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Calculations on the ^2S ground state of the lithium atom

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Extensive variational calculations on the ^2S ground state of the lithium atom are reported. With use of a 352-term Hylleraas-type expansion, the nonrelativistic ground-state energy of ^2S Li I is determined to be $-7.478\,058$ a.u., which lies approximately 3 cm^{-1} above empirical estimates of the nonrelativistic ground-state energy. This variational upper bound to the ground-state energy is the lowest to our knowledge reported to date in the literature. A number of expectation values, including the individual energy terms, the Fermi-contact interaction, the electron density at the nucleus, and the moments $\langle r_i^n \rangle$, $n=1-3$, and $\langle r_{ij}^n \rangle$, $n=1,2$, are also evaluated. The general rates of convergence of the calculation are discussed. The role played by the two doublet spin eigenfunctions is examined, and the importance of including both of these functions for the accurate calculation of the Fermi-contact interaction is discussed.

I. INTRODUCTION

The purpose of this paper is to present the results of extensive variational calculations on the ^2S ground state of Li I. The lithium atom has been the focus of extensive computational studies, particularly at the post-Hartree-Fock level.[1-12] Despite these considerable efforts, the accuracy obtained for the ^2S ground state of Li, and other three-electron systems, is poor in comparison with the results obtained by Pekeris and co-workers for two-electron systems.[13-16] For helium, the nonrelativistic ground-state energy is known to be bounded below by 1 part in 10^9,[17] and a recent calculation has reported an upper bound converged to 1 part in 10^{13}.[18] The best currently available result for the nonrelativistic ground-state energy, E_{NR}, of the lithium atom is several orders of magnitude less accurate than results available for two-electron systems. The most accurate calculations of E_{NR} for ^2S Li are the 100-term Hylleraas wave function of Larsson,[4] the 92-term Hylleraas wave function of Ho,[10] and the 170-term configuration-interaction Hylleraas wave function of Pipin and Woźnicki.[11]

The present investigation was undertaken with several goals in mind. In a series of recent papers[19-24] we have investigated the assessment of local accuracy and attempted to improve the accuracy of various expectation values using nonlinear programming modifications of the standard variational method. Extension of this work to fairly accurate wave functions requires accessibility to accurate reference wave functions, for which a variety of expectations are also available. This study provides such values for the lithium atom.

The present study was also undertaken to explore the general rates of convergence, both for the energy and for several different expectation values. Some attention[25,26] has focused on the careful convergence study made by Larsson[4] for the Fermi-contact term. The present investigation provides some clarification on the convergence of the Fermi-contact term, and amplifies on Bunge's[26] comments.

Also of interest is the possibility of obtaining indirect assessment of the quantum electrodynamic contributions to the ground-state energy. Such an assessment requires very accurate values for the experimental ionization potentials, coupled with accurate calculations of the nonrelativistic ground-state energy, and of the relativistic and mass polarization contributions. The analysis of quantum electrodynamic effects for Li I are limited by the lack of accurate calculations for E_{NR}. An error of several cm^{-1} for E_{NR} is likely to be a significant problem for sorting out Lamb-shift effects on various transitions. For the $2s_{1/2}$-$2p_{1/2}$ transition in Li I, the Lamb shift is estimated (on the basis of unscreened one-electron shifts) to be 2.1 cm^{-1}.[27] To the author's knowledge, no experimental measurement of the shift of the ^2S ground state has been reported, perhaps not surprising, since the shift of the $1S$ ground state of hydrogen and deuterium has only recently been measured with high precision.[28] A recent review of the current status of quantum electrodynamical effects in few electron systems has been given by Drake.[29] In this review, Drake draws attention to the need for more accurate results for Li I and other members of the lithium isoelectronic series.

In addition to the considerations discussed above, the calculation of accurate wave functions has its own intrinsic interest. Accurate wave functions always have potential usefulness as reference points for more approximate computational schemes.

II. THEORY

The underlying computation scheme involved in this study has been presented in several locations in the literature.[3,4,30-32] A brief sketch is provided below. The trial wave function employed is

$$\Psi = \mathscr{A} \sum_{\mu=1}^{N} C_\mu \phi_\mu \chi_\mu \,, \tag{1}$$

where $\mathscr{A}$ is the antisymmetrizer and C_μ the variationally determined expansion coefficients. The basis functions ϕ_μ are of the form

$$\phi_\mu(r_1,r_2,r_3,r_{23},r_{13},r_{12})=r_1^{i_\mu}r_2^{j_\mu}r_3^{k_\mu}r_{23}^{l_\mu}r_{13}^{m_\mu}r_{12}^{n_\mu}\exp(-\alpha_\mu r_1-\beta_\mu r_2-\gamma_\mu r_3)\ , \tag{2}$$

where the exponents $i_\mu,j_\mu,k_\mu,l_\mu,m_\mu,n_\mu$ are each ≥ 0. The Greek symbols α and β will be employed to designate orbital exponents in this work; $\alpha(1)$ and $\beta(1)$ will denote electron-spin states. In Eq. (1), χ denotes the doublet spin eigenfunctions. There are two such functions:

$$\chi=\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3) \tag{3a}$$

or

$$\chi=2\alpha(1)\alpha(2)\beta(3)-\beta(1)\alpha(2)\alpha(3)-\alpha(1)\beta(2)\alpha(3)\ . \tag{3b}$$

The nonrelativistic Hamiltonian is

$$H=\sum_{i=1}^{3}(-\tfrac{1}{2}\nabla_i^2-3/r_i)+\sum_{i=1}^{3}\sum_{j>i}^{3}\frac{1}{r_{ij}}\ . \tag{4}$$

The mass polarization contribution is not included. Atomic units are employed throughout this work.

