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Improved Hylleraas Calculations for Ground State Energies of Lithium Iso–electronic Sequence

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Abstract

The ^2S ground state of lithium iso–electronic sequence is calculated by the use of Hylleraas-type wave functions. A 92 term one-spin wave function was used for lithium atom calculations. The energy obtained was −7.478031 a.u. as compared with the previous best value of −7.478025 a.u. calculated by Larsson. In addition, improved energies for $Z = 4$ to 8 were calculated by the use of 60 term wave functions. This work thus provides the lowest *ab initio* ground state energies for lithium sequence to date.

1. Introduction

Hylleraas-type (HT) wave functions containing r_{ij} factors have been widely used in atomic physics involving both electrons and positrons to represent the correlation effects between electrons and/or between electrons and positrons for bound and scattering states. On the electron side Larsson [1] used a 100-term Hylleraas-type wave function to calculate the ground state of Li atoms. Sims and Hagstrom [2] combined the Hylleraas-type wave functions and configuration interaction type wave functions (CIHT) to calculate the Li and Be ground state energies. The ground states of Li iso–electronic sequence have been calculated by Perkins [3]. In atomic systems involving positrons Houston and Drachman [4], Page and Fraser [5], and Ho [6] have used HT wave functions to calculate the binding energy of the positronium hydride (a diatomic molecule consisting of a positronium atom and a hydrogen atom). Drachman et al. [7] have investigated the possible attachment of positrons to the helium atoms in the ^3S state. Clary used [8] CIHT wave functions to investigate the binding of positrons to two and three electron atoms and ions. In the positron–helium scattering problem HT wave functions have been employed to represent the closed channel part of the wave function [9–11]. A resonant state (quasibound state) of positronium hydride has been calculated by using HT wave functions [6, 12] together with the method of complex rotation [13].

The use of HT wave functions have led to quite accurate results in various branches of atomic physics. Recently, Bunge [14] estimated the nonrelativistic ground state energy of Li atoms from an experimental value and concluded that the convergence of Larsson's calculation is quite slow. In addition, Bunge commented that for an assessment of convergence of the Li Fermi contact term,

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higher numerical precision might be necessary. It is felt, therefore, that Larsson's work should be extended. This paper reports an improved Hylleraas calculation on the Li sequence including the ground state of Li atoms, and thus provide results which are believed to be the best *ab initio* calculation to date.

2. Calculations and Results

Since the ground state wave functions of Li sequence are of $^2S_{1/2}$ type, it is sufficient to use one spin wave function as follows:

$$\psi = A \Sigma C_i r_1^l r_2^m r_3^n r_{23}^p r_{13}^q r_{12}^s e^{-ar_1 - br_2 - cr_3}(\alpha_1\beta_2\alpha_3 - \beta_1\alpha_2\alpha_3) \tag{1}$$

where α and β are the standard notations for spin up and spin down, respectively, and A is the antisymmetrizer for three electron systems

$$A = 1 - (12) - (13) - (23) + (123) + (132). \tag{2}$$

It should be mentioned that Larsson used a two spin wave function for the ground state of Li. The advantage of using two spin wave functions is that no new integrals are involved when the second spin wave function is introduced. The advantage of using one spin wave function, as will be shown later in the text, is that we can obtain a better energy by solving an eigenvalue problem with a smaller dimension.

The best way to investigate the convergence behaviour of the energy is to include all the possible positive (or zero) integers for l, m, n, etc., in Eq. (1). However, such an approach may not be economically practical. Larsson used a method of trial and error to determine the most effective basis set such that the convergence rate was the fastest. In the present calculation, the first 60 terms (shown in Table I) are the same as those of Larsson. However, the nonlinear parameters of Eq. (1) ($a = b = 2.80$ and $c = 0.65$) are those of Perkins, which were optimized using 30-term wave functions. With a 60-term wave function the present work shows the energy obtained by the Perkins parameters is -7.478011 a.u., a value of 1×10^{-6} a.u. lower than Larsson's -7.478010 a.u. Consequently, the Perkins parameters are used throughout this work. It should be mentioned that for numerical check Larsson's parameters ($a = b = 2.76$ and $c = 0.65$) are employed and energies calculated from the first 60 terms are reproduced.

The necessary integrals involved in this work are solved using the method of Perkins [15], and some numerical examples have been published elsewhere [16]. Most integrals have led to exact results suitable for mechanine computations except for the integrals in which the powers of the three interelectronic coordinates are all odd. In those cases an infinite series must be involved and the present work is programmed in such a way that the series is terminated only after a convergence of 12 significant figures is obtained. This compares with the 10 significant figures used in Larsson's work. The higher standard of numerical accuracy will be useful for investigations of the Fermi-contact term of Li atoms.

TABLE I. Expansion terms for the wave function [see Eq. (1)].

