

Hylleraas-type calculations of the ground states of the Li isoelectronic sequence through $Z = 8$

J. F. Perkins

U.S. Army Missile Command, Redstone Arsenal, Alabama 35809

(Received 24 September 1975)

Hylleraas-type (HT) expansions, containing correlation factors of the form r_{ij}^p , have been used to calculate ground states of the Li isoelectronic sequence. A maximum of 30 expansion terms was used with a common set of exponential parameters for all terms in a particular calculation. The ordering of expansion terms was roughly optimized, so that the expansions can be truncated at various lengths to give suitable approximations. About 15 terms of the present HT expansions give results comparable to those of Weiss's 45-term configuration-interaction calculations. For the Li ground state the present 30-term result is poorer than results of other more extensive calculations which include HT expansion terms.

Several types of expansions have been used in variational calculations which account for electron correlation effects in atomic wave functions associated with stationary, quasistationary, and scattering states. These include the configuration-interaction (CI) method, Hylleraas-type (HT) methods, and a combination of the two (CIHT).

An extensive set of CI calculations of the ground states of several members of the He, Li, and Be isoelectronic series was performed by Weiss,¹ who pointed out the relatively slow convergence of the CI method as compared to HT calculations. The HT method has been extensively applied to two-electron systems.² Complexities involved in HT calculations increase rapidly with the number of electrons, but HT calculations have been performed for ${}^3\text{-}^{10}\text{Li}$ and Be.¹¹⁻¹⁶

Extensive calculations of the Li ground state were carried out by Larsson⁵ and by Sims and Hagstrom.¹⁰ The Be ground state has been calculated to high precision by Sims and Hagstrom^{13,16} with the CIHT method; the r_{ij}^p correlation factors of the HT approach are especially well suited to treating the $1s^2$ core, while CI-type expansions are evidently satisfactory for the outer shell. It appears that very few HT or CIHT calculations have been carried out for other members of the Li or Be isoelectronic sequences. Öhrn and Nordling⁴ have treated the Li sequence using HT terms for the core electrons only.

The work reported herein is a set of HT calculations, for expansion lengths up to 30, of the ground states of the Li isoelectronic sequence through $Z = 8$.

Since the calculations are limited to 2S states, it suffices to limit attention to the spatial part of the wave function which is associated with the $\uparrow\uparrow$ spin function. The Pauli principle is satisfied

by antisymmetrizing on electrons one and three. Each expansion term has the form

$$(1 - P_{13})(1 + P_{12})r_1^m r_2^n r_3^t r_{23}^\lambda r_{31}^\mu r_{12}^\nu e^{-\alpha r_1 - \beta r_2 - \gamma r_3},$$

where at most one of the parameters λ , μ , ν is allowed to be nonzero in a given expansion term. Symmetrizing on electrons one and two ensures that the overall function has doublet character; since α and β were assigned a common value it was not necessary to carry out this symmetrization explicitly for all terms. Evaluation of the requisite matrix-element integrals was carried out by methods described previously.⁷ Computations were performed with a CDC-6600 computer.

The selection of expansion terms was made for the Li ground state, with the goal of approximately optimizing the choice and ordering of terms; the same sequence of terms (except for values of exponential parameters) was then used for other members of the isoelectronic sequence. On the basis of previous experience⁷ and the desire for simplicity, a common set of exponential parameters was used for all terms in a particular calculation. The exponential parameters were not explicitly optimized but were chosen for Li on the basis of past experience^{5,7} and were incremented for increasing values of Z in a simple manner related to screening arguments. Tests performed for $Z = 3$ and 8 indicated that a carefully optimized choice of exponential parameters would not substantially improve the energies obtained with 30-term expansions.

As a preliminary step, HT calculations of the Li^+ ground state were performed and an approximately optimized ordering of two-electron expansion terms was obtained. This ordering was then used as a guide in the initial choice of order-

TABLE I. Expansion terms.

No.	$mnl\lambda\mu\nu$	No.	$mnl\lambda\mu\nu$
1	001000	16	201001
2	001001	17	001003
3	111000	18	311001
4	201000	19	221001
5	000010	20	100010
6	001002	21	002001
7	111001	22	000001
8	000000	23	201002
9	002000	24	200000
10	101000	25	200020
11	200010	26	113000
12	000020	27	110000
13	003000	28	101003
14	211001	29	004000
15	001004	30	001010

ing of expansion terms for the Li ground state. The Li expansion terms (prior to symmetrization) were formed by merely multiplying the previously chosen two-electron functions by $e^{-\gamma r_3}$ and various functions such as r_3^t ($t=0, 1, 2, 3, 4$), r_{23} , r_{23}^2 , $r_3 r_{23}$.

