

# PHYSICAL REVIEW A

## GENERAL PHYSICS

THIRD SERIES, VOLUME 40, NUMBER 4

AUGUST 15, 1989

### Calculations on the $^2S$ ground states of some members of the Li I isoelectronic series

Frederick W. King

*Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin 54702*

(Received 4 January 1989)

Extensive variational calculations using Hylleraas-type functions are carried out on the  $^2S$  ground states for the following members of the Li I isoelectronic series: Li I, B III, C IV, N V, O VI, F VII, and Ne VIII. For each species, the nonrelativistic energy, the electronic density at the nucleus, the specific mass shift, the transition isotope shift, the Fermi contact interaction, the diamagnetic susceptibility, the nuclear magnetic shielding factor, moments of  $\langle r_i^n \rangle$  for  $n = -1, 1, 2$ , and 3 and of  $\langle r_{ij}^n \rangle$  for  $n = -1, 1$ , and 2 are reported. The nonrelativistic energies obtained are lower than any previously published values for each member of the Li I series examined. The effect of one versus two spin eigenfunctions in the basis set is examined. The rates of convergence for both the one- and two-spin-eigenfunction basis sets are examined for each expectation value.

#### I. INTRODUCTION

Over the past 30 years remarkable progress has been made on the calculation of the properties of two-electron atoms to spectroscopic accuracy.<sup>1-12</sup> The extremely high accuracy achieved by recent calculations has allowed an assessment of fundamental fine-structure shifts in these atomic systems.<sup>11-14</sup> For atoms with three or more electrons, very few calculations have been carried out where the nonrelativistic energy  $E_{NR}$  is in error by 1 microhartree or less, and no examples are known to the author where an accuracy comparable to that obtained in two-electron systems has been achieved.

In the present work the results of extensive variational calculations employing Hylleraas-type basis functions are reported for the  $^2S$  ground states of the following members of the Li I isoelectronic series: Li I, B III, C IV, N V, O VI, F VII, and Ne VIII. Calculations on the  $^2S$  ground state of Be II have been carried out previously,<sup>15</sup> and this system has not been reconsidered in the present investigation. The  $^2S$  ground state of Li I has been the subject of a previous calculation by the author,<sup>16</sup> but is reexamined in the present work using a somewhat larger basis set than employed in the earlier calculations.

The objectives of the present work are threefold. The first is the construction of wave functions of sufficiently high quality that accurate evaluations of a number of properties of these systems can be made. Two of the properties of special interest are the nonrelativistic energy and the specific mass shift. These two expectation values are required input for a longer-range goal: the semiempirical determination of the Lamb shifts for the  $^2S$  ground states of members of the Li I isoelectronic series.

Accurate relativistic corrections must be evaluated to complete the aforementioned objective, and work is presently in progress on this topic. A second aim is to provide additional information on the rates of convergence of a variety of expectation values. Since two spin eigenfunctions can be employed for these states, the present work provides detailed results on the effect of using one versus two spin eigenfunctions in the basis set. Compact analytic expressions for the radial electronic density functions for the  $^2S$  states of three-electron systems have recently been derived.<sup>17</sup> A third outcome of the present investigation is to provide wave functions that can be utilized to produce radial electronic densities of high accuracy with minimal computational effort.

#### II. THEORY

The theoretical approach employed in this study has been discussed elsewhere in the literature.<sup>18-21</sup> A brief sketch is presented below. The trial wave function employed for each atom is

$$\psi = \mathcal{A} \sum_{\mu=1}^{\mathcal{N}} C_{\mu} \phi_{\mu} \chi_{\mu}, \quad (1)$$

where  $\mathcal{A}$  is the antisymmetrizer,  $\mathcal{N}$  is the number of basis functions, and  $C_{\mu}$  are the variationally determined expansion coefficients. The basis functions are of the form

$$\begin{aligned} \phi_{\mu}(r_1, r_2, r_3, r_{23}, r_{31}, r_{12}) \\ = r_1^{i_{\mu}} r_2^{j_{\mu}} r_3^{k_{\mu}} r_{23}^{l_{\mu}} r_{31}^{m_{\mu}} r_{12}^{n_{\mu}} \exp(-\alpha_{\mu} r_1 - \beta_{\mu} r_2 - \gamma_{\mu} r_3), \end{aligned} \quad (2)$$