Evaluation of the matrix elements $\langle\phi_\mu|H|\phi_\nu\rangle$ can be shown in a straightforward fashion to reduce to the calculation of integrals of the following type:

$$I(i,j,k,l,m,n,\alpha,\beta,\gamma)=\int r_1^i r_2^j r_3^k r_{23}^l r_{13}^m r_{12}^n \times e^{-\alpha r_1-\beta r_2-\gamma r_3}d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ . \tag{5}$$

These integrals in turn can be reduced to the evaluation of the simpler integrals:

$$W(i,j,k,\alpha,\beta,\gamma)=\int_0^\infty x^i e^{-\alpha x}dx\int_x^\infty y^j e^{-\beta y}dy \times\int_y^\infty z^k e^{-\gamma z}dz\ . \tag{6}$$

The evaluation of the I and W integrals has been discussed in several places in the literature.[3,4,31,33,34] The approach of Öhrn and Nordling was employed in the present investigation.

III. COMPUTATIONAL DETAILS

A. Choice of basis functions

One of the principal objectives of the present study was to examine the rate of convergence of the energy expectation value. In order to study this in an unbiased fashion, the initial choice of basis functions was chosen in a systematic manner, without direct consideration of obtaining the optimal energy with the fewest possible number of basis functions.

The following index of the basis function exponents i, j, k, l, m, n is defined:

$$\omega=i+j+k+l+m+n\ . \tag{7}$$

The first 210 terms in the expansion of Eq. (1) involved all possible terms for $\omega=0$ through $\omega=4$, added in increasing order of ω. The basis functions for a given ω were added in the following order: largest n, all other entries for i,j,k,l,m zero; n decreased by 1, m increased by 1, all other entries for i,j,k,l zero; and so on, then followed by terms where n decreased by 2, m and l both increased by 1, etc. For example, the first 16 entries for $\omega=4$ are

$\{000004\}$, $\{000013\}^*$, $\{000022\}^*$, $\{000031\}^*$,

$\{000040\}^*$, $\{000112\}$, $\{000121\}^*$, $\{000130\}^*$,

$\{000220\}$, $\{001003\}$.

An asterisk indicates both doublet spin eigenfunctions are included. For a term where both spin eigenfunctions are possible, if they were both included in the calculation, then they were added as a pair with the first spin eigenfunction [Eq. (3a)] preceding the second [Eq. (3b)]. This pairing was chosen for coding convenience. For such a pair, the spatial component need only be computed once.

TABLE I. Breakdown of the maximum possible number of terms for a given ω [see Eq. (7)] and the actual number of terms employed in the present calculation. Breakdown also includes the numbers of each type of doublet spin eigenfunction included.

ω	Maximum number of terms of spin function 1 [Eq. (3a)] possible	Maximum number of terms of spin function 2 [Eq. (3b)] possible	Number of spin function 1 terms employed in Eq. (1)	Number of spin function 2 terms employed in Eq. (1)	Maximum total number of terms possible in wave function to given ω
0	1	0	1	0	1
1	4	2	4	2	7
2	13	8	13	8	28
3	32	24	32	24	84
4	70	56	70	56	210
5	136	116	63	6	462
6	246	216	19	4	924
7	416	376	17	1	1716
8	671	616	11	0	3003
9	1036	966	10	0	5005
10	1547	1456	9	0	8008
11	2240	2128	2	0	12376

Certain combinations are related by symmetry to previously added terms, and are therefore not included in the basis set. For example, {000103} is excluded because {000013} has already been included.

The total number of possible terms which can be incorporated grows very rapidly for increasing ω, as Table I indicates. To attempt to push the calculations to $\omega = 5$, for which the total number of terms is 462, would have been prohibited by our present computer resources.

After the first 210 terms, the remaining 142 basis functions added were selected so as to incorporate all the terms included by Perkins[8] and by Larsson,[4] and additional basis functions were added specifically to improve the energy convergence. To some extent, the best choice of terms is a matter of guesswork, although experience from the first part of the calculation suggested what basis functions are likely to be more promising than others. The final selection of basis functions did not include all those incorporated by Ho[10] in his accurate wave function. A number of these excluded terms actually had little impact on Ho's calculation, as is apparent from his table of energy versus added basis functions.[10] In addition, some basis functions closely related to Ho's were tried, but these gave negligible improvement in the energy. The final 142 terms in the basis set are tabulated in Table II. Relatively few terms involving the second spin eigenfunction [Eq. (3b)] were in-

TABLE II. Terms 211 to 352 employed in the basis set. An asterisk indicates that the same *ijklmn* function was employed with both spin functions.

