: I found these results quite exciting. Midtdal and I had thought our (24 term) $E_2^{(2)}$ value was fairly accurate, possibly to the sixth decimal place. Then, comparison with Pekeris' values indicated a difference of some units. Now through Knight and Scherr's calculations, the value has not only been corrected (to 6 decimals), but has actually been given to more decimals.

NESBET: In using $(1/Z)$ expansions, nonintegral values of Z could be used for the basic numerical work (Pekeris' calculations, for example) with $(1/Z)$ perhaps equal to roots of Chebyshev polynomials, to give better formulas for interpolation and extrapolation.

HYLLERAAS: I remember a conversation long ago with Ta-You Wu, who firmly believed in the existence of $H^-(1s)(2s)^3S$ as a closed state which I had been unable to produce. In such cases, the use of Z as a continuous parameter might be helpful, because as long as $Z > 1$ the state in question would be closed. In the case of the closed state $(2p)^2\ ^3P$ of H^- I had tried the values of $Z = 1.5$, 1.2, 1.1, however, only after the stability of $Z = 1.0$ had been proved. At an earlier stage the procedure might perhaps have been of some use.

LÖWDIN: The coefficients of the Chebyshev expansion of the energy of the He-like ions in terms of $1/Z$ have been evaluated in Uppsala about one year ago by Klaus Appel and myself.

KIM: I should like to report on a calculation of the interaction of two He atoms in the ground state. [Dong-Yun Kim, *Z. Physik*, **166**, 359 (1962)]. Aside from the normal Heitler-London type