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PHYSICAL REVIEW A VOLUME 6, NUMBER 5 NOVEMBER 1972

Hylleraas-Type Wave Functions for Some Excited Three-Electron *S* States[*]

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(Received 10 April 1972)

The usefulness of Hylleraas-type wave functions for variational calculation of three-electron excited *S* states is investigated. The four lowest $(1s^2ns)\,^2S$ wave functions for lithium are obtained in the same 57-term basis. The calculated energies are $-7.477\,82$, $-7.353\,92$, $-7.318\,37$, and $-7.303\,39$ a.u. compared to the corrected experimental results $-7.478\,07$, $-7.354\,10$, $-7.318\,53$, and $-7.303\,55$ a.u. The largest part (0.000 15 a.u.) of the discrepancies is due to approximations in the core function. For the lowest ^4S state for lithium a 44-term basis was used with the resulting energy $-5.212\,40$. The wave function was analyzed in terms of natural orbitals and found to exhibit strong $2s3s$-$2p3p$ "near degeneracy." The density for the Li state is significantly correlation contracted in the $3s$ region.

I. INTRODUCTION

Variational trial functions with explicit dependence on the interelectronic distance coordinates were introduced by Hylleraas for the He atom.[1] These kinds of wave functions were also used for the lithium ground state,[2] the H_2 molecule[3] and the metastable $\mathrm{He}^-\,^4p^o$ state.[4] Later applications using electronic computers for two-electron[5–7] and three-electron[8–11] atomic ions, the Be ground state,[12–14] and the hydrogen molecule[15] have demonstrated their usefulness for these systems. Hylleraas (Hy) expansions have also been used in the calculation of Bethe-Goldstone-type pair functions in the many-electron theory of atoms and molecules.[12,16,17]

For two-electron atomic ions the original approach of Hylleraas with non-negative powers of r_{12}, r_1+r_2, and r_1-r_2 has been extended to more complicated types of trial functions by Kinoshita,[18] Pekeris,[19] Schwartz,[20] Ermolaev and Sochilin,[21] Frankowski and Pekeris,[22] and others. Contrary to Hy expansions these different methods would lead to very difficult integrals in variational calculations for three or more electrons or in pair function calculations. It is therefore important to keep the Hy form when improving the basis sets. For the two-electron ground state this can be done by choosing some large parameters in the exponent, as is demonstrated in Sec. III.

The $(1s^2ns)\,^2S$ states have been calculated earlier by Öhrn and Nordling [9] and Perkins.[11] The wave functions of Öhrn and Nordling were essentially of the form

$$\psi(1,2,3)=A_3\{\phi(1,2)\varphi(3)\}\,. \qquad (1)$$

φ was optimized by variation of the exponential parameters in a three-term basis, whereas ϕ was taken to be a Hy-type function with only one fixed exponential parameter. In this paper we will instead optimize the core function by variation of the exponential parameters of a four-term Hy-type basis. This optimization is carried out for Li^+. The basis for φ is chosen rather large to make possible a description of four valence orbitals. In addition core-valence correlation is included in an efficient way. This calculation is described in Sec. IV.

The $^4S^e$, $^4P^o$, $^4P^e$ states have been calculated by Holøien and Geltman using only even powers of r_{ij}.[8] The cusp conditions of the Coulomb hole are of no importance in this case since all electrons have the same spin. The Coulomb hole exists then only as a slight modification of the Fermi hole, which has a flat bottom.[23] Benefitting from the simplification obtained when using only even powers of r_{ij}, Holøien and Geltman were able to calculate many states and contribute to the identification of spectral lines for transitions between quartet terms. Here only the lowest state is calculated without any variation of the exponent parameters.

To see how correlation affects charge densities and one- and two-particle expectation values for a state of this kind the ^4S wave function has been analyzed in terms of natural spin orbitals (NSO).[24] A method was used, which was developed in connection with the $(1s^2 2s)\,^2S$ state.[25] For comparison purposes some excited two-electron S states are analyzed also. This is done in Sec. V.

