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# Eigenvalues and expectation values for the $1s^2 2s^2 S$ , $1s^2 2p^2 P$ , and $1s^2 3d^2 D$ states of lithium

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High-precision variational eigenvalues for the  $1s^2 2s^2 S$ ,  $1s^2 2p^2 P$ , and  $1s^2 3d^2 D$  states of lithium are calculated using multiple basis sets in Hylleraas coordinates. Convergence to a few parts in  $10^{10}$ – $10^{11}$  is achieved. The nonrelativistic energies for infinite nuclear mass are  $-7.478\,060\,323\,10(31)$  a.u. for the  $1s^2 2s^2 S$  state,  $-7.410\,156\,521\,8(13)$  a.u. for the  $1s^2 2p^2 P$  state, and  $-7.335\,523\,541\,10(43)$  a.u. for the  $1s^2 3d^2 D$  state. The corresponding specific isotope shifts due to mass polarization are also calculated with similar accuracy. The  $1s^2 2s^2 S$ – $1s^2 2p^2 P$  and  $1s^2 2p^2 P$ – $1s^2 3d^2 D$  transition energies for  ${}^7\text{Li}$  and  ${}^6\text{Li}$ , as well as the isotope shifts, are calculated and compared with experiment. The results yield an improved ionization potential for lithium of  $43\,487.167(4)$   $\text{cm}^{-1}$ . Expectation values of powers of  $r_i$  and  $r_{ij}$  and the delta functions  $\delta(\mathbf{r}_i)$  and  $\delta(\mathbf{r}_{ij})$  are evaluated.

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## I. INTRODUCTION

Lithium, a three-electron atomic system, is the simplest atom with both an open and a closed shell. Lithium also serves as a prototype for other alkali-metal atoms. Among the various computational methods, the variational method in Hylleraas coordinates is particularly powerful in handling complex correlation effects between electrons. Though profound advances have been made in the variational calculation of energies for helium and heliumlike ions [1–3], only a few high-precision calculations for lithium are available. King and Shoup [4] calculated the  ${}^2S$  ground-state energy of lithium using a 352-term Hylleraas-type wave function. King also extended his calculation to the lithium isoelectronic sequences for the ground state and some excited  $S$  states [5]. Due to their use of fixed nonlinear parameters, and perhaps because of problems of near linear dependence in their basis set, the ground-state energy obtained is accurate to only a few parts in  $10^6$ . A significant improvement was made recently by McKenzie and Drake [6], who used a multiple basis set method in the construction of their variational wave function in Hylleraas coordinates. With up to 1134 terms in the basis set, the nonrelativistic eigenvalue of the ground state was improved to an accuracy of one part in  $10^9$ . This work also resolved a long-standing discrepancy with experiment. A combination of configuration interaction (CI) with a Hylleraas-type method was used by Pipin and Bishop [7] in their calculations of the energies for the  $2^2S$ ,  $2^2P$ , and  $3^2D$  states of lithium. With about 1500 terms in their basis sets, they also similarly improved the nonrelativistic ground-state energy and obtained the lowest-energy bounds for the  $2^2P$  and  $3^2D$  states. Lüchow and Kleindienst [8] recently calculated the lithium ground-state energy to a precision of about one part in  $10^8$ , as well as some excited  $S$ -state energies, using the variational method in Hylleraas coordinates. Instead of optimizing the nonlinear parameters, they optimized the dimension of basis sets with the purpose of reducing the size of the basis set to a minimum without significant loss of accuracy. A less accurate method is the full core plus correlation CI calculation of Chung *et al.* [9].

One of the main obstacles in lithium calculations in Hylleraas

coordinates is the difficulty of calculating integrals with several interelectronic distances in the integrand. These integrals converge very slowly in general, that ultimately leads to calculations which are extremely time consuming. Thus a complete optimization of the nonlinear parameters for a large basis set, which is indispensable in obtaining the lowest eigenvalues and is important in avoiding problems of near linear dependence in the basis set, is not an easy task. We have recently discovered an asymptotic expansion method to deal with these slowly convergent integrals [10]. This method has proven to be very successful in accelerating the rate of convergence and thus it removes a major obstacle to further progress. Large-scale variational calculations in Hylleraas coordinates can now be done not only for  $S$  states, but also for non- $S$  states of lithium and lithiumlike ions. The details will be presented elsewhere [10].

The purpose of this paper is to present the results of variational calculations using multiple basis sets in Hylleraas coordinates. The structure of the basis sets is first discussed in Sec. II. The variational eigenvalues are presented in Sec. III, together with the finite mass corrections and estimates of the relativistic and QED shifts. These are then compared with experiment for both the transition frequencies and isotope shifts, and an improved value for the ionization potential of lithium is obtained. Finally, high-precision expectation values for a number of other operators are presented.