No.	*i*	*j*	*k*	*l*	*m*	*n*	No.	*i*	*j*	*k*	*l*	*m*	*n*	No.	*i*	*j*	*k*	*l*	*m*	*n*
211	0	0	1	0	0	4	266	0	0	1	0	2	2	310	0	3	1	0	1	0
212	2	2	1	0	0	0	267	0	1	2	3	0	0	311	0	0	2	0	2	1
213*	3	0	1	0	0	1	268	0	2	0	0	0	3	312	0	0	2	0	1	2
215*	4	0	1	0	0	0	269	0	1	1	5	0	0	313	0	0	0	1	1	3
217*	2	0	1	0	0	2	270	0	5	1	0	1	0	314	0	0	0	1	2	2
219*	1	0	1	0	0	3	271	0	0	1	0	0	7	315	0	0	0	1	3	1
221	0	0	5	0	0	0	272	0	0	1	0	0	8	316	0	0	0	2	2	1
222*	3	0	2	0	0	0	273	0	0	1	0	0	9	317	0	0	1	0	3	1
224*	3	1	1	0	0	0	274	8	0	1	0	0	1	318	0	0	1	1	3	0
226	0	0	1	0	0	5	275	1	0	1	0	0	6	319	0	0	1	2	2	0
227*	4	0	1	0	0	1	276	1	0	1	0	0	7	320	1	0	1	0	0	8
229*	5	0	1	0	0	0	277	0	0	2	0	0	4	321	1	0	1	0	0	9
231*	2	0	1	0	0	3	278	0	0	2	0	0	5	322	6	1	1	0	0	1
233*	3	0	1	0	0	2	279	6	0	1	0	0	0	323	7	1	1	0	0	1
235	0	0	6	0	0	0	280	7	0	1	0	0	0	324	1	1	1	0	2	0
236	0	0	1	0	0	6	281	8	0	1	0	0	0	325	1	1	1	0	0	2
237	0	0	7	0	0	0	282	9	0	1	0	0	0	326	0	1	1	0	1	2
238*	5	0	1	0	0	1	283	4	1	1	0	0	1	327	0	1	1	0	2	1
240	2	1	1	0	0	1	284	5	1	1	0	0	1	328	0	1	1	1	0	2
241	1	1	3	0	0	0	285	3	2	1	0	0	1	329	0	2	1	0	1	1
242	3	1	1	0	0	1	286	3	3	1	0	0	0	330	0	0	1	1	1	2
243	2	2	1	0	0	1	287	0	0	1	0	1	4	331	0	0	1	1	2	1
244	0	1	1	3	0	0	288	3	0	1	0	1	1	332	0	5	0	0	0	0
245	0	2	0	0	2	1	289	4	0	1	0	1	1	333	0	1	4	0	0	0
246	0	0	0	0	0	5	290	2	2	2	0	0	0	334	0	1	0	0	0	4
247	0	0	0	0	5	0	291	0	1	1	0	0	4	335	0	0	1	0	5	0
248	0	2	1	2	0	0	292	0	0	1	0	4	0	336	0	0	1	0	6	0
249	0	1	1	4	0	0	293	0	0	0	0	1	4	337	0	0	1	0	7	0
250	0	2	1	3	0	0	294	0	0	0	1	4	0	338	0	0	1	0	8	0
251	2	3	0	0	0	0	295	0	0	0	0	2	3	339	0	0	1	0	9	0
252	2	2	0	0	1	0	296	0	0	0	0	3	2	340	1	7	1	0	0	0
253	2	2	0	0	0	1	297	0	0	0	0	4	1	341	1	8	1	0	0	0
254	1	4	0	0	0	0	298	0	0	0	2	3	0	342	1	9	1	0	0	0
255	1	3	0	1	0	0	299	0	0	2	0	0	3	343	0	2	1	0	0	5
256	1	3	0	0	0	1	300	0	0	2	0	3	0	344	0	2	1	0	0	6
257	1	2	2	0	0	0	301	1	4	1	0	0	0	345	0	2	1	0	0	7
258	1	2	1	1	0	0	302	1	5	1	0	0	0	346	0	3	1	0	0	5
259	1	2	1	0	1	0	303	1	6	1	0	0	0	347	0	3	1	0	0	6
260	1	2	0	2	0	0	304	0	3	1	0	0	3	348	0	3	1	1	0	0
261	6	0	1	0	0	1	305	0	3	1	0	0	4	349	1	3	0	0	1	0
262	7	0	1	0	0	1	306	0	4	1	0	0	2	350	0	4	1	0	0	3
263	1	0	1	0	0	5	307	0	5	1	0	0	2	351	0	4	1	0	0	4
264	2	0	1	0	0	4	308	0	1	1	0	3	0	352	1	2	1	0	0	2
265	0	0	1	0	1	3	309	0	2	1	0	2	0							

cluded in this set. Although no additional time is required to construct the necessary spatial matrix elements for the second spin eigenfunction, additional resources are expended in the solution of the secular equation. Also, at this point in the calculation, the second doublet spin eigenfunction is having negligible impact on the ground-state energy.

