the inner and outer shells, would not be independent). It is clear, therefore, that relativistic effects are appreciable and an accurate comparison of experiment with HF predictions can only be made when the latter (HF and not H) takes relativity into account. It is well known that use of the Dirac Hamiltonian involves excessive numerical work. It is very likely that the formal similarity of the symmetric Hamiltonian to the nonrelativistic problem would help simplify the HF procedures without appreciably loss in accuracy.

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Logarithmic Terms in the Wave Functions of the Ground State of Two-Electron Atoms

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A variational calculation for the ground state of two-electron atoms is carried out with a function containing the nonconventional terms $\ln(r_1+r_2)$, $[\ln(r_1+r_2)]^2$, and $(r_1^2+r_2^2)^{1/2}$. The convergence of the energy eigenvalues is very good, lending support to the existence of the logarithmic terms in the exact solution of the wave equation.

I. INTRODUCTION

THE energy eigenvalues E of the nonrelativistic Schrödinger wave equation for the ground states of two-electron atoms,

$$\frac{\partial^2\psi}{\partial r_1^2}+\frac{2}{r_1}\frac{\partial\psi}{\partial r_1}+\frac{\partial^2\psi}{\partial r_2^2}+\frac{2}{r_2}\frac{\partial\psi}{\partial r_2}+2\frac{\partial^2\psi}{\partial r_{12}^2}+\frac{4}{r_{12}}\frac{\partial\psi}{\partial r_{12}}+\frac{(r_1^2-r_2^2+r_{12}^2)}{r_1r_{12}}\frac{\partial^2\psi}{\partial r_1\partial r_{12}}+\frac{(r_2^2-r_1^2+r_{12}^2)}{r_2r_{12}}\frac{\partial^2\psi}{\partial r_2\partial r_{12}}+2\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r_{12}}\right)\psi=0, \qquad (1)$$

have been determined variationally[1–4] to a precision of one part in 10^9 to 10^{10}, which is more than two orders of magnitude better than the experimental accuracy. However, the accuracy of the corresponding variational wave functions is still uncertain. An expected *average* accuracy of from $1/10^4$ to $1/10^5$ is not assured for particular regions in space. The purpose of this investigation is to adduce evidence on the analytic nature of the solution $\psi(r_1,r_2,r_{12})$ of Eq. (1). In the absence of the repulsive term $1/r_{12}$ in the potential, Eq. (1) has an analytic solution represented by products of hydrogenic wave functions in each of the variables r_1 and r_2. However, with the inclusion of the repulsive term, it was shown by Bartlett *et al.*[5] that a solution of the form

$$\psi(r_1,r_2,r_{12})=\sum_0^\infty A_{lmn}r_1^l r_2^m r_{12}^n \qquad (2)$$

does *not* exist. The repulsive term thus changes the analytic character of the solution. In studying Eq. (1) in Gronwall's[6] coordinates, where the variable

$$R=(r_1^2+r_2^2)^{1/2} \qquad (3)$$

is introduced, Barlett further proved[7] that a solution of the form

$$\psi=\sum_{p=0}^\infty B_p(r_1,r_2,r_{12})R^{p+\gamma} \qquad (4)$$

also does not exist. Bartlett then shows,[7] on the basis of the work of Pierce,[8] that ψ can be developed formally into an expansion

$$\psi=\sum_{k=0}^\infty C_k(r_1,r_2,r_{12})(\ln R)^k. \qquad (5)$$

Two decades after Gronwall's work,[9] Fock,[10] apparently independently, rederived Gronwall's form of Eq. (1) using Gronwall's coordinates. Like Bartlett, Fock

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also reaches the conclusion that a solution of the form (4) does not exist, and that the equation can be satisfied formally if we use an expansion of the type (5) containing powers of $\ln R$. Fock outlines a procedure by which the functions C_k in (5) can be determined successively. This procedure is very complicated, but it was felt that, if the logarithmic terms appear in the true wave function, their inclusion in a variational function should accelerate convergence. The effect of a term $r_1r_2\cos\theta \ln(r_1+r_2)$, together with three other nonconventional rational terms, in a 24-term variational wave function, was tried by Hylleraas and Midtdal,[11,12] with encouraging results. However, when subsequently Hart and Herzberg included the same group of nonconventional terms in their 20-term variational wave function, no appreciable lowering of the energy was found.[13]

In view of these inconclusive results, and in the absence of a proof of the convergence of the expansion (5), the question as to whether or not logarithmic terms belong to the true wave function remained open. Evidence tending to support the reality of the logarithmic terms has recently been adduced by Ermolaev and Sochilin,[14] who carried out a variational calculation using 37 terms of the Fock[10] type, which included the terms $\ln R$ and $(\ln R)^2$. Their value of $E(2)=-2.9037238$ a.u. for $Z=2$ compares with the value $E(2)=-2.90372388$ a.u. obtained[1] by the use of conventional perimetric coordinates for a determinant[15] of order 125. Their wave functions also yield values for the relativistic corrections which converge rapidly.