## II. CONSTRUCTION OF WAVE FUNCTIONS

The basis set is constructed from the terms

$$\begin{aligned} \phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = & r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} \\ & \times e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \mathcal{Y}_{(l_1 l_2) l_3}^{LM}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi_1, \end{aligned} \quad (1)$$

where

$$\begin{aligned} \mathcal{Y}_{(l_1 l_2) l_3}^{LM} &= r_1^{l_1} r_2^{l_2} r_3^{l_3} \sum_{m_i} \langle l_1 m_1; l_2 m_2 | l_1 l_2; l_3 m_3 \rangle \langle l_1 l_2; l_3 m_3 | LM \rangle Y_{l_1 m_1}(\mathbf{r}_1) \\ &\quad \times Y_{l_2 m_2}(\mathbf{r}_2) Y_{l_3 m_3}(\mathbf{r}_3) \end{aligned} \quad (2)$$

denotes a vector-coupled product of spherical harmonics for the three electrons to form a state of total angular momentum  $L$  and

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \quad (3)$$

is the spin function with the spin angular momentum  $1/2$ , where the indices 1, 2, 3 label the three electrons. Our work shows that the exclusion of the second linearly independent spin function does not affect the final convergence of energy eigenvalues. In (1), the  $\mathcal{Y}_{(l_1 l_2) l_3}^{LM}$  functions include the lowest powers of  $r_1$ ,  $r_2$ , and  $r_3$  in order to ensure correct behavior of the wave function as  $r_i \rightarrow 0$ . The variational wave function is a linear combination of the functions  $\phi$  antisymmetrized by the three-particle antisymmetrizer

$$\mathcal{A} = (1) - (12) - (13) - (23) + (123) + (132). \quad (4)$$

For a given angular momentum  $L$ , the angular coupling for the three electrons is

$$(l_1, l_2, l_3) = (0, 0, 0)_A \text{ for } S \text{ states,}$$

$$(l_1, l_2, l_3) = (0, 0, 1)_A \text{ (0, 1, 0)}_B \text{ for } P \text{ states,}$$

$$(l_1, l_2, l_3) = (0, 0, 2)_A \text{ (0, 1, 1)}_B \text{ for } D \text{ states, etc.}$$

The inclusion of block  $(0, 1, 0)_B$  in the  $P$  state basis sets, which describes the core polarization, is crucial in obtaining adequate convergence. For small basis sets, the gain is barely detectable. However, it becomes essential when the basis sets become large. With only block  $(0, 0, 1)_A$  included, the energy eigenvalue apparently converges to an incorrect value  $-7.410\,136\,34$  a.u., even if the size of the basis set becomes as large as 1500 terms. A similar situation has also been found in two-electron variational calculations [1] when the mass polarization operator is included explicitly in the Hamiltonian. This illustrates that experiments with small basis sets may lead to conclusions that are incorrect as basis sets become large. It also illustrates the need to search for all potentially important classes of terms. In the case of the  $P$  states, the  $(0, 0, 1)_A$  and  $(0, 1, 0)_B$  terms differ only in their exponential scale factors. Although either set by itself becomes asymptotically complete in the limit of infinite basis sets, a finite sequence of calculations may give a false impression of convergence to an energy that is too high. Inclusion of just a few  $(0, 1, 0)_B$  terms for the  $P$  states has an immediate and dramatic effect for large basis sets. A systematic search for other possible such terms did not yield a fur-

ther significant lowering of the energy. However, this is by no means a proof that none exist, only that they were searched for and none found. In the case of the  $3^2D$  state, the inclusion of a  $(0, 2, 0)$  block does not change the pattern of convergence.

In generating the finite basis sets, all terms from (1) are nominally included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leq \Omega \quad (5)$$

and the convergence of the eigenvalues studied as  $\Omega$  is progressively increased. However, terms that may potentially cause near linear dependences should be excluded. For example, if  $l_1 = l_2$  and  $\alpha \approx \beta$ , then terms with  $j_1 > j_2$  should be omitted, as well as terms with  $j_1 = j_2$  when  $j_{23} > j_{31}$ . The presence of the near linear dependences in the basis set can be detected by diagonalizing the positive definite overlap matrix to see if there is an abnormally small or negative eigenvalue.

As in previous work [1,3,6], the total basis set is divided into sectors with different scale factors  $\alpha$ ,  $\beta$ , and  $\gamma$ . These are then separately optimized for each sector. This strategy dramatically improves the accuracy for a given total number of terms in the basis set. However, instead of simply duplicating the terms in each block and assigning independent scale factors as in the helium calculations [1,3], the first block  $(0, 0, L)_A$  is divided into five sectors according to correlations among the three electrons as follows:

$$\text{sector 1: all } j_{12}, \quad j_{23} = 0, \quad j_{31} = 0;$$

$$\text{sector 2: all } j_{12}, \quad j_{23} = 0, \quad j_{31} \neq 0;$$

$$\text{sector 3: all } j_{12}, \quad j_{23} \neq 0, \quad j_{31} = 0;$$

$$\text{sector 4: } j_{12} = 0, \quad j_{23} \neq 0, \quad j_{31} \neq 0;$$

$$\text{sector 5: } j_{12} \neq 0, \quad j_{23} \neq 0, \quad j_{31} \neq 0.$$

This yields significantly better results than the McKenzie-Drake [6] scheme, in which the basis set was partitioned according to the inequalities  $j_\lambda \leq j_\mu \leq j_\nu$  and  $j_{\lambda\mu} \leq j_{\lambda\nu} \leq j_{\mu\nu}$  for the six permutations of the labels  $(\lambda, \mu, \nu) = (1, 2, 3)$ . The present scheme has an obvious significance in terms of which correlations are contained in each sector. A complete optimization of the nonlinear parameters leads to a natural division of the basis set into these five sectors with quite different distance scales. Therefore, a complete optimization is important not only for improving the variational eigenvalues, but also for preserving the numerical stability of the wave function, especially when  $\Omega$  is large.