Several orderings of terms were then tested until a roughly optimized one was found. The effects of certain expansion terms are nonadditive, and as a result the energy improvements resulting from each successive term do not necessarily decrease monotonically. The expansion terms are listed in Table I.

Table II lists results of the present calculations for several expansion lengths and also shows results of other calculations for comparison. Only 15 or less HT terms are sufficient to give convergence as good as the 45-term CI results.¹ The present 30-term HT results for Li, however, are not as well converged as other more extensive HT and CIHT calculations. For most expansion lengths up to the maximum of 30 treated here, the present Li results are better than or close to results of equal-length expansions as reported by Larsson,⁵ though this probably is merely a result of the fact that Larsson presumably did not attempt to optimize the ordering of expansion terms. From the present work it appears that convergence becomes quite slow beyond 30 terms or so, and this seems to be consistent with results of others.

TABLE II. Calculated energies $-E$ (a.u.) for ground states of the Li isoelectronic sequence.

No. of expansion terms	Z	3	4	5	6	7	8
	$\alpha=\beta$	2.80	3.80	4.80	5.80	6.80	7.80
	γ	0.65	1.15	1.65	2.15	2.65	3.15
5		7.474 19	14.314 14	23.399 43	34.726 59	48.294 50	64.102 74
10		7.476 99	14.323 34	23.422 87	34.773 50	48.374 66	64.226 11
15		7.477 64	14.324 03	23.423 53	34.774 12	48.375 25	64.226 68
20		7.477 81	14.324 32	23.423 91	34.774 58	48.375 77	64.227 25
25		7.477 88	14.324 49	23.424 23	34.775 04	48.376 35	64.227 94
30		7.477 93	14.324 57	23.424 36	34.775 22	48.376 57	64.228 19
Exact ^a		7.478 07	14.324 79	23.424 71	34.775 73	48.377 28	64.229 17
Weiss ^b		7.477 10	14.323 50	23.423 12	34.773 84	48.375 09	64.226 61
Onello <i>et al.</i> ^c				23.421 45	34.773 16	48.374 92	64.226 72
Öhrn and Nordling ^d		7.4760	14.3183	23.4164	34.7654	48.3652	64.2160
Larsson ^e		7.478 02					
Larsson ^f		7.477 82					
Sims and Hagstrom ^g		7.478 02					

^a Taken from Ref. 1.

^b 45-term CI, Ref. 1.

^c 58-term $1/Z$ expansion, Ref. 17.

^d Five HT terms for core, uncorrelated expansion for $2s$ orbital, Ref. 4.

^e 100-term HT, Ref. 5.

^f 57-term HT, four lowest 2S states treated with same basis set, Ref. 8.

^g 150-term CIHT, four lowest 2S states treated with same basis set, Ref. 10.

- ¹A. W. Weiss, Phys. Rev. 122, 1826 (1961); Astrophys. J. 138, 1262 (1963).
- ²For a recent paper listing references to two-electron HT calculations, see Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A 11, 1479 (1975). In the interest of brevity, no attempt is made here to list references to the rather extensive literature on two-electron HT calculations.
- ³H. M. James and A. S. Coolidge, Phys. Rev. 49, 688 (1936).
- ⁴Y. Öhrn and J. Nordling, Ark. Fys. 31, 471 (1966).
- ⁵S. Larsson, Phys. Rev. 169, 49 (1968).
- ⁶S. Larsson and E. A. Burke, Phys. Rev. 184, 248 (1969).
- ⁷J. F. Perkins, Phys. Rev. A 5, 514 (1972).
- ⁸S. Larsson, Phys. Rev. A 6, 1786 (1972).
- ⁹T. Ahlenius and S. Larsson, Phys. Rev. A 8, 1 (1973).
- ¹⁰J. S. Sims and S. A. Hagstrom, Phys. Rev. A 11, 418 (1975).
- ¹¹L. Szasz and J. Byrne, Phys. Rev. 158, 34 (1967).
- ¹²R. F. Gentner and E. A. Burke, Phys. Rev. 176, 63 (1968).
- ¹³J. S. Sims and S. Hagstrom, Phys. Rev. A 4, 908 (1971).
- ¹⁴J. F. Perkins, Phys. Rev. A 8, 700 (1973).
- ¹⁵J. S. Sims and R. C. Whitten, Phys. Rev. A 8, 2220 (1973).
- ¹⁶J. S. Sims and S. A. Hagstrom, Int. J. Quantum Chem. IX, 149 (1975).
- ¹⁷J. S. Onello, L. Ford, and A. Dalgarno, Phys. Rev. A 10, 9 (1974).