where the exponents  $i_\mu, j_\mu, k_\mu, l_\mu, m_\mu,$  and  $n_\mu$  are each  $\geq 0$ . In Eq. (1),  $\chi_\mu$  denotes the doublet spin eigenfunctions, which take the form

$$\chi_\mu = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \quad (3a)$$

or

$$\chi_\mu = 2\alpha(1)\alpha(2)\beta(3) - \beta(1)\alpha(2)\alpha(3) - \alpha(1)\beta(2)\alpha(3). \quad (3b)$$

The nonrelativistic Hamiltonian employed is

$$H = \sum_{i=1}^3 \left[ -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}}, \quad (4)$$

where  $Z$  is the nuclear charge of the species. The mass polarization contribution is not included in  $H$ ; it is evaluated using first-order perturbation theory. Atomic units (atom based) are employed throughout (including all table entries) unless a statement to the contrary is made [the molar diamagnetic susceptibility, the transition isotope shift, and hyperfine coupling constant being three exceptions to the use of atomic units (atom)]. Atom-based atomic units are inherent in atomic calculations, and may be converted to standard atomic units by incorporating the appropriate nuclear-mass factor. This is illustrated later for the Fermi contact term. Details on the evaluation of the required matrix elements have been given elsewhere.<sup>18-20,22-24</sup>

### III. COMPUTATIONAL DETAILS

#### A. Choice of basis functions

Define

$$\omega = i + j + k + l + m + n, \quad (5)$$

where the set  $\{i, j, k, l, m, n\}$  are the exponents appearing in Eq. (2). All possible choices leading to values of  $\omega = 0, 1, 2, 3,$  and  $4$  were included in the calculation for each atom studied. This leads to a total of 210 basis functions. The ordering of these 210 terms is discussed elsewhere.<sup>16</sup> Basis functions that include the second spin eigenfunction [Eq. (3b)] are included unless excluded by symmetry. Beyond  $\omega = 4$ , the maximum possible number of terms increases rapidly. A table of the number of basis functions as a function of  $\omega$ , including the breakdown into numbers for the two spin eigenfunctions, can be found in Ref. 16. For each atom, terms 211 to 401 were the same as those employed previously for calculations on Be II (see Table I of Ref. 15), except for CIV, NV, OVI, FVII, and Ne VIII for which terms 370, 377, 378, 379, 388, 389, 394, and 395 were excluded. The remaining terms employed are shown Table I. An asterisk on an entry in Table I signifies that the spatial component is repeated with the second spin eigenfunction included. When both spin eigenfunctions occur for a particular spatial component, they are computed together as a pair, which results in a considerable reduction of computational effort. For Li I, all entries in Table I were employed; for B III, terms up to number 503 were included in the basis set. For each of the other atoms studied, all entries were employed excluding terms 486, 487, 522, 523, and 569, and any entry

for which one member of the set  $\{i, j, k, l, m, n\}$  has a value which exceeds 6.

The orbital exponents for each atom were kept fixed during the course of the calculation, that is,  $\alpha_\mu = \beta_\mu = \alpha$  and  $\gamma_\mu = \gamma$ . The values of  $\alpha$  and  $\gamma$  were selected as follows. For Li I, the present calculations were carried out using software substantially different from our previous calculations<sup>16,22</sup> on Li I. The fixed exponents employed in that work and also used elsewhere<sup>19</sup> are close to optimal, and were used again in the present calculations. This provided a substantial check on the new software. For each of the other atoms investigated, the 30-term Hylleraas basis set of Perkins<sup>25</sup> was optimized on a grid accurate to 0.01. The resulting values of  $\alpha$  and  $\gamma$  are given in Table II. Although the choice of exponents will obviously change with the size of the test basis set, the exponents appearing in Table II are expected to be close to the optimal values. This is suggested by some preliminary trial and error work with different-size test basis sets for Li I.

