made using Eq. (13). The best over-all agreement between the present results and previous measurements seems to be obtained if the results of Risch (see reference c of Table I) are used. It should also be pointed out that the previous results quoted in Table I are obtained by a completely different method than the present measurement and are the result of averaging a number of observations for elements with atomic number 81 (Tl^{208}) and 83 (Bi^{212}). The value of ω_{KL} obtained for thallium ($Z=81$) in the present work is considerably lower than the value quoted for lead ($Z=82$). Kinsey[6] gives values of $\omega_{L_{II}}$ and $\omega_{L_{III}}$ from which the number for ω_{KL} ($Z=81$) given in Table I is calculated using Eq. (3). This number is smaller than the one measured in the present experiment by about 15%. The cause for the disagreement may be that the L_{III} shell yield given by Kinsey is too small. Recent measurements[9] of this number give somewhat larger values in this region of atomic numbers. The measurement of ω_{LL} for $Z=78$ is compared with an L_I subshell yield measured by Roos and quoted in reference 9. (It is assumed that this yield is ν_{L_I} rather than ω_{L_I} as quoted in reference 9. This assumption is reasonable since ω_{L_I} should be only about one third as large due to the effect of Coster-Kronig transitions.) The agreement between these two numbers is only fair and may be accidental because of the large experimental error quoted for the previous measurement.

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Two-Electron Atoms. I. Perturbation Study of the Ground State

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A variational perturbation method used by Hylleraas has been extended to include 70-term basis sets as approximations to the first-order wave function of the two-electron atomic species. An upper limit of -0.15766625^{+} a.u. has been found for the second-order perturbation energy coefficient. It is estimated that this value is converged to at least two units in the seventh decimal place. A value of the third-order perturbation energy coefficient of 0.00869868 a.u. is calculated from the same variational first-order wave function. A number of expectation values to first-order for certain operators [e.g., $\delta(\mathbf{r}_1)$, $\delta(\mathbf{r}_{12})$, p_1^4, r_1^n, $\cos\theta_{12}$, etc.] are computed, and compared, where possible, to known values. A variety of basis sets is studied, including a set that contains negative powers of the metric variables ("Kinoshita" type) and one that contains only positive powers ("Hylleraas" type). A scheme is proposed that uses first and higher order expectation values for the analysis and characterization of approximate wave functions. This scheme, which is not restricted to two electrons, also opens the possibility of a nonenergetic variational procedure for obtaining wave functions.

I. INTRODUCTION

An upper limit for the second-order perturbation energy coefficient, ϵ_2, of the two-electron atomic species is found here which is the deepest so far reported. It is estimated that the value of[1]

$$\epsilon_2=-0.15766625^{+}\text{ a.u.} \tag{1}$$

is converged to at least two units in the seventh decimal place. The method employed is due to Hylleraas,[2] and is admirably adapted to retaining the full numerical accuracy available with an electronic computer. First-order approximations to other properties of interest are also found, and in Sec. IV a proposal is made for the application of perturbation theory results to the analysis and characterization of approximate wave functions.

Conventional Schrödinger perturbation theory presents an atomic wave function as an expansion in powers of the nuclear charge Z:

$$\psi=\sum_n Z^{-n}\psi_n, \tag{2}$$

where the sum to a particular n is called the nth order wave function. This expansion leads to what might be called a perturbation expansion for the expectation value of an operator. Thus, the expansion through first order of the expectation value of an operator is given in obvious notation by

$$\langle\Omega\rangle_0+Z^{-1}\langle\Omega\rangle_1=\int d\tau\,\psi_0^*\Omega\psi_0+2Z^{-1}\int d\tau\,\psi_1^*\Omega\psi_0. \tag{3}$$

Recently a fund of information on such perturbation expansion terms of various expectation values averaged over the ground states of the first few members of the two-electron isoelectronic sequence has become avail-

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[1] Atomic units (of length, the Bohr radius; of energy, $2Rhc$) are used throughout.