II. WAVE FUNCTIONS

The two-electron wave functions are of the form

$$\psi = \sum\nolimits_\nu c_\nu A_2[\phi_\nu(\vec{r}_1, \vec{r}_2)(\alpha\beta \pm \beta\alpha)] \,,$$
$$\phi_\nu(\vec{r}_1, \vec{r}_2) = r_1^i r_2^j e^{-ar_1 - br_2} r_{12}^k \,, \tag{2}$$
$$A_2 = e - (12) \,.$$

The plus sign in the spin function is used for triplet functions and the minus sign for singlet functions.

The three-electron wave functions for the ^2S states are of the form

$$\psi = \sum\nolimits_\nu A_3[\phi_\nu(\vec{r}_1, \vec{r}_2, \vec{r}_3)(c_{1\nu}S_1 + c_{2\nu}S_2)] \,,$$
$$\phi_\nu(\vec{r}_1, \vec{r}_2, \vec{r}_3) = r_1^i r_2^j r_3^k e^{-ar_1 - br_2 - cr_3} r_{23}^l r_{13}^m r_{12}^n \,, \tag{3}$$
$$A_3 = e - (12) - (13) - (23) + (123) + (132) \,,$$
$$S_1 = \alpha\beta\alpha - \beta\alpha\alpha \,; \quad S_2 = 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha \,.$$

Usually $C_{2\nu}$ is chosen to be zero. This does not affect the completeness.[10] On the other hand, including the term with S_2, i.e., allowing $C_{2\nu} \neq 0$, does not lead to the calculation of any new integrals. In the present calculations for the $(1s^2 ns)\,^2S$ states only one spin function is used ($C_{2\nu} = 0$). For the ^4S wave functions we use the spin function $S_3 = \alpha\alpha\alpha$.

The nonrelativistic Hamiltonian for three electrons can be written, using Hartree atomic units,

$$\mathcal{H} = \sum_{i=1}^{3} \left(-\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \frac{1}{u_i} \right) \,, \tag{4}$$
$$u_1 = r_{23} \,, \quad u_2 = r_{13} \,, \quad u_3 = r_{12} \,.$$

The kinetic part can be transformed[26,27,10]

$$\sum_{i=1}^{3} \nabla_i^3 = \sum_{i=1}^{3} \left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} + 2\frac{\partial^2}{\partial u_i^2} + \frac{4}{u_i} \frac{\partial}{\partial u_i} \right)$$
$$+ \sum_P \left(\frac{r_i^2 + u_k^2 - r_j^2}{u_k r_i} \frac{\partial^2}{\partial r_i \partial u_k} \right)$$
$$+ \sum_P \frac{1}{2} \frac{u_i^2 + u_k^2 - u_j^2}{u_i u_k} \frac{\partial^2}{\partial u_i \partial u_k} \,. \tag{5}$$

No terms with more than one r_{ij} factor at a time have been used. These are necessary for a complete basis[25] but have proved to be of little importance for the energy.[9]

III. TWO-ELECTRON IONS

In calculations using Hy-type functions it has been noted that with $a = b$ in Eq. (2), the best value of a will increase as the number of terms in the expansions is increased.[5,28] Bartlett *et al.*,[29] Fock,[30] and others have pointed out that the exact wave function cannot be expressed in a Hy series with only one exponential parameter. The value of $\| H\psi - E\psi \|$ will be infinite at $r_1 = 0$, $r_2 = 0$, and $r_{12} = 0$. It then seems justified to try Hy terms with large exponent factors and high powers of r_{12} to gain flexibility near these points. In Table I such an attempt is demonstrated. Terms 1–21 are ordinary Hy-type functions with a constant exponent parameter, $a = b = 1.80$ for He and $a = b = 2.70$ for Li^+. In the following exponent parameters multiplied by 2 and 4 have been included also. The energy after 39 terms (Table II) is better than that of Kinoshita who also used 39 terms. The result is, however, somewhat worse than that of Davidson using 44 terms[28] of which 10 were of Kinoshita type. It should be mentioned, however, that the large exponent parameters are chosen rather arbitrarily. It is quite possible that a shorter expansion can be obtained using other combinations of powers and exponential parameters.