#### B. Accuracy controls

An extensive discussion of accuracy controls relevant to the calculations reported in this work has been given elsewhere.<sup>15,16</sup> Checking the new software used for the present calculations against results generated by an earlier code, provided an extensive test of the possibilities of significant figure loss in the construction of the individual matrix elements.

In a parallel study, analytic expressions have been derived for the radial electronic density for  $^2S$  atomic states described by Hylleraas-type wave functions.<sup>17</sup> The radial density has been used to evaluate several expectation values, including the moments  $\langle r_i^n \rangle$  and the electronic density at the nucleus,  $\rho(0)$ , for basis sets incorporating over 200 terms. The agreement found between the two independent approaches was generally 10–12 significant figures or better, for a variety of matrix elements. This provides an indirect check on the accuracy of a significant number of matrix elements employed in the present study.

The calculations for Li I, B III, F VII, and Ne VIII were carried out on a Honeywell DPS8/49 computer at the University of Wisconsin–Eau Claire. The calculations for CIV, NV, and OVI were carried out on a Cray XMP/48 computer at the National Center for Supercomputer Applications at the University of Illinois at Urbana–Champaign. All calculations were carried out in double precision.

### IV. RESULTS

The principal results of the calculations are collected in Tables III–IX. The following shorthand notation for expectation values is employed:

$$\langle \mathcal{O}_i \rangle \equiv \left\langle \psi \left| \sum_{i=1}^3 \mathcal{O}_i \right| \psi \right\rangle, \quad (6a)$$

$$\langle \mathcal{O}_{ij} \rangle \equiv \left\langle \psi \left| \sum_{i=1}^3 \sum_{j>i}^3 \mathcal{O}_{ij} \right| \psi \right\rangle, \quad (6b)$$

and  $\psi$  is normalized. Besides the energy components, and moments  $\langle r_i^n \rangle$  and  $\langle r_j^n \rangle$ , Tables III–IX also report the electron density at the nucleus

$$\rho(0) = \langle \delta(r_i) \rangle, \quad (7)$$

the Fermi contact interaction

$$f = 4\pi \langle \delta(r_i) \sigma_{zi} \rangle, \quad (8)$$

the expectation value required for the evaluation of the

TABLE I. Terms 402 to 602 employed in the basis set. An asterisk indicates that the same  $i, j, k, l, m, n$  function was employed with both spin functions.