The complete basis sets thus contain five sectors for  $S$  states, and six sectors for  $P$  and  $D$  states when the  $(0, 1, 0)_B$  or  $(0, 1, 1)_B$  blocks are included. Finally, the size of each sector is separately controlled by assigning to each an  $\Omega_i$  value according to

$$\{\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5\} = \{\Omega, \Omega, \Omega, \Omega, \Omega\}, \quad L = 0$$

$$\{\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5, \Omega_6\} = \{\Omega, \Omega, (\Omega, 7)_{\min}, (\Omega, 7)_{\min}, (\Omega, 7)_{\min}, \Omega - 2\}, \quad L = 1$$

$$\{\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5, \Omega_6\} = \{\Omega, \Omega, \Omega, \Omega, \Omega, (\Omega - 2, 3)_{\min}\}, \quad L = 2,$$

TABLE I. Nonrelativistic energies for the  $1s^2 2s^2 S$ ,  $1s^2 2p^2 P$ , and  $1s^2 3d^2 D$  states of lithium, in atomic units.

$\Omega$	No. of terms	$E(\Omega)$	$R(\Omega)$
$1s^2 2s^2 S$			
2	18	-7.477 311 711 30	
3	50	-7.477 984 835 87	
4	120	-7.478 052 568 65	9.938
5	256	-7.478 059 384 23	9.938
6	502	-7.478 060 203 73	8.317
7	918	-7.478 060 310 46	7.678
8	1589	-7.478 060 321 56	9.611
$\infty$		-7.478 060 323 10(31)	
$1s^2 2p^2 P$			
2	19	-7.409 722 805 8	
3	55	-7.410 100 606 3	
4	138	-7.410 150 289 3	7.604
5	306	-7.410 155 458 5	9.611
6	622	-7.410 156 380 9	5.604
7	1174	-7.410 156 500 2	7.733
8	1715	-7.410 156 518 4	6.540
$\infty$		-7.410 156 521 8(13)	
$1s^2 3d^2 D$			
2	19	-7.335 271 380 14	
3	57	-7.335 484 754 84	
4	148	-7.335 520 359 81	5.993
5	340	-7.335 523 158 86	12.720
6	586	-7.335 523 488 10	8.502
7	1002	-7.335 523 534 71	7.064
8	1673	-7.335 523 540 35	8.253
$\infty$		-7.335 523 541 10(43)	

where  $(a, b)_{\min}$  denotes  $\min(a, b)$ . The resulting truncations of the basis set in the indicated sectors have been carefully studied to verify that they do not significantly affect the eigenvalue convergence pattern.

### III. RESULTS

#### A. Nonrelativistic eigenvalues

The nonlinear parameters are optimized by calculating analytically the derivatives

$$\frac{\partial E}{\partial \alpha} = 2 \left\langle \Psi \left| H \left| \frac{\partial \Psi}{\partial \alpha} \right. \right. \right\rangle - 2E \left\langle \Psi \left| \frac{\partial \Psi}{\partial \alpha} \right. \right\rangle, \quad (6)$$

where  $\alpha$  represents any nonlinear parameter,  $H$  is the Hamiltonian of lithium, and the normalization  $\langle \Psi | \Psi \rangle = 1$  is assumed. Newton's method is used to locate the zeros of the first derivatives. Provided the initial  $\alpha_i$ ,  $\beta_i$ , and  $\gamma_i$  are chosen close to a minimum, the procedure converges in a few iterations.

Table I lists the results for the nonrelativistic energies, together with a detailed account of the convergence process as the size of the basis set is enlarged. The ratio  $R(\Omega)$  is defined by

$$R(\Omega) = \frac{E(\Omega - 1) - E(\Omega - 2)}{E(\Omega) - E(\Omega - 1)}. \quad (7)$$

If  $R(\Omega)$  were a constant  $R$ , then the series would converge as a geometric series to the value

$$E(\infty) = E(\Omega_{\max}) + \frac{E(\Omega_{\max}) - E(\Omega_{\max} - 1)}{R - 1}. \quad (8)$$

The values of  $R$  listed in Table I are not constant, but they vary smoothly enough with  $\Omega$  to be useful in extrapolating the energies to the limit  $\Omega \rightarrow \infty$ . The extrapolations were done by assuming the functional form [1]

$$R(\Omega) = 1 + \frac{a}{\Omega^b} \quad (9)$$

and determining the parameters  $a$  and  $b$  by a least-squares fit to the tabulated values. The extrapolation converges for  $b < 1$ . For example, for the  $2^2 S$  state,  $a = 12.23$  and  $b = 0.238$  to give the extrapolated ( $\Omega = \infty$ ) result in Table I. In general, a tabulation of  $R(\Omega)$  provides a sensitive test of the quality of the calculation because imperfections in the optimization of the nonlinear parameters or numerical instabilities due to the existence of near linear dependence in the basis set cause these ratios to become erratic.