II. VARIATIONAL SOLUTION INCLUDING LOGARITHMIC TERMS

We have carried out a systematic study of the effect of the logarithmic terms on the convergence of the energy eigenvalues in a variational calculation. The purpose was to test the expected acceleration of convergence in case the logarithmic terms actually belong to the true solution. Using the Hylleraas notation

$$s=r_1+r_2,\quad t=r_2-r_1,\quad u=r_{12}, \tag{6}$$

the Fock expansion is

$$\psi=e^{-(k/2)s}\{1+C_1s+C_2u+C_3s(s^2+t^2)^{1/2}+C_4u(s^2+t^2)^{1/2} +C_5su+C_6s^2+C_7t^2+C_8u^2+C_9(u^3/(s^2+t^2)^{1/2}) +C_{10}[\tfrac{1}{2}(s^2+t^2)-u^2]\ln[(s^2+t^2)/2]+\cdots\}. \tag{7}$$

From the differential equation (1), we know that in the exact solution the following relations hold:

$$C_1=-Z+\tfrac{1}{2}k,\quad C_2=\tfrac{1}{2}. \tag{8}$$

Following Hylleraas,[16] we scale the variables by introducing a function φ defined by

$$\psi(s,u,t)=\varphi(ks,ku,kt). \tag{9}$$

For φ we take, for the symmetrical case,

$$\varphi=e^{-\frac{1}{2}s}P(s,t,u,(s^2+t^2)^{1/2},\ln s), \tag{10}$$

$$P=\sum_{\substack{n,l,m,\\ i,j}} C(n,l,m,i,j)s^nt^{2l}u^m(s^2+t^2)^{i/2}(\ln s)^j. \tag{11}$$

For the antisymmetrical case, odd powers of t are used. The C's and the scaling parameter k are determined from Hylleraas'[16] variational form: The variation

$$\delta(k^2M-kL-\lambda N)=0, \tag{12}$$

$$M=\int_0^\infty ds\int_0^s du\int_0^u dt[u(s^2-t^2)(\varphi_s^2+\varphi_t^2+\varphi_u^2) +2s(u^2-t^2)\varphi_s\varphi_u+2t(s^2-u^2)\varphi_t\varphi_u], \tag{13}$$

$$L=\int_0^\infty ds\int_0^s du\int_0^u dt\{2su-[(s^2-t^2)/2Z]\}\varphi^2, \tag{14}$$

$$N=\tfrac{1}{8}\int_0^\infty ds\int_0^s du\int_0^u (s^2-t^2)\varphi^2dt, \tag{15}$$

$$\lambda=E/Z^2,\quad E\equiv-\epsilon^2. \tag{16}$$

yields relations[17] between the coefficients $C(n,l,m,i,j)$, from which the elements of the determinant are determined. The roots λ of the determinant yield the energy eigenvalues E, by (16).

The indices n, l, m, i, j were arranged in groups ω

TABLE I. Ordering of the indices for the symmetrical case.

k	n	$2l$	m	i	j	ω	k	n	$2l$	m	i	j	ω
1	0	0	0	0	0	0	16	0	2	1	0	0	3
2	0	0	1	0	0	1	17	1	2	0	0	0	3
3	1	0	0	0	0	1	18	0	0	2	1	0	3
4	0	0	2	0	0	2	19	1	0	1	1	0	3
5	1	0	1	0	0	2	20	2	0	0	1	0	3
6	2	0	0	0	0	2	21	0	2	0	1	0	3
7	0	2	0	0	0	2	22	−1	0	3	0	0	3
8	0	0	1	1	0	2	23	−1	2	1	0	0	3
9	1	0	0	1	0	2	24	−2	0	3	0	0	3
10	−1	0	2	0	0	2	25	−2	2	1	0	0	3
11	−1	2	0	0	0	2	26	0	0	2	0	1	3
12	0	0	3	0	0	3	27	2	0	0	0	1	3
13	1	0	2	0	0	3	28	0	2	0	0	1	3
14	2	0	1	0	0	3	29	0	0	1	1	1	3
15	3	0	0	0	0	3							

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TABLE II. Values of the energy parameter ϵ^2 in atomic units (a.u.) for various orders n of the determinant. $E=-2\epsilon^2$ Ry.