Table I indicates how many terms for a given value of ω are included in the calculation, for each of the two spin eigenfunctions. For values of ω beyond 4, only a very small proportional of all possible terms have been included in the calculation.

An orbital exponent optimization was investigated for several small basis set expansions.[35] The outcome was that most exponents were close to the values employed by Larsson,[4] Perkins,[8] and Ho.[10] The entire present calculation was carried out with the set $\alpha=\beta=2.76$ and $\gamma=0.65$ employed by Larsson. This set was selected because it would afford the possibility of providing some important checks on the accuracy of the present computations.

B. Accuracy controls

There are four major accuracy considerations involved in the present calculations. These are (i) the accuracy of the W integrals [Eq. (6)], (ii) the accuracy of the I integrals [Eq. (5)], (iii) the resulting accuracy of the individual matrix elements, and (iv) the accuracy of the solution of the secular equation and of the resulting lowest eigenvalue. The possibility of linear dependence of the basis set was also explored.

For positive values of the exponent set i,j,k in Eq. (6), the W integrals are given by simple closed formulas, and have been evaluated to 18 significant figures in the present calculation. For negative values of $i+j$ and $i+j+k$, the algorithm of Öhrn and Nordling[31] was used. This algorithm involves an infinite summation of positive terms. The convergence criterion was set to obtain approximately 18 significant figures. Some exploration of the effect of the convergence cutoff was made for representative W integrals. For the W integrals, we expect that 16 (or better) significant figures have been obtained.

Since the functional dependence of the I integrals on the W integrals is not completely trivial, particularly for the situation where l,m,n are all odd in Eq. (5), no attempt was made to carry out an error analysis on the I integrals directly in terms of the errors in the W integrals. Instead, the effect of the W convergence cutoff criterion on the I integrals was investigated directly, by computing a variety of I integrals with different values of the W-integral cutoff.

The evaluation of the I integrals breaks up into two distinct cases. For the case where l, m, and n are not *all* odd, the I integrals can be calculated in closed form. For the situation where l, m, and n are all odd, the I integrals involve an infinite summation. This infinite summation represents a major bottleneck in the calculations. In the present computations, the convergence criterion on the infinite summation for the all odd l, m, n case was set to obtain approximately 18 significant figures, although a conservative estimate is 16 significant figures. Numerical tests were made on representative I integrals to test the effect of different values of the convergence cutoff.

Of principal interest is what happens to the calculated energy as the cutoffs for the W and I integrals are changed. Several different tests on some small-term wave functions were explored. Care was taken to include basis functions in the test set which would lead to a number of all odd l, m, n exponents for the I integrals. From these investigations we have confidence that the cutoffs employed for the W and I integrals have no impact on the number of reported significant figures for the energy and the expectation values given.

Instead of attempting a direct error analysis on a typical matrix element, an alternative procedure was implemented. The number of significant figures for the matrix elements was deliberately cut in stages from 18 to 12. This is perhaps an important indicator of significant figure control because it is carried out on the full 352-term wave function, a situation obviously not possible for the W and I integral convergence criteria discussed above. When the matrix element input was restricted to 14 significant figures, all calculated expectation values were unchanged to seven significant figures, with changes typically in the 9th to 11th significant figures, except for the Fermi-contact interaction and $\langle r_i^3\rangle$, which were both altered in the eighth significant figure. Reduction of the number of significant figures for the input matrix elements to 12 led to final expectation values which were changed by no more than 2 in the ninth significant figure. The exceptions were the aforementioned two expectation values: they were changed by 6 (Fermi interaction) and 4 ($\langle r_i^3\rangle$) in the sixth significant figure.

Two diagonalization routines were employed (and some preliminary calculations done with other routines). The final results reported were based on Nesbet's procedure.[36] As the wave function was constructed, the Nesbet routine was checked against the EIGEN diagonalization subroutine. Cutoff tolerances in both routines were tested to see their effect on the calculated expansion coefficients. The final set of expansion coefficients is believed accurate to better than seven significant figures.

As a final check on potential significant figures loss, the individual positive and negative contributions to the energy and each of the reported expectation values were added separately. Three to four significant figures are typically lost in the addition of both components, except for the moments $\langle r_i^3\rangle$, $\langle r_{ij}\rangle$, and $\langle r_{ij}^2\rangle$, for which five significant figures are lost.

For a large part of the calculation, the ratio $\lambda_{\min}/\lambda_{\max}$ ($\lambda_{\min}$ equals the smallest eigenvalue, $\lambda_{\max}$ equals the largest eigenvalue) of the overlap matrix was monitored as the basis set was expanded. This serves as a means to ascertain possible problems with near-linear dependence in the basis set. Because of computational limitations, it was not possible to follow this ratio to the very end of the 352-term wave function.

All of the calculations were carried out on the Honeywell DPS 8/44 computer at the University of Wisconsin—Eau Claire (UWEC). The calculations were carried out in double precision (HEX mode) which yields 18 significant figures.