All the numerical calculations were performed on an IBM RISC/6000 350 workstation using double precision (approximately 16 decimal digits). For the  $2^2 S$  state, the CPU time for a complete calculation, including the calculation of all the derivatives, is about 5 h for the 1589-term basis set. However, as a check, the final calculations of wave functions and energies were done in quadruple precision (approximately 32 decimal digits).

The overall accuracy we have achieved for the nonrelativistic eigenvalues of lithium is a few parts in  $10^{11}$  for the  $2^2 S$  and  $3^2 D$  states and a few parts in  $10^{10}$  for the  $2^2 P$  state. A comparison with selected previous calculations in Table II shows the significant improvement that has been achieved. For example, our 306-term calculation for the  $2^2 P$  state is better than 1454-term CI-Hylleraas result of Pipin and Bishop [7]. The ground state energy obtained is about two orders of magnitude more precise than the best previous value of McKenzie and Drake [6]. As for the configuration interaction result of Jitrik and Bunge [20], their lower value is apparently an artifact of their extrapolation [6]. On the other hand, the method used by Chung *et al.* [9] for obtaining the  $2^2 P$  state energy cannot guarantee to yield an upper bound to the eigenvalue. Our results for  $2^2 P$  and  $3^2 D$  states have improved the best previous calculations of Pipin and Bishop [7] by about three orders of magnitude.

#### B. Finite mass corrections

In order to account for finite nuclear mass effects, we rescale the Hamiltonian according to  $r \rightarrow (m/\mu)r$  and include the mass polarization term explicitly in the Hamiltonian such that

$$H = -\frac{1}{2} \sum_{i=1}^3 \nabla_i^2 - Z \sum_{i=1}^3 \frac{1}{r_i} + \sum_{i>j}^3 \frac{1}{r_{ij}} - \frac{\mu}{M} \sum_{i>j}^3 \nabla_i \cdot \nabla_j, \quad (10)$$

in units of  $2R_M$ , where  $R_M = (1 - \mu/M)R_\infty$ , and  $\mu = mM/(m + M)$  is the electron reduced mass and  $M$  is the

TABLE II. Comparison with other calculations for the nonrelativistic energies of lithium, in atomic units. HR denotes the Hylleraas result.

Author	Method	$1s^2 2s^2 S$	$1s^2 2p^2 P$	$1s^2 3d^2 D$
Larsson [11]	100-term HR	-7.478 025		
Ahlenius and Larsson [12]	78-term HR		-7.409 99	
Sims and Hagstrom [13]	150-, 120-term CI-HR	-7.478 023	-7.410053	
Ahlenius and Larsson [14]	97-term HR		-7.410 078	
Muszyńska <i>et al.</i> [15]	139-, 120-term CI-HR	-7.478 044	-7.410 097	
Ho [16]	92-term HR	-7.478 031		
Pipin and Woźnicki [17]	170-term CI-HR	-7.478 044	-7.4101 06	
King and Shoup [4]	352-term HR	-7.478 058		
Kleindienst and Beutner [18]	310-term HR	-7.478 058 24		
King [5]	602-term HR	-7.478 059		
King and Bergsbaken [19]	296-term HR	-7.478 059 53		
Jitrik and Bunge [20]	Extrapolated CI	-7.478 062 4(7)		
Chung <i>et al.</i> [9]	Full core plus correlation	-7.478 059 7(9)	-7.410 157 8(9)	-7.335 5239
McKenzie and Drake [6]	1134-term HR	-7.478 060 326(10)		
Pipin and Bishop [7]	1618-term CI-HR	-7.478 060 1	-7.410 155 4	-7.335 5231
Lüchow and Kleindienst [8]	976-term HR	-7.478 060 25		
Tong <i>et al.</i> [21]	Extrapolated MCHF	-7.478 060 9	-7.410 153 1	
Present work		-7.478 060 323 10(31)	-7.410 156 521 8(13)	-7.335 523 541 10(43)

nuclear mass. This procedure in effect sums to infinity the perturbation series in  $\mu/M$ . The resulting total energies can be expressed in the form

$$E_M(\text{Li } 2^2S) = -7.478\,060\,323\,10(31) + 0.301\,842\,809(15) (\mu/M) - 1.500(72) (\mu/M)^2, \quad (11)$$

$$E_M(\text{Li } 2^2P) = -7.410\,156\,521\,8(13) + 0.246\,737\,81(71) (\mu/M) - 1.54(30) (\mu/M)^2, \quad (12)$$

$$E_M(\text{Li } 3^2D) = -7.335\,523\,541\,10(43) + 0.288\,928\,837(66) (\mu/M) - 1.361(99) (\mu/M)^2. \quad (13)$$

For  ${}^7\text{Li}$ ,  $\mu/M = 7.820\,203 \times 10^{-5}$ , and for  ${}^6\text{Li}$ ,  $\mu/M = 9.121\,677 \times 10^{-5}$ . The coefficient of  $\mu/M$  above is the expectation value of  $-\sum_{i>j}^3 \nabla_i \cdot \nabla_j$  calculated for infinite nuclear mass and the next coefficient is obtained by subtracting the term of  $\mu/M$  from the directly calculated total energy shift due to mass polarization. The corresponding result for the  $\text{Li}^+ 1^1S$  core is

$$E_M(\text{Li}^+ 1^1S) = -7.279\,913\,412\,669\,3 + 0.288\,975\,786\,393\,60 (\mu/M) - 1.277\,369\,3 (\mu/M)^2. \quad (14)$$

The nonrelativistic ionization energies are given by the differences between Eqs. (11)–(13) and Eq. (14).