$Z \diagdown n$	59	101	170	246	Extrapolated
1	0.52775048	0.52775098	0.5277510150	0.52775101635	0.52775101638
2	2.903724351	2.9037243763	2.903724377011	2.9037243770326	2.9037243770333
3	7.279913365	7.2799134110	7.279913412613	7.2799134126660	7.2799134126678
4	13.65556617	13.6555662359	13.65556623834	13.655566238418	13.655566238421
5	22.030971499	22.0309715771	22.030971580128	22.030971580235	22.030971580239
6	32.406246508	32.4062465982	32.406246601762	32.406246601889	32.406246601894
7	44.781445045	44.7814451447	44.781445148618	44.781445148763	44.781445148768
8	59.156595012	59.1565951183	59.15659512259	59.156595122749	59.156595122755
9	75.53171225	75.5317123593	75.53171236378	75.531712363950	75.531712363957
10	93.90680639	93.9068065101	93.90680651485	93.906806515025	93.906806515031

which contain all elements satisfying the bound

$$n+l+m+j\leqslant\omega. \tag{17}$$

The index i is either 0 or 1; n is a positive or negative integer such that

$$n+\omega\geqslant 1. \tag{18}$$

The power j of the logarithmic terms in (11) is restricted by the condition

$$n+l+m+i\geqslant 2j. \tag{19}$$

Negative powers of s enter only when $i=j=0$. A sample of the sequence of indices adopted is shown in Table I.

The expansion (11) differs from the Fock expansion in that we use $\ln s$ instead of Fock's $\ln[(s^2+t^2)^{1/2}]$. Since, however, $|t|<s$, the difference $\ln[1+(t^2/s^2)]$ is not singular at the triple point. We also use negative powers of s instead of Fock's negative powers of $(s^2+t^2)^{1/2}$. We found that when negative powers of $(s^2+t^2)^{1/2}$ are used, the vector becomes unstable as we proceed to higher orders. On the other hand, the negative powers of s are essential, and without them the eigenvalues λ are inferior.

III. DISCUSSION OF RESULTS

Table II gives the energy eigenvalues ϵ^2 in a.u. for $Z=1$ to $Z=10$, and for determinants up to order 246. The determinant 246 contains all the terms possible in our scheme, with $\ln s$ and $(\ln s)^2$. The scaling factor k in (7) was given the values 0.44 for $Z=1$, 0.91 for $Z=2$, and 1.00 for $Z>2$. The computations were carried out on the computer GOLEM in 38-decimal-accuracy (single-precision of the GOLEM). The values[18] given in Table II are better than anything published hitherto. Thus, for $n=101$, $Z=2$, the value of $\epsilon^2=2.9037243763$ is higher than the value[2] of $\epsilon^2=2.903724375$ obtained from a *sparse* determinant of order 1078, and Schwartz's value[4] of $\epsilon^2=2.90372437616$ obtained from a *full* determinant of order 189, in which were included the nonconventional terms $s^{l/2}$, $l=0, 1, 2, \cdots$.

We interpret the manifestly rapid convergence of the eigenvalues shown in Table II as evidence supporting the reality of the logarithmic terms in the exact solution of the wave equation (1).

An indication of the accuracy of the wave functions can be obtained from the degree to which they satisfy conditions (8). This is shown in Table III. It will be noticed that the improvement with increasing order n of the determinant is not uniform.

TABLE III. The degree to which the coefficients C_1 and C_2 in Eq. (7) satisfy the relations $C_1-\frac{1}{2}k=-Z$, and $C_2=\frac{1}{2}$, which follow from (1).

	$Z \diagdown n$	29	59	101	170	246
$C_1-\frac{1}{2}k$	1	−0.9360	−1.0181	−1.0011	−1.0013	−0.9987
	2	−1.9918	−1.9997	−1.9995	−1.9992	−1.9992
	3	−2.9998	−3.0016	−2.9996	−2.9916	−2.9892
	4	−4.0488	−3.9979	−3.9985	−3.9932	−3.9877
C_2	1	0.4001	0.5852	0.5459	0.5163	0.5010
	2	0.5171	0.5161	0.5033	0.4992	0.4998
	3	0.5128	0.5078	0.5003	0.4981	0.4992
	4	0.5163	0.5078	0.4993	0.4976	0.4990

The influence of the radical $(s^2+t^2)^{1/2}$ in the expansion (11) is shown in Table IV, which gives the eigenvalues ϵ^2 when this radical is omitted. It is seen, by comparison with Table II, that without the radical the ϵ^2 values are poorer for comparable orders n of the determinant.