TABLE III. Expectation values for the ^2S ground state of Li I. $\langle \mathcal{O}_i \rangle = \langle \sum_{i=1}^{3} \mathcal{O}_i \rangle$ and $\langle \mathcal{O}_{ij} \rangle = \langle \sum_{i=1}^{3} \sum_{j>i}^{3} \mathcal{O}_{ij} \rangle$. All values are in a.u.

Expectation value	Number of terms					
	84	150	210	280	320	352
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.477 845	7.477 927	7.478 006	7.478 051	7.478 054	7.478 058
$\left\langle \frac{-3}{r_i} \right\rangle$	−1.715 396(1)[a]	−1.715 408(1)	−1.715 431(1)	−1.715 431(1)	−1.715 431(1)	−1.715 432(1)
$\langle 1/r_{ij} \rangle$	2.198 269	2.198 227	2.198 295	2.198 207	2.198 202	2.198 208
$\langle r_i \rangle$	4.992 291	4.992 367	4.989 491	4.989 653	4.989 669	4.989 579
$\langle r_i^2 \rangle$	1.838 295(1)	1.838 796(1)	1.835 204(1)	1.835 522(1)	1.835 583(1)	1.835 514(1)
$\langle r_i^3 \rangle$	9.286 100(1)	9.294 062(1)	9.255 906(1)	9.260 143(1)	9.261 378(1)	9.260 858(1)
$\langle r_{ij} \rangle$	8.673 893	8.674 023	8.668 346	8.668 657	8.668 687	8.668 507
$\langle r_{ij}^2 \rangle$	3.690 388(1)	3.691 433(1)	3.684 270(1)	3.684 905(1)	3.685 026(1)	3.684 889(1)
$\langle \delta(\mathbf{r}_i) \rangle$	1.381 507(1)	1.381 857(1)	1.383 263(1)	1.384 207(1)	1.384 136(1)	1.384 150(1)
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	2.887 942	2.895 211	2.902 746	2.902 411	2.902 691	2.904 079

[a] The notation (n) signifies $\times 10^n$.

IV. RESULTS

The principal results of the calculations are assembled in Tables III and IV. The shorthand notation for expectation values is employed:

$$\langle \mathcal{O}_i \rangle \equiv \left\langle \Psi \left| \sum_{i=1}^{3} \mathcal{O}_i \right| \Psi \right\rangle , \qquad \langle \mathcal{O}_{ij} \rangle \equiv \left\langle \Psi \left| \sum_{i=1}^{3} \sum_{j>i}^{3} \mathcal{O}_{ij} \right| \Psi \right\rangle , \tag{8}$$

and Ψ is normalized. Besides the energy components, and moments of r_i^n and r_{ij}^n, Table III also gives the electron density at the nucleus:

$$\rho(0) = \langle \delta(\mathbf{r}_i) \rangle , \tag{9}$$

and the Fermi-contact interaction

$$f = 4\pi \langle \delta(\mathbf{r}_i)\sigma_{zi} \rangle . \tag{10}$$

TABLE IV. Ground-state energy and scale factor for wave functions of different size.

Number of terms	Energy	Scale factor η [Eq. (11)]
28	−7.475 984	1.000 073
84	−7.477 845	1.000 111
150	−7.477 927	1.000 070
210	−7.478 006	1.000 023
280	−7.478 051	1.000 004
320	−7.478 054	1.000 003
352	−7.478 058	1.000 001

Table IV lists the ground-state energy and scale factor η defined by

$$\eta = -\frac{\frac{1}{2}\langle V \rangle}{\langle T \rangle} , \tag{11}$$

where $\langle V \rangle$ and $\langle T \rangle$ are the potential energy and kinetic energy, respectively. All reported expectation values have been appropriately scaled using the values of η tabulated in Table IV.

Calculations were also carried out with only the single spin eigenfunction given by Eq. (3a) included in the basis set. The basis set for this calculation was ordered in exactly the same manner discussed above. The results obtained for the various expectation values are presented in Table V.

V. DISCUSSION

A. General convergence characteristics

A general feature of the present calculations is the very slow convergence observed for the energy, and most of the reported expectation values. This is not a totally unexpected result, particularly in light of the results of Larsson,[4] and Ho.[10] The present calculations clearly indicate just how poor the overall convergence is, beyond the Larsson expansion.

There is no question that approximately the same ground-state energy could have been obtained with fewer terms in the expansion, assuming the restriction to the fixed orbital exponents employed in the present calculations. A number of terms in the basis set have very minor impact on the ground-state energy. The slow convergence of the calculation is not governed totally by the presence of these energetically unimportant basis functions.

TABLE V. Expectation values for the ^2S ground state of Li I, for wave functions involving only one spin eigenfunction [Eq. (3a)].