### C. Comparison with experiment

Table III lists the  $2^2S-2^2P$  and  $2^2P-3^2D$  transition energies for  ${}^7\text{Li}$  and  ${}^6\text{Li}$  and the isotope shifts. Also included are estimates of the relativistic and QED shifts. High-precision values for the relativistic correction of  $O(\alpha^2)$  are

TABLE III. Comparison of the  $2^2S-2^2P$  and  $2^2P-3^2D$  transition energies for  ${}^7\text{Li}$  and  ${}^6\text{Li}$  and the isotope shifts, in units of  $\text{cm}^{-1}$ .

Contribution	$2^2S-2^2P$	$2^2P-3^2D$
	${}^7\text{Li}$	
$E_\infty$	14 903.161 76(29)	16 380.045 93(30)
$\mu/M$	-2.111 245(12)	-0.556 813(12)
$(\mu/M)^2$	0.000 02(41)	0.000 18(42)
$\alpha^2$ <sup>a</sup>	3.040(70)	-0.311(20)
$\alpha^3$ <sup>b</sup>	-0.30	0.045
Total	14 903.791(70)	16 379.223(20)
Experiment	14 903.871 689(10) <sup>c</sup>	16 379.204 4 <sup>d</sup>
Difference	-0.081(70)	0.019(20)
	${}^6\text{Li}$	
$E_\infty$	14 903.161 76(29)	16 380.045 93(30)
$\mu/M$	-2.462 608(14)	-0.649 480(14)
$(\mu/M)^2$	0.000 03(56)	0.000 25(58)
$\alpha^2$	3.040(70)	-0.311(20)
$\alpha^3$	-0.30	0.045
Total	14 903.439(70)	16 379.131(20)
Experiment	14 903.520 341(13) <sup>c</sup>	
Difference	-0.081(70)	
	Isotope shift	
${}^7\text{Li}-{}^6\text{Li}$	0.351 35(41)	0.092 60(42)
Experiment	0.351 348(16)	

<sup>a</sup>Reference [9] and present work.

<sup>b</sup>QED shift from Ref. [24].

<sup>c</sup>Reference [26].

<sup>d</sup>Reference [23].

TABLE IV. Expectation values of various powers of  $r_i$ ,  $r_{ij}$ , and the delta functions  $\delta(\mathbf{r}_i)$  and  $\delta(\mathbf{r}_{ij})$  for lithium. The subscript  $\infty$  stands for the infinite nuclear mass case and the subscript  $M$  stands for the finite nuclear mass case for  ${}^7\text{Li}$ . Units are  $a_0^n$  and  $(\mu/m)^{-n}a_0^n$  for these two cases, where  $n$  is the corresponding power and is  $-3$  for  $\delta(\mathbf{r}_i)$  and  $\delta(\mathbf{r}_{ij})$ ,  $a_0$  is the Bohr radius, and  $\mu/m=0.999\,921\,797\,97$ . Numbers in parentheses denote uncertainties in the final figures quoted.

Quantity	$1s^22s^2S$	$1s^22p^2P$	$1s^23d^2D$
$\langle r_i^{-2} \rangle_\infty$	30.240 965 15(25)	29.900 988 78(42)	29.869 480 81(66)
$\langle r_i^{-2} \rangle_M$	30.240 882 97(25)	29.900 892 57(42)	29.869 395 28(66)
$\langle r_i^{-1} \rangle_\infty$	5.718 110 883 61(13)	5.638 905 934 4(15)	5.487 098 963 82(21)
$\langle r_i^{-1} \rangle_M$	5.718 099 230 81(13)	5.638 905 200 7(15)	5.487 088 739 23(21)
$\langle r_i \rangle_\infty$	4.989 523 148 59(75)	5.871 364 34(18)	11.629 225 31(16)
$\langle r_i \rangle_M$	4.989 545 825 97(75)	5.871 203 46(18)	11.629 227 56(16)
$\langle r_i^2 \rangle_\infty$	18.354 614 517(72)	27.948 236 4(16)	126.532 360 8(15)
$\langle r_i^2 \rangle_M$	18.354 790 429(72)	27.946 521 2(16)	126.532 340 4(15)
$\langle r_{ij}^{-1} \rangle_\infty$	2.198 212 002 47(71)	2.096 404 780 42(65)	1.790 249 821 20(18)
$\langle r_{ij}^{-1} \rangle_M$	2.198 224 235 15(71)	2.096 441 151 23(65)	1.790 264 319 04(18)
$\langle r_{ij} \rangle_\infty$	8.668 396 813 4(36)	10.412 089 29(33)	21.865 558 89(32)
$\langle r_{ij} \rangle_M$	8.668 412 553 6(36)	10.411 746 02(33)	21.865 542 47(32)
$\langle r_{ij}^2 \rangle_\infty$	36.847 838 063(39)	56.049 467 7(44)	253.141 928 3(31)
$\langle r_{ij}^2 \rangle_M$	36.848 033 170(39)	56.045 890 6(44)	253.141 728 8(31)
$\langle \delta(\mathbf{r}_i) \rangle_\infty$	13.842 543(53)	13.676 064(17)	13.703 681(50)
$\langle \delta(\mathbf{r}_i) \rangle_M$	13.736 442(53)	13.676 014(17)	13.703 643(50)
$\langle \delta(\mathbf{r}_{ij}) \rangle_\infty$	0.544 329 0(37)	0.532 286 4(57)	0.533 728 3(50)
$\langle \delta(\mathbf{r}_{ij}) \rangle_M$	0.544 335 4(37)	0.532 291 6(57)	0.533 734 3(50)

