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Logarithmic Terms in the Wave Functions of the 2^1S and 2^3S States of Two-Electron Atoms

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Following our previous attempt to analyze the convergence rate of variational calculations for the ground state of two-electron atoms, the nonconventional terms $\ln(r_1+r_2)$ and $[\ln(r_1+r_2)]^2$ were inserted into the 2^1S and 2^3S states, with the proper exponentials. The convergence of the energy eigenvalues seems to indicate that logarithmic terms are important in these states also.

INTRODUCTION

IN a previous paper,[1] we concluded that when logarithmic terms are included to find the second root for the 2^1S states, the results obtained by conventional representation do not appreciably improve. The author felt that better results can be obtained by satisfying the proper asymptotic behavior for large r_1 and r_2 as well as the singular behavior around the origin. So in addition to the logarithmic terms, the proper exponential terms were included in the expansions.

METHOD OF SOLUTION

The author carried out calculations using the Hylleraas variational form as in the previous paper, namely, the scaled variables s, t, u:

$$s=r_1+r_2,\qquad t=r_2-r_1,$$

$$u=r_{12},\qquad \psi(s,u,t)=e^{-s/2}\phi(ks,ku,kt),$$

and

$$\phi=\sum_{n,l,m,j}C(n,l,m,j)s^nt^lu^mf(tc)(\ln s)^j,$$

where $f(tc)$ is the hyperbolic sine or cosine, depending on the parity of l and the symmetry of the state. We used the same selection rules as before for the arrangement of the indices n, l, m, and j; allowing n to be negative. Terms involving $(s^2+t^2)^{1/2}$ were excluded because of the lack of an efficient numerical algorithm for handling the corresponding integrals. Without these terms the natural grouping is $p=19$, 47, 98, and 174. A sample of indices for $p=19$ is shown in Table. I.

The constants c and k were computed to two decimal places only, in such a way as to optimize the energy value E for the determinant of order 19. When we checked these values later for higher-order determinants, we found that up to two decimals c and k do not change, and that higher-order approximations are insensitive to small changes in c and k, with the exception of $Z=1$, in which c and k had to be optimized further. The constants c and k are given in Table II.

TABLE I. The ordering of indices for determinant $p=19$.

p	n	l	m	j
1	0	0	0	0
2	0	0	1	0
3	0	1	0	0
4	1	0	0	0
5	0	0	2	0
6	0	1	1	0
7	0	2	0	0
8	1	0	1	0
9	1	1	0	0
10	2	0	0	0
11	−1	0	2	0
12	−1	1	1	0
13	−1	2	0	0
14	0	0	2	1
15	0	1	1	1
16	0	2	0	1
17	1	0	1	1
18	1	1	0	1
19	2	0	0	1

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[1] K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966).

TABLE II. Values of parameters c and k.

	Z	1	2	3	4	5	6	7	8	9	10
Para	c	0.87	0.49	0.41	0.37	0.35	0.34	0.33	0.33	0.33	0.32
	k	0.52	0.64	0.68	0.70	0.71	0.72	0.72	0.73	0.73	0.73
Ortho	c	0.88	0.53	0.43	0.38	0.37	0.36	0.35	0.35	0.34	0.34
	k	0.55	0.67	0.69	0.70	0.71	0.72	0.72	0.73	0.73	0.73

TABLE III. Values of the energy parameter ϵ^2 in atomic units for various order of determinants, for para (2^1S).

$Z\backslash p$	19	47	98	174	Extrapolated.
1	0.499685	0.4997977	0.49988897	0.49991672	0.499921
2	2.145896	2.1459735	2.1459740383	2.1459740457	2.14597404582
3	5.040789	5.0408760	5.0408767177	5.0408767445	5.04087674575
4	9.184767	9.1848728	9.1848738573	9.1848738927	9.1848738944
5	14.578413	14.5785268	14.5785279950	14.5785280293	14.5785280305
6	21.221897	21.2220162	21.2220176420	21.2220176965	21.2220176992
7	29.115291	29.1154141	29.1154155764	29.1154157084	29.1154157257
8	38.258632	38.2587555	38.2587571540	38.2587572999	38.2587573191
9	48.651950	48.6520597	48.6520614719	48.6520616307	48.6520616514
10	60.295209	60.2953381	60.2953398511	60.2953400389	60.2953400688

RESULTS

Tables III and IV give energy eigenvalues ϵ^2 in atomic units (a.u.) for $Z=1$ to $Z=10$ for determinants up to order 174 for para, and up to order 98 for ortho. The values of 174 for ortho are not given because checks indicate that they are unreliable in single precision floating (about 14 decimal places on the CDC 6600) and their behavior does not differ enough to justify the cost of higher-precision evaluation.

Because of the slow rate of convergence for $Z=1$, 2^3S was also evaluated by a determinant of order[2] 174:

$$\epsilon^2(174)=0.49991526 \quad \text{and} \quad (\epsilon^2)_{\text{extr}}=0.499926.^2$$

All results for determinants of order 174 were checked in double precision (28 decimal figures).