No.	$i$	$j$	$k$	$l$	$m$	$n$	No.	$i$	$j$	$k$	$l$	$m$	$n$
402	0	0	7	0	0	0	502*	0	1	2	1	1	0
403*	7	0	1	0	0	1	504*	0	1	2	2	0	0
405*	0	1	2	3	0	0	506*	0	1	3	0	0	1
407*	0	1	1	5	0	0	508*	0	1	3	0	1	0
409*	0	5	1	0	1	0	510*	0	1	3	1	0	0
411	0	0	1	0	0	9	512*	0	2	0	0	0	3
412*	8	0	1	0	0	1	514*	0	2	0	0	1	2
414	0	0	2	0	0	4	516*	0	2	0	0	2	1
415	0	0	2	0	0	5	518*	0	2	0	0	3	0
416*	8	0	1	0	0	0	520*	0	2	0	1	0	2
418*	9	0	1	0	0	0	522*	0	2	0	1	1	1
420*	4	1	1	0	0	1	524*	0	2	0	1	2	0
422*	5	1	1	0	0	1	526*	0	2	0	2	0	1
424*	3	2	1	0	0	1	528*	0	2	0	2	1	0
426	3	3	1	0	0	0	530*	0	2	0	3	0	0
427*	0	0	1	0	1	4	432*	0	2	1	0	1	1
429*	3	0	1	0	1	1	534*	0	2	1	1	0	1
431*	4	0	1	0	1	1	536*	0	2	1	1	1	0
433	2	2	2	0	0	0	538*	0	2	2	0	0	1
434*	0	3	1	0	0	3	540*	0	2	2	0	1	0
436*	0	3	1	0	0	4	542*	0	2	2	1	0	0
438*	1	0	1	0	0	8	544*	0	3	0	0	0	2
440*	1	0	1	0	0	9	546*	0	3	0	0	1	1
442*	6	1	1	0	0	1	548*	0	3	0	0	2	0
444*	7	1	1	0	0	1	550*	0	3	0	1	0	1
446*	0	0	1	0	8	0	552*	0	3	0	1	1	0
448*	0	0	1	0	9	0	554*	0	3	0	2	0	0
450*	1	7	1	0	0	0	556*	0	4	0	0	0	1
452*	1	8	1	0	0	0	558*	0	4	0	0	1	0
454*	1	9	1	0	0	0	560*	0	4	0	1	0	0
456*	0	2	1	0	0	6	562	1	1	0	0	0	3
458*	0	2	1	0	0	7	563*	1	1	0	0	1	2
460*	0	3	1	0	0	6	565*	1	1	0	0	2	1
462*	0	4	1	0	0	3	567*	1	1	0	0	3	0
464*	0	4	1	0	0	4	569	1	1	0	1	1	1
466*	0	1	0	1	3	0	570*	1	1	0	1	2	0
468*	0	1	0	2	0	2	572*	1	1	1	0	1	1
470*	0	1	0	2	1	1	574	1	1	1	1	1	0
472*	0	1	0	2	2	0	575	1	1	2	0	0	1
474*	0	1	0	3	0	1	576*	1	1	2	0	1	0
476*	0	1	0	3	1	0	578*	1	2	0	0	0	2
478*	0	1	0	4	0	0	580*	1	2	0	0	1	1
480*	0	1	1	0	1	2	582*	1	2	0	0	2	0
482*	0	1	1	0	2	1	584*	1	2	0	1	0	1
484*	0	1	1	1	0	2	586*	1	2	0	1	1	0
486*	0	1	1	1	1	1	588*	1	2	0	2	0	0
488*	0	1	1	1	2	0	590*	1	3	0	0	0	1
490*	0	1	1	2	0	1	592*	1	3	0	0	1	0
492*	0	1	1	2	1	0	594*	1	3	0	1	0	0
494*	0	1	2	0	0	2	596*	1	4	0	0	0	0
496*	0	1	2	0	1	1	598	2	2	0	0	0	1
498*	0	1	2	0	2	0	599*	2	2	0	0	1	0
500*	0	1	2	1	0	1	601*	2	3	0	0	0	0

TABLE II. Orbital exponents employed in the Hylleraas expansion.

Species	Orbital exponents	
	$\alpha$	$\gamma$
Li I	2.76	0.65
B III	4.65	1.60
C IV	5.95	2.24
N V	6.95	2.75
O VI	7.96	3.27
F VIII	8.97	3.77
Ne VIII	9.97	4.28

specific mass shift (mass polarization correction)  $\langle \nabla_i \cdot \nabla_j \rangle$ , and the scale factor  $\eta$ , defined by

$$\eta = \frac{-\frac{1}{2}\langle V \rangle}{\langle T \rangle}, \quad (9)$$

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  $\eta$  presented in the tables.

Extensive calculations were made in the present study to assess the necessity of including both spin eigenfunctions in the basis set in order to achieve accurate expectation values. The results obtained by retaining only the first spin eigenfunction [Eq. (3a)] have been deposited with the Physics Auxiliary Publication Service.<sup>26</sup>

TABLE III. Expectation values for the  $^2S$  ground state of Li I.  $\langle O_i \rangle \equiv \langle \sum_{i=1}^3 O_i \rangle$  and  $\langle O_{ij} \rangle \equiv \langle \sum_{i=1}^3 \sum_{j>i}^3 O_{ij} \rangle$ . All values are in atomic units (atom). The notation  $[n]$  signifies  $\times 10^n$ .