[2] E. Hylleraas, Z. Physik **65**, 209 (1930).

TABLE I. Some first-order expectation values, in atomic units.

	K	H	S	Other
$2k$	2.55	2.73	2.0	...
$-\epsilon_2$	0.157666254	0.157666149	0.125331979	0.1576664[a]
$-\epsilon_2^0$	0.125332617	0.125332144	0.125331979	0.12534[b]
ϵ_3	0.008698679	0.008698674	−0.005215406	0.008690[a]
$Mm^{-1}Z^{-1}\mathcal{E}_m$	0.133293412	0.133293679	0	0.13327[a]
$-\pi Z^{-2}\delta(\mathbf{r}_1)$	0.6677846	0.6678131	0.6698709	0.667639614[c,d,e] 0.6675[a]
$-\pi Z^{-2}\delta(\mathbf{r}_{12})$	0.2429172	0.2428040	0.1529560	0.2431[a]
$-\delta(r_2-r_1)$	0.2102302	0.2102390	0.2099754	...
$-Z^{-3}p_1^4$	4.0911498	4.0912292	4.091449	4.09111691[c,e] 4.092[a]
$-(\alpha Z)^{-2}E_2$	0.0814216757	0.0814258583	0	0.08141[a]
$-r_1^{-1}-r_2^{-1}$	0.624999998	0.624999812	0.624999998	0.625[c,d,e]
$Z^2(r_1+r_2)$	1.124999976	1.124998477	1.125000002	1.125[c,e]
$Z^3(r_1^2+r_2^2)$	4.78124998	4.78123054	4.781250000	4.78125[c,d,e,f]
Z^2r_{12}	1.02968827	1.02968741	0.872551061	...
$-Z^3\mathbf{r}_1\cdot\mathbf{r}_2$	0.378616569	0.378618085	0	0.379[f]

[a] From an analysis of Pekeris' data. See present footnote 9.
[b] See footnote 17.
[c] Exact values from footnote 5.
[d] Exact values from footnote 6.
[e] Exact values from footnote 7.
[f] Values from footnote 3.

able both from theoretical calculations[2–9] and from analysis of experimental data.[10] The $\langle\Omega\rangle_0$ part of Eq. (2) is usually easily computed, and in special cases so is the $\langle\Omega\rangle_1$ part.[3–7] In general, in order to find the $\langle\Omega\rangle_1$ conveniently, an approximate form for ψ_1 is required. Aside from calculations of the third-order energy coefficient, ϵ_3, the only previous direct calculation of an $\langle\Omega\rangle_1$ from a ψ_1 for the two-electron system is due to Dalgarno and Stewart.[3,4]

The Hylleraas method employed is a variational perturbation procedure. The variational wave function is an approximation to ψ_1. In addition to computing a bounded ϵ_2 (and an approximate, but presumably not bounded ϵ_3), this approximate ψ_1 has been used in Eq. (3) to compute approximate values for $\langle\Omega\rangle_1$. These $\langle\Omega\rangle_1$ not only have an intrinsic interest, but they may turn out to have some interesting applications as discussed below. Thus, it seemed worthwhile to extend the work of Hylleraas to other and larger basis sets.

II. PROCEDURE AND RESULTS

Three basically different basis sets are considered here. The first set, referred to as K, includes 70 of the 80 terms employed by Kinoshita.[11] The second set, referred to as H, includes 70 terms of the "Hylleraas" type.[12] The third set is a group of 70 term sets based on an expansion whose form is given in a conventional notation by

$$\psi_1=\sum_l \psi_1^l(r_1,r_2)P_l(\cos\theta_{12}). \qquad (4)$$

When the summation is cut off at $l=0, 1, 2 \cdots$, the sets are referred to as S, P, D $\cdots$.[13] The actual P used included 40 $l=0$ (s-type) terms and 30 $l=1$ (p-type) terms. The actual D used included 40 s-type terms, 20 p-type terms, and 10 $l=2$ (d-type) terms. The best limiting ϵ_2 value that can be obtained from an infinity-term S is called the s limit, (ϵ_2^0); from an infinity-term P is called the p limit, (ϵ_2^1), etc. All the basis sets include a scaling factor, kZ, where k is a variation parameter.