In applications to the n^2S states it was desirable to have as short an expansion as possible for the $1s^2$ core. For that purpose the exponent parameters were varied in a four-term expansion. One exponent parameter was varied at a time. When the procedure had converged rather well an energy -7.27976 a.u. was obtained. Five more functions were added and the exponent parameters of these terms were varied while those of the first four were kept fixed. The energy was then -7.27987 compared to the accurate result -7.27991.[19] It is thus possible to get a good result with only a few basis functions of Hy type. On the other hand, if these

TABLE I. Basis for ^1S ground state, two electrons ($a = Zx$; $b = Zy$).

No.	(ijk)	x	y
1–21	(000), (100), (200), (110), (210), (220), (001), (101), (201), (111), (211), (221), (002), (102), (202), (112), (212), (222), (300), (301), (003)	0.9	0.9
22–25	(000), (001), (002), (003)	0.9	1.8
26–29	(000), (001), (002), (003)	0.9	3.6
30–32	(400), (401), (004)	0.9	0.9
33–36	(000), (001), (002), (003)	1.8	1.8
37	(004)	0.9	1.8
38	(004)	0.9	3.6
39	(004)	1.8	1.8
40–45	(310), (103), (311), (302), (203), (113)	0.9	0.9
46–50	(000), (001), (002), (003), (004)	1.8	3.6

TABLE II. Energies for ^1S ground states, two electrons.

No. of terms	$-E$ (a.u.) He	$-E$ (a.u.) Li$^+$
21	2.903 702	⋯
25	2.903 7157	⋯
29	2.903 7180	⋯
32	2.903 7185	7.279 9023
36	2.903 7225	7.279 9096
39	2.903 7234	7.279 9115
45	2.903 7237	7.279 9122
50	2.903 7239	7.279 9125
Kinoshita (Ref. 18)	2.903 7225	⋯
Davidson (Ref. 28)	2.903 7239	⋯
Pekeris (Ref. 19)	2.903 7244	7.279 9134

terms are used in longer expansions to get very good accuracy, it is very difficult to choose effective new basis functions. Also one easily runs into hidden linear dependencies.

IV. $1s^2ns$ STATES

The four-term Li$^+$ basis for the core function is combined with a flexible valence basis for φ [Eq. (1)]. It is expected that Slater-type functions $re^{-r/2}$, $r^2e^{-r/3}$, $r^3e^{-r/4}$, and $r^4e^{-r/5}$ will be rather good, at least for 3*s*, 4*s*, and 5*s*. To these we add functions with a somewhat higher exponent parameter to be able to describe the core-penetrating 2*s* orbital and improve the description of the other orbitals. Since it is known that the function $re^{-0.65r}$ is very suitable for the 2*s* orbital we chose parameters as fractions of 1.3; thus, we add $re^{-1.3r/2}$, $r^2e^{-1.3r/3}$, $r^3e^{-1.3r/4}$, and $r^4e^{1.3r/5}$. To these we add $e^{-1.5r}$ to get additional flexibility in the core (Table III). The energies given by these $4\times(4+4+1)=36$ basis functions are already rather good and superior to those of Öhrn and Nordling. The ionization energies can be obtained by subtracting the Li$^+$ energy of the four-term function. The differences are close to the Hartree-Fock (HF) virtual orbital energies for Li$^+$.