Expectation value	Number of terms					
	100	200	300	400	500	602
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.477 902	7.478 004	7.478 032	7.478 057	7.478 059	7.478 059
$\langle -\frac{3}{r_i} \rangle$	-1.715 392 7[1]	-1.715 431 2[1]	-1.715 431 1[1]	-1.715 432 2[1]	-1.715 432 5[1]	-1.715 432 9[1]
$\langle \frac{1}{r_{ij}} \rangle$	2.198 122	2.198 305	2.198 248	2.198 208	2.198 208	2.198 211
$\langle r_i \rangle$	4.993 516	4.989 451	4.989 621	4.989 604	4.989 576	4.989 538
$\langle r_i^2 \rangle$	1.840 032[1]	1.835 181[1]	1.835 571[1]	1.835 547[1]	1.835 518[1]	1.835 474[1]
$\langle r_i^3 \rangle$	9.305 778[1]	9.255 858[1]	9.261 691[1]	9.261 049[1]	9.260 791[1]	9.260 364[1]
$\langle r_{ij} \rangle$	8.676 288	8.668 265	8.668 594	8.668 558	8.668 502	8.668 427
$\langle r_{ij}^2 \rangle$	3.693 874[1]	3.684 224[1]	3.685 004[1]	3.684 954[1]	3.684 897[1]	3.684 809[1]
$\langle \delta(r_i) \rangle$	1.381 471[1]	1.383 074[1]	1.384 374[1]	1.384 166[1]	1.384 175[1]	1.384 182[1]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	2.921 148	2.910 311	2.906 911	2.905 315	2.906 026	2.906 359
$\langle \nabla_i \cdot \nabla_i \rangle$	-3.028 219[-1]	-3.021 920[-1]	-3.019 761[-1]	-3.018 559[-1]	-3.018 471[-1]	-3.018 467[-1]
$\eta$	1.000 088 9	1.000 021 9	1.000 012 4	1.000 001 9	1.000 001 0	1.000 000 7
Energy	-7.477 902	-7.478 004	-7.478 032	-7.478 057	-7.478 059	-7.478 059

### A. Nuclear magnetic shielding constant

The nuclear magnetic shielding constant (diamagnetic shielding factor) is determined from the formula

$$\sigma = \frac{1}{3}\alpha^2 \left\langle \psi \left| \sum_{i=1}^3 \frac{1}{r_i} \right| \psi \right\rangle, \quad (10)$$

where  $\alpha$  is the fine-structure constant, whose value is taken as<sup>27</sup>  $7.297\,353\,08 \times 10^{-3}$ . Values of  $\sigma$  are tabulated in Table X.

### B. Diamagnetic susceptibility

The molar diamagnetic susceptibility is defined by

$$\chi = -\frac{1}{6}N_A \alpha^2 a_0^3 \left\langle \psi \left| \sum_{i=1}^3 r_i^2 \right| \psi \right\rangle, \quad (11)$$

where  $N_A$  is Avogadro's constant and  $a_0$  is the Bohr radius. Using the values<sup>27</sup>  $N_A = 6.022\,136\,7 \times 10^{23} \text{ mol}^{-1}$  and  $a_0 = 0.529\,177\,249 \times 10^{-8} \text{ cm}$  leads to  $\chi$  in units of  $\text{cm}^3 \text{ mol}^{-1}$  as

$$\chi = -0.792\,015\,3(4) \times 10^{-6} \left\langle \psi \left| \sum_{i=1}^3 r_i^2 \right| \psi \right\rangle, \quad (12)$$

and the expectation value is expressed in atomic units. For the  $^2S$  ground states of the atomic system studied in this work, the values of  $\chi$  are tabulated in Table X. Adjustment for finite nuclear mass has not been made to the entries listed in Table X.

TABLE IV. Expectation values for the  $^2S$  ground state of B III. The notation  $[n]$  signifies  $\times 10^n$ .