It is interesting to compare the rate of convergence with the values obtained by Pekeris by method C (without logarithmic terms and with unequal exponents). For $Z=2$, 2^1S state, the determinant of order 19 gives a lower energy value then Pekeris'[3] value with a determinant of order 56; $p=47$ is better than the extrapolated value (order over 220). However, in ortho states the improvement is smaller: $Z=2$, 2^3S state, $p=47$ compares with Pekeris'[3] value of about order 100 and $p=98$ is better than his extrapolated value (order over 220). The same is true for $Z=3$ (Pekeris[4]). In addition to this research the method was applied to higher excited states. The results from 3^1S up to 6^1S for $Z=2$ are given in Table V. Comparison of these results with Pekeris[3] shows that the expansions with logarithmic terms produce comparable number of eigenvalues as the expansions with conventional terms, but the former produce much higher accuracy. From these results it seems that the logarithmic terms are important even in excited states, but more important in para states, than in ortho.

TABLE IV. Values of the energy parameter ϵ^2 in atomic units for various order of determinants, for ortho (2^3S).

$Z\backslash p$	19	47	98	Extrapolated
1	0.499705	0.4998408	0.49989535	0.499932
2	2.175225	2.1752293	2.175229375	2.1752293785
3	5.110723	5.1107272	5.110727366	5.1107273713
4	9.297161	9.2971664	9.297166581	9.2971665867
5	14.733891	14.7338971	14.733897338	14.7338973467
6	21.420749	21.4207556	21.420755890	21.4207559003
7	29.357674	29.3576814	29.357681724	29.3576817350
8	38.544639	38.5446470	38.544647305	38.5446473180
9	48.981630	48.9816380	48.981638314	48.9816383270
10	60.668638	60.6686462	60.668646568	60.6686465820

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[2] The extrapolation is made on an assumption that the successive ratios of differences are nearly constant (which is true with the exception of $Z=1$), and uses the Pekeris formula [C. L. Pekeris, Phys. Rev. **112**, 1652 (1958)] for 4 terms and the Aitken scheme for 3 terms.

[3] C. L. Pekeris, Phys. Rev. **127**, 509 (1962).

[4] C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

TABLE V. The excited singlet S states of helium. Values of the nonrelativistic energy parameter ϵ^2 in atomic units; p denotes the order of the determinant; c and k, the exponent coefficients. Pekeris's (Ref. 3) values are given for comparison.

p	3^1S $c=0.68$ $k=0.61$	4^1S $c=0.77$ $k=0.55$	5^1S $c=0.82$ $k=0.55$	6^1S $c=0.84$ $k=0.54$
47	2.06127077	2.03358633	2.02117361	...
98	2.0612719785	2.0335866187	2.0211766540	2.01455842
174	2.0612719892	2.0335866982	2.0211767784	2.01456292
Extrap.	2.06127198933	2.033586728	2.0211767837	...
		Pekeris' values		
56	2.06113355	2.03345646	2.02106034	2.0144436
120	2.06122632	2.03353215	2.02112309	2.0145124
220	2.06125581	2.03356302	2.02115033	2.0145364
Extrap.	2.06127053	2.03358470	2.02117522	2.0145617

EVALUATION OF INTEGRALS

We compute the following integrals:

$$I=\int_0^\infty s^n e^{-s}\ln^j s ds \int_0^s u^l du \int_0^u t^m e^{ct} dt,$$

or

$$I=\int_0^\infty s^n e^{-s}(\ln s)^j ds \int_0^s t^m e^{ct}\left(\frac{s^{l+1}-t^{l+1}}{l+1}\right) dt;$$

putting $t=sx$,

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

$$\times\int_0^1 x^m \exp(c\cdot sx)(1-x^{l+1})dx,$$

$$I=(l+1)^{-1}\int_0^1 x^m(1-x^{l+1})dx$$

$$\times\int_0^\infty s^{m+n+l+2}\exp[-s(1-cx)](\ln s)^j ds,$$

or

$$I=(l+1)^{-1}\sum_{\rho=0}^{j}\binom{j}{\rho}K(k,j-\rho)(-)^\rho$$

$$\times\int_0^1\frac{\ln^\rho(1-cx)[x^m-x^{m+l+1}]dx}{(1-cx)^{k+1}},$$

where

$$k=n+m+l+2,\qquad K(k,j)=\int_0^\infty \exp(-s)s^k(\ln s)^j ds.$$

Call

$$L(a,k,n,j)\equiv\int_0^1\frac{x^n[\ln(1+ax)]^j dx}{(1+ax)^{k+1}}.$$

Then

$$I=(l+1)^{-1}\sum_{\rho=0}^{j}\binom{j}{\rho}(-)^\rho[L(-c,k,m,\rho)$$

$$-L(-c,k,m+l+1,\rho)]K(k,j-\rho).$$

Since in this scheme $0\leq j\leq 4$, this formula is very convenient to use in the computations. For a given a, the $L(a,k,n,j)$ and $K(k,j)$ were computed and stored in fast memory. Since

$$L(a,k,n,j)=(-)^j(\partial^j/\partial k^j)[L(a,k,n,0)],$$

recurrence relations were used. First

$$L(a,0,0,j)=\int_0^1\frac{[\ln(1+ax)]^j}{1+ax}dx=\frac{\ln^{j+1}(1+a)}{a(j+1)}$$

was computed; then two recurrence relations for $L(a,k,n,0)$ were differentiated j times with respect to k to produce the needed three-dimensional relations.

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