In terms 37–44 core-correlation terms have been introduced. Terms with large n and small c have been included to account for eventual core-valence correlation for the $(1s^24s)$ and $(1s^25s)$ states. In the set of core-valence-correlation terms 48–55, some terms with large n and small c were originally included, but since they lead to very little energy decrease for all states they were deleted. Terms 45–47 are included to improve the valence orbital description. Terms 56 and 57 could be interpreted as either core correlating or core-valence correlating. It was found in the Li$^+$ calculation, however, that the term (010 2.7 1.9) does not improve the energy of the four-term function. Further, if two terms were added (Nos. 58 and 59) where the valence orbital corresponded to 3*s* and 4*s*, no energy increment was obtained for the $(1s^23s)$ and $(1s^24s)$ states. This ought to be the case if we were dealing with core correlation. Thus, none of the terms added after No. 44 improve the core part of the wave function. It, therefore, seems justified to add the remaining energy error in the Li$^+$ function ($=-1.54\times10^{-4}$ a.u.). The results then obtained (Table IV) are in good agreement with spectroscopic results corrected for relativistic effects, the mass polarization, and the Lamb shift.[31,32]

The ionization energies are given in Table V. As we see, the HF energies are quite close for the ^2S states, particularly for the excited ones, but not for the ^4S state. This shows that the ^2S states

TABLE III. Basis functions for the $(1s^2ns)^2S$ states.

No.	$(ijklmn\ a\ b\ c)$
1–36	$(00n000\ \ 2.181\ \ 3.640\ \ c)$, $(11n000\ \ 2.605\ \ 3.400\ \ c)$, $(00n001\ \ 2.879\ \ 3.030\ \ c)$, $(00n002\ \ 2.810\ \ 4.620\ \ c)$; $(n\ \ c)=(0\ \ 1.5)$, $(1\ \ 0.65)$, $(2\ \ 0.43)$, $(3\ \ 0.33)$, $(3\ \ 0.25)$, $(4\ \ 0.26)$, $(4\ \ 0.20)$
37–44	$(00n100\ \ 2.7\ \ 2.7\ \ c)$; $(n\ \ c)=(0\ \ 0.65)$, $(1\ \ 0.38)$, $(2\ \ 0.28)$, $(3\ 0.22)$, $(0\ \ 1.2)$, $(1\ \ 0.65)$, $(2\ \ 0.38)$, $(3\ \ 0.28)$
45–47	$(00n000\ \ 2.7\ \ 2.7\ \ c)$; $(n\ \ c)=(1\ \ 1.3)$, $(2\ \ 0.65)$, $(0\ \ 0.65)$
48–50	$(000200\ \ 2.7\ \ 2.7\ \ c)$; $c=1.5$, 0.65, 0.9
51–54	$(01n100\ \ 2.7\ \ 2.7\ \ c)$; $(n\ \ c)=(0\ \ 0.65)$, $(1\ \ 0.38)$, $(0\ 0.9)$, $(0\ \ 1.5)$, $(0\ \ 0.65)$
55	$(010100\ \ 2.7\ \ 1.9\ \ 0.65)$
56–57	$(011000\ \ 2.7\ \ 1.9\ \ 1.5)$, $(011000\ \ 2.7\ \ 1.9\ \ 0.65)$
58–59	$(012000\ \ 2.7\ \ 1.9\ \ 0.35)$, $(013000\ \ 2.7\ \ 1.9\ \ 0.27)$

TABLE IV. Energies $-E$ (a.u.) for $(1s^2ns)$ wave functions. The line after 59 shows the result after -1.54×10^{-4} a.u., representing the error of the core function, has been added.

No. of terms	n = 2	3	4	5
36	7.476 019	7.353 548	7.318 231	7.303 328
40	7.477 211	7.353 783	7.318 315	7.303 368
44	7.477 303	7.353 819	7.318 331	7.303 375
47	7.477 503	7.353 858	7.318 345	7.303 382
55	7.477 681	7.353 897	7.318 360	7.303 389
57	7.477 819	7.353 917	7.318 366	7.303 392
59	7.477 819	7.353 917	7.318 366	7.303 392
+ core error	7.477 973	7.354 071	7.318 520	7.303 546
expt. (Refs. 31 and 32)	7.478 069	7.354 099	7.318 530	7.303 550
Perkins (Ref. 11)	⋯	7.353 5	7.317 5	⋯
Öhrn, Nordling (Ref. 9)	7.4760	7.352 7	7.314 2	⋯

TABLE V. Ionization energies $-E$(a.u.) obtained in this paper compared to HF energies and experimental ionization energies (Ref. 34).