Expectation Value	Number of Terms 50	100	150	200	251
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.477 789	7.477 976	7.478 039	7.478 049	7.478 056
$\langle -3/r_i \rangle$	−1.715 344(1)	−1.715 414(1)	−1.715 426(1)	−1.715 429(1)	−1.715 432(1)
$\langle 1/r_{ij} \rangle$	2.197 864	2.198 189	2.198 187	2.198 195	2.198 203
$\langle r_i \rangle$	4.996 092	4.990 405	4.989 972	4.989 737	4.989 623
$\langle r_i^2 \rangle$	1.843 152(1)	1.835 878(1)	1.835 781(1)	1.835 619(1)	1.835 574(1)
$\langle r_i^3 \rangle$	9.342 459(1)	9.258 473(1)	9.261 567(1)	9.261 439(1)	9.261 602(1)
$\langle r_{ij} \rangle$	8.681 394	9.670 122	8.669 246	8.668 825	8.668 595
$\langle r_{ij}^2 \rangle$	3.700 144(1)	3.685 613(1)	3.685 431(1)	3.685 102(1)	3.685 009(1)
$\langle \delta(\mathbf{r}_i) \rangle$	1.381 017(1)	1.383 725(1)	1.384 386(1)	1.384 281(1)	1.384 149(1)
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	2.915 014	3.075 229	2.952 384	2.932 850	2.936 683
Energy	−7.477 789	−7.477 976	−7.478 039	−7.478 049	−7.478 056

B. Basis set selection and convergence rate

As indicated in Sec. III, the optimal strategy to obtain the lowest energy with the minimal basis set was not pursued. This is obvious from a comparison of the results reported in Table IV with the summary of several of the most accurate calculations published for the ground state of Li, Table VI. In particular, the energy obtained from Larsson's 100-term and Ho's 92-term wave functions (see Table VI) are superior to the energy obtained from the 210-term wave function of the present study. The systematic selection of all terms to $\omega = 4$ (giving rise to the 210-term wave function), avoids the difficult, if not impossible task of deciding the likely impact that a given term will have on the energy. In addition, the selection of basis functions that are important for improving the energy important region, may be far less appropriate for improving expectation values that emphasize other regions of configuration space. The systematic inclusion of all terms to $\omega = 4$ gives a clear picture of the very slow convergence of the energy, and of most of the other calculated expectation values.

Beyond term 210, basis functions were added according to their expected impact on the energy. The 25 terms of Larsson involving $\omega > 4$ were included. From the final 352-term wave function, the 100-term wave function of Larsson was calculated. Complete agreement was found with Larsson's reported energy and Fermi-contact interaction,[4] and with the published coefficients,[6] to what is believed are an appropriate number of significant figures. A

TABLE VI. Upper bounds to the nonrelativistic ground-state energy of ^2S Li I. The wave functions are listed in chronological order. (CI denotes configuration interaction.)

Wave function	Type	Number of terms	Energy
Weiss[a]	CI	45	−7.477 10
Larsson[b]	Hylleraas (single spin function)	60	−7.478 010
	Hylleraas (both doublet spin functions)	100	−7.478 025
Sims and Hagstrom[c]	Combined CI-Hylleraas	150	−7.478 02
Perkins[d]	Hylleraas	30	−7.477 93
Muszyńska *et al.*[e]	Combined CI-Hylleraas	139	−7.478 044
Ho[f]	Hylleraas	92	−7.478 031
Pipin and Woźnicki[g]	Combined CI-Hylleraas	170	−7.478 044
Present work	Hylleraas (single spin function)	251	−7.478 056
Present work	Hylleraas (both doublet spin functions)	352	−7.478 058
Empirical estimates for the nonrelativistic ground-state energy			−7.478 068[h] −7.478 073[i]

[a] Reference 2.
[b] Reference 4.
[c] Reference 7.
[d] Reference 8.
[e] Reference 9.
[f] Reference 10.
[g] Reference 11.
[h] Reference 37.
[i] Reference 26.

number of Larsson's smaller wave functions were also checked in the early stages of the calculations.

Although attempts were made to select those basis functions that would have significance for the energy bound, many of these terms had relatively minor bearing on the energy. These terms did, however, provide a useful guide as to what types of additional terms to avoid. The rate of convergence is definitely affected by the selection process. For example, the last 22 terms selected improved the energy by $\sim 3.6\ \mu$hartree, whereas the 49 terms immediately preceding these, improved the energy by $\sim 3.5\ \mu$hartree. Experience in basis function selection does have an important relationship to the overall convergence of the calculation.

The basis set included a number of terms where $\{l_\mu, m_\mu, n_\mu\}$ in Eq. (2) were all nonzero, and a number that would lead to the *all* odd case for the I integrals. The former selection leads to a much more involved calculation, particularly for the matrix elements of the kinetic energy. The second of the aforementioned sets implies a heavy computational burden, because of the infinite series involved in the evaluation of the resulting I integrals. It was found that terms with all nonzero $\{l_\mu, m_\mu, n_\mu\}$ generally made only minor contributions to the convergence of the energy. A similar remark seems valid for the other expectation values calculated in this study. This observation is supported in part, from the results presented in Table III, and from the calculation of these same expectation values from many other wave functions not tabulated in Table III. For other expectation values that are particularly sensitive to correlation effects, such as the mass polarization, the above observation requires further investigation.