not available. For the  $2^2S$  and  $2^2P$  states, the relativistic corrections to the ionization energies were taken from the restricted configuration-interaction calculations of Chung *et al.* [9], relative to a common  $\text{Li}^+(1s^2\,{}^1S)$  parent ion. However, the accuracy of their calculations is not clear since their result for the  $\text{Li}^+(1s^2\,{}^1S)$  ion was in error by  $-1.35\text{ cm}^{-1}$  ( $-6.16\text{ }\mu\text{a.u.}$ ) relative to the high-precision variational result of Pekeris [22]. This error cancels from the  $1s^22s^2S-1s^22p^2P$  transition frequency only if it remains the same when a  $2s$  or  $2p$  electron is added to form neutral lithium. If the cancellation is no better than 95%, then the relativistic correction to the  $2^2S-2^2P$  transition frequency is  $2.761+0.279=3.040\pm 0.07\text{ cm}^{-1}$ . Since Chung *et al.* [9] do not quote an uncertainty, our value of  $\pm 0.07\text{ cm}^{-1}$  should only be taken as a reasonable estimate. For the nonpenetrating  $3^2D_J$  state, the relativistic ionization energy can be simply estimated from the one-electron Dirac energy

$$\Delta E_{\text{rel}} = -\frac{\alpha^2 Z^4}{2n^3} \left( \frac{1}{j+1/2} - \frac{3}{4n} \right) \quad (15)$$

with  $Z=1$ . Thus

$$\Delta E_{\text{rel}}(3d_{5/2}) = -0.018\,036\text{ cm}^{-1},$$

$$\Delta E_{\text{rel}}(3d_{3/2}) = -0.054\,108\text{ cm}^{-1},$$

yielding the center of gravity average  $\Delta E_{\text{rel}}(3d) = -0.0325\text{ cm}^{-1}$ . For comparison, the spin-averaged relativistic shift for the  $1s3d\,{}^1D_2$  and  ${}^3D_J$  states of helium is accurately known to be  $-0.027\,785\,9\text{ cm}^{-1}$  [1]. We take the difference from  $\Delta E_{\text{rel}}(3d)$  of  $0.0047\text{ cm}^{-1}$  to be an upper limit on the uncertainty in  $\Delta E_{\text{rel}}(3d)$  since the closed-shell  $1s^2\,{}^1S$  core

in lithium makes Eq. (15) a better approximation than for helium. The  $3^2D_J$  fine-structure splitting is much more accurately predicted to be  $0.036\,07\text{ cm}^{-1}$  in comparison with the observed splitting of  $0.036\,01\text{ cm}^{-1}$  [23].

The QED corrections of order  $\alpha^3$  in Table III contain two parts. One is from a recent calculation by Feldman and Fulton [24] for the radiative corrections using a Hartree-Fock approximation. The numerical values are  $0.24\text{ cm}^{-1}$  for the  $2^2S$  state and  $-0.048\text{ cm}^{-1}$  for the  $2^2P$  state. However, these corrections are the radiative contributions not included in the Johnson-Blundell-Sapirstein calculations [25]. The remaining part of  $O(\alpha^3)$  included implicitly in [25] must also be taken into account. Explicitly, the full two-electron QED shift from the Araki-Sucher terms is

$$\Delta E_{L,2}^{\text{MD}}(nl) = \alpha^3 \left( \frac{164}{15} + \frac{14}{3} \ln \alpha \right) \Delta \delta(12)_{nl} - \frac{14}{3} \alpha^3 [Q(1s^2nl) - Q(1s^2)], \quad (16)$$

as calculated by McKenzie and Drake [6], where

$$\Delta \delta(12)_{nl} = \langle \delta(\mathbf{r}_{ij}) \rangle_{1s^2nl} - \langle \delta(\mathbf{r}_{12}) \rangle_{1s^2},$$

$$Q = (1/4\pi) \lim_{a \rightarrow 0} \langle r_{ij}^{-3}(a) + 4\pi(\gamma + \ln a) \delta(\mathbf{r}_{ij}) \rangle,$$

$\gamma$  is Euler's constant,  $a$  is the radius of a sphere about  $r_{ij}=0$  excluded from the integration, and a summation over  $i>j$  from 1 to 3 is assumed. The terms evaluated by Feldman and Fulton [24] are

TABLE V. Contributions to the ionization energy of  $\text{Li}(1s^2 2s^2 S)$ . Corrections are relative to  $\text{Li}^+(1s^2 1S)$ .