	^2S 2*s*	3*s*	4*s*	5*s*	^4S 3*S*
HF	0.196 30[a]	0.073 80[a]	0.038 47[a]	0.023 51[a]	0.095 11[b]
This paper	0.198 06	0.074 16	0.038 61	0.023 63	0.101 67
Expt.	0.198 15	0.074 19	0.038 62	0.023 64	⋯

[a] The virtual Li$^+$ orbital energies are taken.

[b] Orbital energy for ^4S state, in this case very close to the difference between the HF total energies for $(1s2s3s)$ ^4S and $(1s2s)$ ^3S for Li$^+$.

TABLE VI. Basis functions and successive energies for the lowest ${}^4S$ state ($a=3.0$, $b=1.07$, $c=0.38$) compared to results from other methods.

No.	*ijklmn*	$-E$ (a.u.)	No.	*ijklmn*	$-E$ (a.u.)
1	012000	5.190 709	26	112001	5.211 725
2	112000	5.191 181	27	032000	5.211 735
3	212000	5.191 215	28	014000	5.211 744
4	002000	5.200 593	29	011100	5.211 982
5	022000	5.201 969	30	012003	•••
6	011000	5.202 930	31	022100	5.212 014
7	010000	5.203 077	32	012200	5.212 014
8	013000	5.203 931	33	202000	5.212 016
9	001000	5.204 228	34	033000	5.212 018
10	000000	5.204 240	35	001200	5.212 167
11	123000	5.204 245	36	002002	5.212 168
12	021000	5.204 251	37	042000	5.212 169
13	012001	5.205 249	38	001300	5.212 325
14	012100	5.208 349	39	011010	5.212 326
15	012010	5.208 356	40	001400	5.212 381
16	001100	5.211 277	41	011020	5.212 382
17	023000	5.211 283	42	004000	5.212 385
18	003000	5.211 396	43	001500	5.212 392
19	102000	5.211 396	44	011200	5.212 396
20	122000	5.211 400	HF (this paper)		
21	111000	5.211 400			5.204 454
22	113000	5.211 402	Holøien, Geltman (Ref. 8)		
23	012002	5.211 616			5.211 05
24	012001	5.211 651	Expt. (Ref. 34)		5.203 ± 0.011
25	312000	5.211 653			

to a much larger degree than the ${}^4S$ state has the structure of a Li$^+$ core surrounded by a valence orbital which is very little penetrating into the core and very little affected by correlation. For the ${}^2S$ states the correlation correction to the density is with certainty largest for the ground state where it is at most 2%.[33]

V. LOWEST ${}^4S$ STATE

A. Wave Function

The basis functions and energies are given in Table VI. On the Slater parameters were used in the exponentials, i.e., 3.0, 1.07, and 0.38. As can be seen, terms which particularly correlate the 2s and 3s electrons contribute much. The energy obtained is somewhat better than the result of Holøien and Geltman. The latter made an extensive variation of the exponential parameters in a set with thirty basis elements, of which ten had one r_{ij} to an even power.

TABLE VII. Occupation numbers of ${}^4S$ ground state.

s type	0.999 773(K), 0.953 495(M) 0.953 314(L), 0.000 014(LM), 0.000 003(KL), 0.000 002, 0.000 001
3x p-type	0.046 514(L), 0.046 371(M) 0.000 211(KL), 0.000 059(KLM), 0.000 022 (KLM), 0.000 001
5x d-type	0.000 089(L), 0.000 083(M), 0.000 008(KL), 0.000 003(KL)
Sum, $s+p+d$	2.999 964

TABLE VIII. Occupation numbers for excited Li$^+$ states (for each occupation number there correspond two NO; for singlets, one of each spin).