Table I tabulates the results. Comparison values obtained from an analysis[9] of the very accurate expectation values found by Pekeris[14] are also tabulated, as well as some from other sources, and such exact values as are available. Note that

$$\nabla_1\cdot\nabla_2\psi_0=-Z^2\cos\theta_{12}\psi_0, \qquad (5)$$

so that

$$\langle\mathcal{E}_m\rangle_1=\langle\nabla_1\cdot\nabla_2\rangle_1=-Z^2\langle\cos\theta_{12}\rangle_1, \qquad (6)$$

where $\mathcal{E}_m$ is the mass polarization; and, of course,

$$\langle r_{12}^{-1}\rangle_1=2\epsilon_2. \qquad (7)$$

The E_2 (a retardation correction) has been discussed by Dalgarno and Stewart[3,4] and by Pekeris.[14]

III. DISCUSSION

A. The K and H Basis Sets

The optimum k values were readily determined to within a few hundredths of a unit for both the K and H basis sets. Each of the k values is greater than unity, as may be seen from Table I, so that the conventional

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[3] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A247**, 245 (1958).
[4] A. Dalgarno and A. L. Stewart, Proc. Phys. Soc. (London) **75**, 441 (1960).
[5] M. Cohen and A. Dalgarno, Proc. Roy. Soc. (London) **A261**, 565 (1961).
[6] C. Schwartz, Ann. Phys. (New York) **6**, 156–180 (1959).
[7] C. W. Scherr (unpublished).
[8] C. Schwartz, Phys. Rev. **126**, 1015 (1962).
[9] C. W. Scherr and J. N. Silverman, J. Chem. Phys. **37**, 1154 (1962).
[10] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).
[11] T. Kinoshita, Phys. Rev. **115**, 366 (1959).
[12] That is, only positive powers of the metric variables.

[13] The first-order wave function used by Dalgarno and Stewart and referred to above was an F-type.
[14] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

TABLE II. A comparison with some exact values, in atomic units.

Operator	Exact theoretical value	Value obtained via K	Relative error
$r_1^{-1}+r_2^{-1}$	-0.625	-0.624999998	2.7×10^{-9}
$Z^2(r_1+r_2)$	-1.125	-1.12499998	2.2×10^{-8}
$Z^3(r_1^2+r_2^2)$	-4.78125	-4.78124998	4.1×10^{-9}
$Z^3(4r_1r_2+r_1^2+r_2^2)\cos\theta_{12}$	-2.40625	-2.40624943	2.4×10^{-7}
$Z^3(4+Zr_1+Zr_2)r_1r_2\cos\theta_{12}$	-3.12890625	-3.12890148	1.5×10^{-6}
$Z^2(r_1+r_2)\cos\theta_{12}$	-0.4375	-0.437499808	4.4×10^{-7}
$Z^3(11r_1r_2-Zr_1^3-Zr_2^3)\cos\theta_{12}$	-6.15234375	-6.15232381	3.2×10^{-6}
$Z^{-3}p_1^4$	$-4.091116916\ldots$	-4.0911498	8.0×10^{-6}
$4\pi Z^{-2}\delta(\mathbf{r}_1)$	$-2.670558458\ldots$	-2.6711384	2.2×10^{-4}