Contribution	Value (a.u.)
$E_\infty(1s^2 1S)$	-7.279 913 412 669 3
$-E_\infty(1s^2 2s^2 S)$	7.478 060 323 10(31)
$-\Delta E_{\text{Breit}}^a$	0.000 012 58(30)
$-\Delta E_{\text{finite mass}}$	-0.000 016 500 28(44)
$-\Delta E_{\text{QED}}^b$	-0.000 001 1
Total	0.198 141 89(30)
Ionization energy <sup>c</sup>	0.198 142 114(20)
Difference	-0.000 000 22(30)

<sup>a</sup>Reference [9].

<sup>b</sup>Reference [24].

<sup>c</sup>Revised value from Table IV.

$$\Delta E_{L,2}^{\text{FF}}(nl) = \alpha^3 \left( \frac{129}{15} - \frac{3\pi}{2} + \frac{14}{3} \ln \alpha \right) \Delta \delta(12)_{nl} - \frac{14}{3} \alpha^3 [Q(1s^2 nl) - Q(1s^2)]. \quad (17)$$

The difference of

$$\delta E_{L,2}(nl) = \alpha^3 \left( \frac{7}{3} + \frac{3\pi}{2} \right) \Delta \delta(12)_{nl} \quad (18)$$

must be added to their QED shift to find the total contribution of  $O(\alpha^3)$ . Numerical values for  $\langle \delta(\mathbf{r}_{ij}) \rangle_{1s^2 nl}$  are listed in Table IV, and from our variational calculations for  $\text{Li}^+(1s^2)$  state,  $\langle \delta(\mathbf{r}_{12}) \rangle_{1s^2} = 0.533 722 5a_0^3$ . Thus  $\delta E_{L,2}(2s) = 0.006 37 \text{ cm}^{-1}$  and  $\delta E_{L,2}(2p) = -0.000 863 \text{ cm}^{-1}$ . However, formula (3.15) of Ref. [24], which gives the  $1/Z$  expansion for  $\langle \delta(\mathbf{r}_{ij}) \rangle_{1s^2 2p}$ , cannot be used reliably for lower  $Z$  and their values based on Hartree-Fock wave functions are also of low accuracy. If we replace their values of  $\Delta \delta(12)_{nl}$  by the accurate ones from Table IV, the difference of

$$\alpha^3 \left( \frac{129}{15} - \frac{3\pi}{2} + \frac{14}{3} \ln \alpha \right) [\Delta \delta(12)_{nl} - \Delta \delta(12)_{nl}^{\text{DFF}}], \quad (19)$$

where DFF denotes their Hartree-Fock value, gives a further shift of  $0.008 45 \text{ cm}^{-1}$  for the  $2s$  state and  $0.004 13 \text{ cm}^{-1}$  for the  $2p$  state. Adding the two  $2s$ - $2p$  differences of  $-0.007 23 \text{ cm}^{-1}$  and  $-0.004 32 \text{ cm}^{-1}$  to their tabulated difference of  $-0.29 \text{ cm}^{-1}$  gives a final QED correction for the

TABLE VI. Estimate of the ionization energy for the ground state of lithium. Corrections are relative to  $\text{Li}^+(1s^2 1S)$ .

Contribution	Value (a.u.)
$E_\infty(1s^2 1S) - E_\infty(1s^2 3d^2 D)$	0.055 610 128 43(43) <sup>a</sup>
$-\Delta E_{\text{Breit}}(1s^2 3d^2 D)$	0.000 000 148(20) <sup>b</sup>
$-\Delta E_{\text{finite mass}}(1s^2 3d^2 D)$	-0.000 004 344 64(61) <sup>a</sup>
$E_{\text{exp}}(1s^2 3d^2 D) - E_{\text{exp}}(1s^2 2s^2 S)$	0.142 536 182 <sup>c</sup>
Total	0.198 142 114(20)

<sup>a</sup>Present work, including both normal and specific mass shifts.

<sup>b</sup>From the spin-averaged Dirac energy.

<sup>c</sup>From the experimental transition energies, using  $R_\infty = 109 737.315 709(18) \text{ cm}^{-1}$  [23].

$2^2S-2^2P$  transition frequency of  $-0.30 \text{ cm}^{-1}$ . For the  $3^2D$  state, the one-electron QED correction is only  $2.32 \times 10^{-6} \text{ cm}^{-1}$  and can be neglected.