It was found that basis terms involving a single interelectronic coordinate function, r_{ij}^n, generally had the most bearing on the energy, particularly when coupled with $\{i,j,k\}$ sets such as $\{0,0,1\}$ and $\{i,0,1\}$, with $i>0$. The importance of these combinations should, of course, be expected.

C. Convergence of expectation values

The results presented in Table III for the kinetic-energy expectation value might at first glance appear to suggest that this expectation value is converging to around 7.478 060, that is, an approximate uncertainty of $\sim 2\times 10^{-6}$ a.u. This is probably a false conclusion for two reasons. The slow convergence of the overall calculation is operative for this expectation value. Secondly, if the empirical estimates for the nonrelativistic ground-state energy given in Table VI are accepted, the uncertainty in the reported kinetic energy is closer to $\sim 1\times 10^{-5}$ a.u.

The electron-nuclear potential energy has the fastest convergence of any expectation value reported in Table III. The uncertainty for this expectation value appears to be $\sim 1\times 10^{-5}$ a.u. The electron-electron potential energy is uncertain to $\sim 1\times 10^{-5}$ a.u. The convergence of this expectation value is clearly nonmonotonic.

For the moments $\langle r_i^n \rangle$ with $n=1$ to 3, the convergence is nonmonotonic for each n reported. The matrix elements appear to have converged to $\sim 1\times 10^{-4}$, 1×10^{-3}, and 5×10^{-3} for $n=1$, $n=2$, and $n=3$, respectively. Not too surprisingly, the absolute uncertainties in the moments increase with increasing n. The larger n, the poorer the convergence. The standard unconstrained variational procedure deals best with the "energy important region" of configuration space. Typically, expectation values of the kinetic energy, electron-electron potential energy, and the electron-nuclear potential energy will converge most quickly, directly reflecting the aforementioned fact. As the higher moments focus attention away from the energy important region, the asymptotic characteristics of the wave function have a greater bearing on the accuracy of the computed moments.

The moments of r_{ij}^n for $n=1$ and $n=2$ also show nonmonotonic convergence. The estimated uncertainties in these expectation values are $\sim 2\times 10^{-4}$ and $\sim 2\times 10^{-3}$ for $n=1$ and $n=2$, respectively.

The electron density at the nucleus, and the Fermi-contact interaction, both exhibit nonmonotonic convergence. The associated uncertainties are $\sim 2\times 10^{-4}$ a.u. for $\rho(0)$, and $\sim 2\times 10^{-3}$ for the Fermi-contact interaction.

The energy convergence is noted to be very slow, and not particularly uniform. The ground-state energy calculated in the present investigation is the most accurate value reported to date for Li I. The present energy is approximately 3 cm^{-1} lower in energy than the very accurate recent calculation of Pipin and Woźnicki.[11] A chronological ordering of several of the most accurate calculations presented in Table VI indicates the progress made on the lithium ground state over the last twenty-five years.

Three empirical estimates of the nonrelativistic ground-state energy have been presented in the literature,[26,37,38] of which the smallest and largest values are given in Table VI. If these values are accepted, the present calculated energy is 2.4 to 3.3 cm^{-1} above the true nonrelativistic ground-state energy. Bunge[26] has estimated the nonrelativistic ground-state energy by subtracting from the experimental energy, estimates of the relativistic, specific isotope shift, and the Lamb-shift corrections. The specific isotope shift employed by Bunge was the value calculated by Prasad and Stewart.[39] A slightly more accurate value can be deduced from the experimental level isotope shift measurements of Lorenzen and Niemax.[40] From their data, the specific isotope shift is calculated to be 2.4×10^{-5} a.u., which increases Bunge's estimate by one in the last quoted figure given in Table VI. The estimate of Woźnicki and co-workers[37] was obtained by combining the results of Pekeris's calculation on Li$^+$ with the relativistically adjusted experimental ionization energy. There are no highly accurate calculations of the principal relativistic contributions to the ground-state energy of Li I available in the literature. For this reason, and the earlier cited comments on the lack of availability of an accurate Lamb-shift correction, it is not possible to assess the accuracy of either of the empirical estimates of the nonrelativistic ground-state energy reported in Table VI.

D. Effects of one versus two spin eigenfunctions

Table VI indicates the energy obtained with only one of the two spin eigenfunctions, that of Eq. (3a), included in the calculation. This wave function contains 251 terms, and the resulting energy is only very slightly higher than the value obtained from the 352-term wave function employing both spin eigenfunctions. Larsson[4] found a similar behavior; the addition of 40 terms containing the second spin eigenfunction [Eq. (3b)] to his 60-term single-spin eigenfunction wave function lowered the energy by 1.5×10^{-5} a.u. It appears, at least insofar as the energy is concerned, that the second spin eigenfunction has little overall impact on the calculation. Delves[41] has suggested a cautionary note in this regard, and this reference may be pursued for further elaboration.

For the other expectation values considered in this work, except the Fermi-contact interaction, which is discussed in detail below, the results presented in Table V for the 251-term single spin eigenfunction expansion are in fairly close agreement with the results presented in Table III for the 352-term function.