No.	ℓmnpqs	No.	ℓmnpqs	No.	ℓmnpqs
1	001000	21	000200	41	101003
2	101000	22	000110	42	110000
3	111000	23	020100	43	112000
4	201000	24	110100	44	200000
5	001001	25	004000	45	202000
6	001002	26	000001	46	100001
7	000000	27	002001	47	102001
8	000100	28	100000	48	200001
9	002000	29	102000	49	021100
10	010100	30	000101	50	030100
11	001003	31	010200	51	201003
12	001100	32	011100	52	005000
13	003000	33	000300	53	211000
14	101001	34	001200	54	001006
15	301000	35	001005	55	302000
16	001004	36	401000	56	300000
17	221000	37	401001	57	000400
18	111001	38	501000	58	100100
19	201001	39	101002	59	311000
20	301001	40	201002	60	301002

Table II shows the energies for Li atoms together with the wave functions used. The selection of basis functions is done mainly by trial and error. Five basis are added, at a time, to the existing wave function of N terms. A program is written such that the contribution from each of these five terms out of the $N + 5$ term wave function is tested. Terms which give small contributions will not be used for further consideration. This procedure differs slightly from the one used by Larsson in which only one term was tested at a time. These procedures, of course, are not rigorous since terms which have small contributions at an earlier stage may have larger contributions at a later time. Up to a total of 92 terms are used in this work and result is compared with previous calculations (see Table III). It is seen that the present work provides the lowest energy to date, a value of −7.478031 a.u. It should be mentioned that the use of one spin wave function will not affect the completeness of the wave function [1]. The

TABLE II.   Energies of Li atoms for various numbers of basis functions ($\alpha = \beta = 2.8$, $\gamma = 0.65$).

No.	ℓmnpqs	-E(a.u.)	No.	ℓmnpqs	-E(a.u.)
61	211001	7.478015	77	020300	7.478024
62	311001	7.478015	78	020400	7.478024
63	411001	7.478016	79	020500	7.478024
64	113000	7.478016	80	211002	7.478024
65	114000	7.478017	81	211003	7.478025
66	115000	7.478017	82	211004	7.478027
67	101004	7.478019	83	211005	7.478027
68	101005	7.478019	84	211006	7.478028
69	101006	7.478019	85	020600	7.478028
70	010300	7.478020	86	030300	7.478028
71	010400	7.478021	87	030400	7.478028
72	010500	7.478021	88	030500	7.478028
73	010600	7.478022	89	040200	7.478028
74	000500	7.478022	90	040300	7.478029
75	000600	7.478023	91	040400	7.478029
76	020200	7.478023	92	000201	7.478031

advantage of using one spin wave function is that one can obtain the same energy by solving an eigenvalue problem with smaller dimension. For example, Table II shows that a wave function of 81 terms leads to a result of −7.478025 a.u. the value obtained by Larsson who solved an eigenvalue problem with a dimension of 100. The use of smaller dimension eigenvalue equations would

TABLE III.   Ground state energy of Li atoms.

Author	Method	Energy
		-E(a.u.)
present	92-term Hylleraas	7.478031
Larsson [1]	100-term Hylleraas	7.478025
Sims and Hagstrom [2]	150-term Hylleraas configulation interaction	7.478025
Exact [14]		7.478073

reduce the cost of selecting the best basis terms, and the round off errors for solving eigenvalue problems are also minimized.

This work also provides an improved calculation for the ground state energies of Li iso–electronic sequence for $Z = 4$ to $Z = 8$. The results are shown in Table IV and they are obtained by the use of the first 60 terms in the trial wave function (see Table I). The nonlinear parameters are the same as Perkins [3]. The results, with no surprise, are lower than those of Perkins since the present

TABLE IV. Ground state energies of Li isoelectronic sequence (calculated by the use of 60 term wave functions).

					-E(a.u.)	
Z	a	b	c	present	Perkins [3]	Exact [17]
4	3.80	3.80	1.15	14.324696	14.32457	14.32479
5	4.80	4.80	2.65	23.424523	23.42436	23.42471
6	5.80	5.80	2.15	34.775418	34.77522	34.77573
7	6.80	6.80	2.65	48.376798	48.37657	48.37728
8	7.80	7.80	3.15	64.228435	64.22819	64.22917

work employs larger expansion sets, and hence provides the lowest *ab initio* energies to date. It is seen, however, that the energies are still considerably different from the exact values [17]. It indicated that the convergence is quite slow, and it may also indicate that the nonlinear parameters, obtained by multiplying appropriated screen factors for high Z ions, may not be the optimized values for energy calculations. No attempt is made, however, in this work to optimize the nonlinear parameters either.

3. Summary and Discussion

The present work provides improved calculations for the ground state energies of Li iso–electronic sequence by the use of Hylleraas-type wave functions. It is seen that the present values are lower than previous calculations. However, they are still quite far away from the non-relativistic estimations. These indicate that the convergence of energy is very slow. Several approaches to improve the speed of convergence are hence worthwhile to try. For example, more terms like Nos. 22 and 92, for which the interparticle coordinate indices *pqs* are allowed to be nonzero simultaneously, should be tested. This of course would require longer computer time since the integrals involved are quite cumbersome. The second approach to increase the speed of convergence is to employ an asymptotic wave function like the one used in H⁻ calculation [18]. Since Li atoms are also loosely

bound species, it is expected that the convergence would improve considerably if asymptotic wave functions are used. It is anticipated that more work on Li energy will be done, and the improved wave functions would then be used to investigate the convergence behaviour of the Fermi-contact term for Li atoms.

Acknowledgment

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