TABLE IV. Values of the energy parameter ϵ^2 for $Z=2$, when the term $(s^2+t^2)^{1/2}$ in the expansion (11) is dropped.

n	ϵ^2
43	2.9037239
73	2.903724345
121	2.9037243745
174	2.90372437687
Extrpl.	2.903724377066

When we use the same representation (10), (11) to get the second root for the 2^1S states, the results are not appreciably better than those obtained by method B from the conventional perimetric representation[2,3]; similarly for the antisymmetrical solution for the 2^3S

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[18] For a determinant of order 29 we get $\epsilon^2=2.9037230$, which is close to the value $\epsilon^2=2.9037233$ of A. Ermolaev and G. Sochilin for $n=30$.

state. This would indicate that the logarithmic terms are significant mainly for the 1^1S states, where both electrons are close to the nucleus.

APPENDIX: EVALUATION OF THE INTEGRALS

In evaluating (12) with the representation (10) and (11), we have to compute integrals of the type

$$I=(n,m,l,i,j)$$

$$=\int_0^\infty s^n e^{-s}ds\int_0^s u^l du\int_0^u t^m(t^2+s^2)^{1/2}(\ln s)^j dt. \quad \text{(A1)}$$

Changing the order of integration, we have

$$I=\int_0^\infty e^{-s}s^n(\ln s)^j ds\int_0^s t^m(t^2+s^2)^{1/2}dt\int_t^s u^l du. \quad \text{(A2)}$$

Performing the integration over u, and putting $t=sx$ we obtain

$$I=\frac{1}{l+1}\int_0^\infty e^{-s}s^{n+l+i+m+2}(\ln s)^j ds$$

$$\times\int_0^1 x^m(1+x^2)^{i/2}(1-x^{l+1})dx. \quad \text{(A3)}$$

With

$$K(k,j)=\int_0^\infty e^{-s}s^k(\ln s)^j ds \quad \text{(A4)}$$

and

$$L(n,i)=\int_0^1 x^n(1+x^2)^{i/2}dx, \quad \text{(A5)}$$

(A3) becomes

$$I=[1/(l+1)]K(n+l+i+m+2,\,j)$$

$$\times[L(m,i)-L(m+l+1,\,i)]. \quad \text{(A6)}$$

Formula (A6) was actually used in the computation of the integrals. $K(k,j)$ and $L(n,i)$ were tabulated separately, and fetched from the fast memory.

Since

$$K(k,j)=(d^j/dk^j)\Gamma(k+1), \quad \text{(A7)}$$

we have the recursion relation

$$K(k,j)=kK(k-1,\,j)+jK(k-1,\,j-1), \quad \text{(A8)}$$

from which $K(k,j)$ can be computed if we know $K(1,j)$.

In order to evaluate $K(1,j)$ we first computed

$$S_n=\sum_{k=1}^\infty \frac{1}{k^n} \quad \text{(A9)}$$

to 40 decimals, using the Euler-Maclaurin summation formula. Since

$$d\Gamma(x)/dx=\Gamma(x)\Psi(x), \quad \text{(A10)}$$

we have

$$\Gamma^{(j)}(x)=\sum_{i=0}^{j-1}\binom{j-1}{i}\Gamma^{(j-i-1)}(x)\Psi^{(i)}(x), \quad \text{(A11)}$$

yielding for $x=2$

$$\Gamma^{(j)}(2)=\sum_{i=0}^{j-1}\binom{j-1}{i}\Gamma^{(j-i-1)}(2)\Psi^{(i)}(2). \quad \text{(A12)}$$

Equation (A12) gives a recursion relation for $\Gamma^{(j)}(2)$, if we know $\Psi^{(i)}(2)$. But

$$\Psi^{(j)}(2)=(-)^j(1-S_{j+1}), \quad \text{(A13)}$$

with S_1 equal to Euler's constant.

The integrals $L(n,i)$ defined in (A5) were also obtained from recursion relations. Putting $x^2=z$ in (A5) we get

$$L(n,i)=(\tfrac{1}{2})\int_0^1 z^{(n-1)/2}(1+z)^{i/2}dz, \quad \text{(A14)}$$

or

$$(i+2)L(n,i)=-4\times 2^{i/2}+(i+n+1)L(n,\,i+2), \quad \text{(A15)}$$

$$(i+n+1)L(n,i)=4\times 2^{i/2}-(n-1)L(n-2,\,i). \quad \text{(A16)}$$

We have

$$L(0,0)=\tfrac{1}{2},\quad L(0,1)=\tfrac{1}{2}[\sqrt{2}+\ln(1+\sqrt{2})], \quad \text{(A17)}$$

$$L(1,0)=\tfrac{1}{2},\quad L(1,1)=\tfrac{1}{3}(2\sqrt{2}-1), \quad \text{(A18)}$$

from which all the $L(n,i)$ with $i\geqslant 0$ can be computed by (A15) and (A16). For negative values of i the procedure is similar.