interpretation of a scaling factor as introducing "shielding" does not apply in this case. The lower value of ϵ_2 obtained via K as well as the better reproduction of the exactly known expectation values seems to allow the conclusion that the present K is superior to the H types investigated. However, it would be premature to generalize from this result.[15] It is very difficult to assess the degree of convergence of the computed ϵ_2. An attempted extrapolation from the data of 40-, 50-, 60-, 70-, and 80-term K basis sets failed as the 80-term results were beginning to be in some doubt in the eighth or ninth decimal due to accumulation of roundoff.[16] An indication of the accuracy of the calculation can be obtained by comparing how well the $\langle\Omega\rangle_1$ are found for those cases where the exact results are known. A consideration of Table II shows that these cases seem to form three groups, one whose relative errors (for K) are of the order 10^{-8} to 10^{-9} (operators of the form $r_1^n+r_2^n$, $n\geqslant-1$), one whose relative errors are of the order 10^{-6} to 10^{-7} (operators typically involving $\cos\theta_{12}$), and one whose relative errors are of the order 10^{-4} to 10^{-5} [p_1^4 and $\delta(\mathbf{r}_1)$]. The first group owe their accuracy to their dependence only on s-type terms (see subsection B). The third group are discussed in the next paragraph. The operator used to furnish ϵ_2 involves $\cos\theta_{12}$, and is probably a member of the second group. In fact, ϵ_2 may be the best converged member of the second group, as the form of ψ_1 (i.e., the variational wave function) is tailored specifically to the needs of computing ϵ_2. This would furnish an approximate upper limit for the relative error of the computed ϵ_2.

It is not surprising that the relative errors of the expectation values of the operators of the third group are large. The expectation values of these operators are sensitive to the goodness of ψ_1 near the nucleus. This is obvious in the case of $\delta(\mathbf{r}_1)$, and, as shown elsewhere,[4,7]

$$\langle p_1^4\rangle_1=8\pi Z\langle\delta(\mathbf{r}_1)\rangle_1+1.25Z^3. \tag{8}$$

It is interesting to note that for this third group the values recovered from Pekeris' calculations are qualitatively no better. Thus, the relative error of the $\langle\delta(\mathbf{r}_1)\rangle_1$ found from the analysis of his data is 2.2×10^{-4}. Likewise, for $\langle p_1^4\rangle_1$ the relative error is 2.0×10^{-4}. To see just how poor a first-order wave function is near the nucleus, consider the coefficients of the constant and linear terms in the unnormalized H after the exponentials have been expanded in a power series

$$\begin{aligned}\psi&=\psi_0+Z^{-1}\psi_1+\cdots\\&=(1-1.1124Z^{-1})-(1-1.11485Z^{-1})Z(r_1+r_2)\\&\qquad+0.4630r_{12}+\cdots,\end{aligned} \tag{9}$$

so that for $Z=2$,

$$\psi=1-1.9186(r_1+r_2)+1.0433r_{12}+\cdots, \tag{10}$$

whereas the exact solution should start with

$$\psi=1-Z(r_1+r_2)+0.5r_{12}+\cdots. \tag{11}$$

Note from Eqs. (9) and (11) that in the limit of infinite Z the coefficient of r_1+r_2 approaches the correct value, but the coefficient of r_{12} remains incorrect.

B. S, P, and D, and ε_2^0

The best ϵ_2^0 value[17] computed from a 70-term S was -0.125331979. The minimum was insensitive to k and was given indifferently by any k in the range of about 0.9 to 1.4. The reported value of unity was picked arbitrarily. Because of the limited interest of the P and D results, they are not presented in Table I. The P was optimized at $k=1.8$ and gave an $\epsilon_2=-0.151778065$. The D was optimized at $k\approx1.8$ and gave an $\epsilon_2=-0.155390431$. These compare well with Schwartz's values[8] of $\epsilon_2^0=-0.12527$, $\epsilon_2^1=-0.1516$, and $\epsilon_2^2<-0.1550$.

It follows from Eq. (4) that the S part of any ψ_1 is given by

$$\psi_1^0=\int\psi_1P_0(\cos\theta_{12})d\cos\theta_{12}, \tag{12}$$

due to the orthogonality of the Legendre polynomials. This S part can be used to compute estimates of ϵ_2^0,

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[15] The superiority may be an artifact, and some better choice of the 70 terms used in H might lead to an improvement in its results. This point was investigated to some extent.

[16] For what it may be worth, an 80-term K identical in its selection of terms with the 80 of Kinoshita gave an ϵ_2 of -0.15766631, and $\epsilon_3=0.00869875$.