State	Type	Occupation numbers	Sum
	s	0.561 236, 0.438 205, 0.000 138, 0.000 004	
2^1S	$p(3x)$	0.000 279, 0.000 108, 0.000 004	0.999 995
	$d(5x)$	0.000 017, 0.000 004	
	s	0.530 071, 0.469 741, 0.000 039, 0.000 001	
3^1S	$p(3x)$	0.000 092, 0.000 047, 0.000 001	0.999 996
	$d(5x)$	0.000 003, 0.000 001	
	s	0.999 779, 0.000 002	
2^3S	$p(3x)$	0.000 211	0.999 999
	$d(5x)$	0.000 007	
	s	0.999 959	
3^3S	$p(3x)$	0.000 038	0.999 999
	$d(5x)$	0.000 002	

B. Natural Analysis

The occupation numbers and characteristics of NSO are given in Table VII. The largest occupation number belongs to an NO localized in the K shell. Since this occupation number is close to unity it can be expected that the NO of its cogeminal is very close to the NO of the total wave function. The former are degenerate in pairs since the spatial part of the geminal is antisymmetric in $\vec{r}_1$ and $\vec{r}_2$.[35] As can be seen in Table VII the second and third s-type NO and the first two of p and d type are paired. The occupation numbers of the p pair are comparatively large. We have here an example of an $ss' \rightarrow pp'$ "near degeneracy,"[36] in this case for electrons with the same spin. The spin is, however, not essential for this kind of correlation, since it is of long-range type rather than of cusp

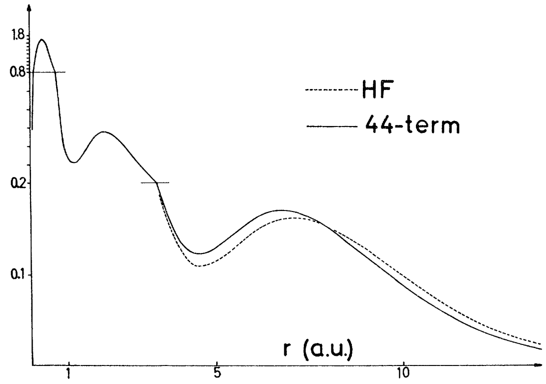

FIG. 1. Actual radial density distribution for ${}^4S$ state of lithium compared to the HF result. Note changes of scale.

type. The $ss' \rightarrow dd'$ correlation is rather weak. The two d orbitals are localized to the L and M shells just like the two p orbitals. The small probability of d-type compared to p-type correlation is, of course, due to the high kinetic energy of the L-shell d orbital.

Of the remaining occupation numbers some have the same size as the Li^{+} ^3S occupation numbers (Table VIII), and the corresponding NO are also similar. This is also the case for the ^2S ground state.[25,33] In this case some of the occupation numbers for p-type natural spin orbitals (NSO) are of the same size as those for the Li$^+$ ground state and the others of the same size as those for the 2^1S and 2^3S states. The occupation numbers and NSO thus have transferability properties to a certain extent.

The strongly occupied NSO are more localized than the corresponding Hartree-Fock (HF) orbitals. An ns HF orbital has $n-1$ nodes and the excited ones have "bumps" in the inner-shell region (on a radial density distribution plot). The K-shell NO is similar to HF $1s$. The NO with second largest occupation number is localized almost completely to the M shell, whereas the NO with third largest occupation number has a large peak in the L shell and two very small peaks in the K and M regions.

The density has been plotted in Fig. 1. There is almost no contraction compared to HF in the K and L shells but a significant one in the M shell. For comparison the $1s^22s$ state showed a contraction in the valence region[28] of at most 2% in the radial density distribution, a difference which is just big enough to be visible in a diagram.

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*Research supported by Statens Naturvetenskapliga Forskningsråd (the Swedish Natural Science Research Council).

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