E. Fermi-contact interaction

It is well known that the Fermi-contact interaction represents a sensitive test of the accuracy of the wave function, particularly for the region of configuration space close to the nucleus. The Fermi-contact interaction for the lithium atom has received considerable attention in the literature. Harriman[42] summarizes the results of almost 50 calculations. The recent review by Lindgren[43] provides additional discussion. The difficulty of determining an accurate value for the Fermi-contact interaction is readily apparent from these articles and the references included therein.

Larsson[4] has reported the most accurate value for the Fermi-contact interaction. He has also carried out a careful study of the convergence of this property. The final value reported by him was 2.906 a.u., in close agreement with the experimental value of 2.9062 given in the same paper. Hibbert labeled the convergence of Larsson's Fermi-contact interaction *erratic*.[25] It is clear from Larsson's calculation that the convergence is not monotonic. On the other hand, it is not at all clear from the final results of Larsson's calculation, that the Fermi-contact term has stabilized to 2.906 a.u.

Bunge[26] has addressed the above question in a clear and succinct fashion. He points out on the basis of a rough order-of-magnitude analysis of significant figure loss, that the Fermi-contact interaction reported by Larsson is uncertain to ~ 0.002 a.u. Bunge also emphasizes the critical dependence of the Fermi term on the numerical precision of the overall calculation.

The present calculation indicates that the convergence of the Fermi-contact interaction is not monotone for the basis set employed. As discussed above, we did explore the effects of tolerance changes in the diagonalization procedure to see its effect on the Fermi-contact interaction. The studies involving deliberate truncation of the number of significant figures of the input matrix elements gives us confidence that the error of the reported Fermi interaction is below that of the Larsson calculation.

The present results indicate that the 100-term wave function of Larsson has not yielded a value for the Fermi-contact interaction stabilized to 2.906 a.u. As indicated above, we have been able to reproduce this value from a subset of the final expansion. It appears that the overall slow convergence of the calculation has a considerable bearing on the Fermi-contact term.

The effect of both doublet spin eigenfunctions has a significant bearing on the calculated value of the Fermi term. Comparison of the results in Tables III and V provides evidence that the particular spin-dependent property under consideration is rather sensitive to the presence of the second spin eigenfunction, even though it has little impact on the energy and other spin-independent properties. Given the very slow speed of convergence of the Fermi term for the wave function with a single spin eigenfunction (see Table V), it is difficult, if not impossible, to predict just how large a basis set would be required for the accurate calculation of this property using a single-spin eigenfunction in the basis set. This is particularly true when the nonmonotonic nature of the convergence is noted.

The experimental value of f reported by Larsson differs slightly from other values reported in the literature.[44,45] Considering the uncertainty associated with the nuclear moment of ^{7}Li, and the corresponding measured value of the hyperfine splitting,[46] the experimental value of f is taken to be 2.9096±0.0001 a.u. A slight correction for the effects of finite nuclear mass introduces a factor of approximately $(1-3m_e/M_{^7\text{Li}})\sim 0.999\,765$, where m_e is the electron mass and $M_{^7\text{Li}}$ is the nuclear mass of ^{7}Li. This refinement lowers the value reported in Table III to 2.9034 a.u. The present calculation leads to a value too low by 0.006 a.u. (0.2% error). The value of 2.9034 together with the estimated uncertainty of ~ 0.002 given above in Sec. V C, does not quite overlap with the experimental result for f. This difference may suggest the need for a larger error of $\sim 6\times10^{-3}$ a.u. in the computed Fermi-contact term, and be another indicator of the poor convergence observed for this property.

F. Extrapolation

Several extrapolation procedures were considered in the present study. An extrapolation was employed using several energy values, E_N, for wave functions with N terms, with N suitably chosen in a manner analogous to Schiff *et al.*[47] This procedure gave unrealistic results due to the lack of smooth variation exhibited by the E_N values. Plotting E_N versus N^{-1} showed the best trend, but the resulting "curve" was sufficiently nonsmooth as to not be particularly useful for extrapolation purposes. The approach suggested by Goldman[48] of examining E_N versus ΔE_N, where $\Delta E_N = E_N - E_{N-1}$, yielded a totally erratic plot of no value for extrapolation purposes. The nonmonotonic convergence, particularly over the last 100 terms, makes attempts at extrapolation in the present calculation not worthwhile.

VI. CONCLUSIONS

The present study has reported the results of extensive calculations on the ground state of ^2S Li I. The calculated energy of −7.478058 a.u. is the lowest to date for this system.

The two general observations from the calculations can be summarized as follows. (i) Very slow convergence was observed for the overall calculation, and in particular, for the Fermi-contact interaction. (ii) The need to include both spin eigenfunctions to accurately determine the Fermi-contact interaction is clearly shown, and this supports previous statements in the literature to this effect, made on the basis of much smaller wave functions.

In view of both the slow convergence of the present calculation, and the difficulty of assessing the correctness of the empirical estimates of the nonrelativistic ground-state energy, an accurate lower bound estimate of the energy seems to be highly desirable. Such a calculation involves considerable computational and mathematical complexities, which to date, have not been addressed in the literature.

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