[17] This value should agree with the value obtained by C. W. Scherr, J. Chem. Phys. **33**, 317 (1960), by direct summation of the perturbation series terms. It does not as Scherr has one integral, the "Contribution to ϵ_2 from doubly ionized states [from terms] with $l=0$," incorrect by a factor of 2 (see C. Schwartz, reference 8). When this error is taken into account Scherr would obtain 0.12534 in agreement with the value obtained here.

the s limit ϵ_2, via

$$\epsilon_2{}^0=\int d\tau\, \psi_0{}^*r_{12}{}^{-1}\psi_1{}^0. \qquad (13)$$

The s limit so computed from K is deeper than that computed from S. Even though all 70 terms of K contribute to the s limit, this result is somewhat hard to understand. The difficulty may lie in the possibility that the $\epsilon_2{}^0$ value computed via Eq. (13) is not a bound, and/or it may lie in an inefficient choice of terms for S.

Any operator such as $r_1{}^n+r_2{}^n$ which does not depend on $\cos\theta_{12}$ can be expected to be obtained with high precision from an S as its total $\langle\Omega\rangle_1$ depends only on the $\psi_1{}^0$ part of ψ_1. A glance at Table I shows that these operators are obtained correct to more than nine significant figures.

It is shown elsewhere[7] that

$$4\epsilon_2{}^0=-2\langle\delta(t)\rangle_1-0.921875, \qquad (14)$$

where $t=r_2-r_1$. The $\epsilon_2{}^0$ computed in this fashion comes out to be -0.125353, indicating convergence to two units in the fifth decimal place. This is probably a pessimistic estimate due to the difficulty involved in obtaining a good value for a delta function.

IV. A POSSIBLE APPLICATION

These first-order corrections can be used to compute good estimates of an expectation value when Z is large. In addition to this obvious application, they could also be used:

(1) to investigate how well an approximate wave function describes the various regions of its configuration space;

(2) to investigate, for a particular region of configuration space, which approximate wave function among a collection of them does best; and, as is suggested by F. A. Matsen (private communication),

(3) to determine which terms in a basis set are effective and which are ineffective in contributing to the calculation of the expectation value of a particular operator.

These uses can be implemented in two ways:

(1) by comparing the computed expectation values with exactly known values, and

(2) by computing the expectation values of an operator, Ω, for a series of Z values, and then, by a procedure involving differences,[10] obtaining estimates for $\langle\Omega\rangle_0$, $\langle\Omega\rangle_1$, $\langle\Omega\rangle_2$, etc. These estimates will be obtained with an rms deviation. For a correction term of a given order, the smaller that rms deviation, the better the approximate wave function, at least in the region of configuration space most important to the operator in question.[18]

For example, a recent paper by Nesbet[19] has very clearly and effectively shown how the expectation value of an operator which does not commute with the Hamiltonian can depend very sensitively on terms which have a negligible effect on the energy.

An intriguing aspect of uses (2) and (3) above in connection with implementation (2) is that they offer a nonenergetic variational criterion (via minimizing the rms deviation) for determining a wave function. These ideas are, of course, not restricted to two-electron systems but can be applied just as well to a many-electron system.

V. CONCLUDING REMARKS

This work is being extended, employing different basis sets, to the excited singlet and triplet S and P states of the two-electron atom. It is planned to explore the possibilities raised in Sec. IV in numerical detail. The calculations were performed on a CDC 1604 located on this campus.

Note added in proof. The authors have extended the investigation to include a 100-term basis set using a double precision calculation. An ϵ_2 value, provisionally regarded as being converged to 8 decimal places, of -0.1576664048 has been obtained, and an ϵ_3 value of $+0.0086989907$.

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[18] The authors are pleased to acknowledge that part of the above material in this section arose from discussions with Dr. Jeremiah N. Silverman.

[19] R. K. Nesbet, Phys. Rev. **118**, 681 (1960).