High-precision measurements for the  $2^2S-2^2P$  transition frequency were performed recently by Sansonetti *et al.* [26]. The measurement for the  $2^2P-3^2D$  transition frequency is from Ref. [23]. For  $^7\text{Li}$ , the differences between theory and experiment in Table III are  $-0.081(70) \text{ cm}^{-1}$  and  $0.019(20) \text{ cm}^{-1}$  for these two transitions. These discrepancies reflect the limited accuracy assigned to the  $\alpha^2$  relativistic shifts from Ref. [9].

The  $^7\text{Li}$ - $^6\text{Li}$  isotope shift in Table III does not suffer from similar uncertainties since the pure  $\alpha^2$  relativistic correction cancels exactly and relativistic reduced mass and recoil corrections are only of order  $\alpha^2[(\mu/M)_{^6\text{Li}} - (\mu/M)_{^7\text{Li}}] \approx 1.5 \times 10^{-4} \text{ cm}^{-1}$ . The specific isotope shift therefore comes predominantly from the first-order term of  $O(\mu/M)$  in Eqs. (11)–(13), though the small second-order term of  $O((\mu/M)^2)$  is also important in bringing theory and experiment into agreement. This is indicated by the excellent agreement between theory and experiment for the  $2^2S-2^2P$  isotope shift.

#### D. The lithium ionization potential

An improved ionization energy for the  $2^2S$  ground state of lithium can now be obtained since the absolute ionization energy of the  $3^2D$  state can be calculated to an accuracy of  $\pm 0.004 \text{ cm}^{-1}$  or better and combined with the experimental  $2^2S-2^2P$  and  $2^2P-3^2D$  transition frequencies. The principal uncertainty is from the relativistic correction to the  $3^2D$  ionization energy. The result from Table IV corresponds to an ionization potential of  $43 487.167(4) \text{ cm}^{-1}$ . This agrees with, but is more accurate than, the values  $43 487.15(2) \text{ cm}^{-1}$  [27] and  $43 487.19(2) \text{ cm}^{-1}$  [28] obtained by direct extrapolation to the series limit. A more accurate value for  $\Delta E_{\text{rel}}(3d)$  would allow a corresponding improvement in the ionization potential.

The various theoretical contributions to the ionization potential are summarized in Table V. Since the nonrelativistic energies and finite mass correction are now well established, the difference of  $0.22 \mu\text{a.u.}$  probably comes from  $\Delta E_{\text{Breit}}$ . A more accurate calculation of this term is clearly necessary.

#### E. Other expectation values

Expectation values of  $r_i^n$  and  $r_{ij}^n$  for various values of  $n$ , as well as expectation values of  $\delta(\mathbf{r}_i)$  and  $\delta(\mathbf{r}_{ij})$ , are useful in testing the accuracy of other approximation methods such as CI or quantum Monte Carlo calculations [29,30]. The cases of  $\langle r_i^{-1} \rangle$  and  $\langle r_{ij}^{-1} \rangle$  may be quite accurate because these terms appear in the Hamiltonian and are determined in part by the virial theorem, but this is not the case for other values of  $n$ . Table VI lists high-precision expectation values for  $n$  in the range  $-2 \leq n \leq 2$  for  $r_i^n$  and in the range  $-1 \leq n \leq 2$  for  $r_{ij}^n$ , as well as expectation values for  $\delta(\mathbf{r}_i)$  and  $\delta(\mathbf{r}_{ij})$ . The corresponding results when the mass polarization is included in the Hamiltonian are also listed in Table VI. The matrix elements are defined by

$$\langle r_i^n \rangle = \left\langle \Psi \left| \sum_{i=1}^3 r_i^n \right| \Psi \right\rangle ,$$

$$\langle r_{ij}^n \rangle = \left\langle \Psi \left| \sum_{i=1}^3 \sum_{i>j}^3 r_{ij}^n \right| \Psi \right\rangle ,$$

with similar definitions for  $\langle \delta(\mathbf{r}_i) \rangle$  and  $\langle \delta(\mathbf{r}_{ij}) \rangle$ . For the  $2^2S$  state, the infinite nuclear mass results in Table VI agree with the previous calculations of King [5], but the expectation values have converged to several more significant figures, as indicated by the extrapolation uncertainties in parentheses. For the  $2^2P$  and  $3^2D$  states, expectation values of comparable accuracy are not available for comparison.

#### IV. SUMMARY AND CONCLUSIONS

With the use of an asymptotic expansion method for the evaluation of integrals, high-precision large-scale variational calculations using Hylleraas coordinates are now possible for the lithium atom and other three-electron systems with modest computing resources. Our calculations demonstrate that

the use of multiple basis sets greatly accelerates the rate of convergence. The complete optimization of the nonlinear parameters in the basis sets is important in maintaining the linear independence of the basis sets and thus preserving the numerical stability of the wave function. The nonrelativistic energies we have obtained are the lowest upper bounds to date. The extension of these results to the lithium isoelectronic sequence is currently under way.

Excellent agreement between theory and experiment for the  $^7\text{Li}$ - $^6\text{Li}$  isotope shift has been achieved and an improved value for the ionization potential obtained. The main source of error in the transition frequencies arises from matrix elements of the Breit interaction. Improvements here would allow more stringent tests of the QED terms and improved accuracy for the ionization potential. Work in this direction is in progress.

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