Expectation value	Number of terms					
	30	100	200	300	400	503
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	2.342 310 6[1]	2.342 440 3[1]	2.342 453 2[1]	2.342 457 0[1]	2.342 460 2[1]	2.342 460 4[1]
$\langle -\frac{5}{r_i} \rangle$	-5.112 819 2[1]	-5.112 752 7[1]	-5.112 761 0[1]	-5.112 762 1[1]	-5.112 762 6[1]	-5.112 762 7[1]
$\langle \frac{1}{r_{ij}} \rangle$	4.281 981	4.278 721	4.278 545	4.278 480	4.278 423	4.278 419
$\langle r_i \rangle$	2.280 464	2.283 067	2.282 870	2.282 850	2.282 849	2.282 848
$\langle r_i^2 \rangle$	3.388 967	3.399 178	3.398 127	3.398 100	3.398 099	3.398 093
$\langle r_i^3 \rangle$	6.869 624	6.906 564	6.902 561	6.902 680	6.902 638	6.902 609
$\langle r_{ij} \rangle$	3.832 429	3.836 948	3.836 548	3.836 504	3.836 502	3.836 499
$\langle r_{ij}^2 \rangle$	6.807 428	6.827 424	6.825 381	6.825 333	6.825 330	6.825 319
$\langle \delta(\mathbf{r}_i) \rangle$	7.106 810[1]	7.137 276[1]	7.142 308[1]	7.146 520[1]	7.145 873[1]	7.145 863[1]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	3.195 865[1]	3.154 936[1]	3.147 160[1]	3.146 389[1]	3.147 815[1]	3.147 788[1]
$\langle \nabla_i \cdot \nabla_i \rangle$	-6.261 573[-1]	-6.086 252[-1]	-6.070 166[-1]	-6.063 944[-1]	-6.061 096[-1]	-6.060 892[-1]
$\eta$	1.000 139 9	1.000 032 9	1.000 010 6	1.000 005 2	1.000 000 8	1.000 000 4
Energy	-23.423 106	-23.424 403	-23.424 532	-23.424 570	-23.424 602	-23.424 604

TABLE V. Expectation values for the  $^2S$  ground state of C IV. The notation  $[n]$  signifies  $\times 10^n$ .

Expectation value	Number of terms					
	100	200	300	400	500	561
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	3.477 537 6[1]	3.477 548 1[1]	3.477 548 7[1]	3.477 550 7[1]	3.447 550 9[1]	3.477 550 9[1]
$\langle -\frac{6}{r_i} \rangle$	-7.485 718 4[1]	-7.485 720 1[1]	-7.485 720 1[1]	-7.485 720 3[1]	-7.485 720 3[1]	-7.485 720 3[1]
$\langle \frac{1}{r_{ij}} \rangle$	5.306 432 0	5.306 238 8	5.306 227 1	5.306 188 4	5.306 184 4	5.306 184 1
$\langle r_i \rangle$	1.812 810	1.812 794	1.812 795	1.812 795	1.812 796	1.812 796
$\langle r_i^2 \rangle$	2.098 807	2.098 787	2.098 795	2.098 795	2.098 798	2.098 797
$\langle r_i^3 \rangle$	3.309 217	3.309 300	3.309 256	3.309 243	3.309 252	3.309 249
$\langle r_{ij} \rangle$	3.027 859	3.027 839	3.027 841	3.027 841	3.027 843	3.027 843
$\langle r_{ij}^2 \rangle$	4.214 139	4.214 142	4.214 155	4.214 153	4.214 160	4.124 159
$\langle \delta(\mathbf{r}_i) \rangle$	1.269 181[2]	1.269 312[2]	1.269 763[2]	1.269 600[2]	1.269 652[2]	1.269 640[2]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	6.291 225[1]	6.284 167[1]	6.281 042[1]	6.282 295[1]	6.281 925[1]	6.281 609[1]
$\langle \nabla_i \cdot \nabla_i \rangle$	-7.616 322[-1]	-7.608 664[-1]	-7.603 996[-1]	-7.602 017[-1]	-7.601 849[-1]	-7.601 836[-1]
$\eta$	1.000 011 6	1.000 002 8	1.000 002 2	1.000 000 3	1.000 000 2	1.000 000 2
Energy	-34.775 376	-34.775 481	-34.775 487	-34.775 507	-34.775 509	-34.775 509

TABLE VI. Expectation values for the  $^2S$  ground state of N v. The notation  $[n]$  signifies  $\times 10^n$ .

Expectation value	Number of terms					
	100	200	300	400	500	561
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	4.837 675 8[1]	4.837 684 5[1]	4.837 687 3[1]	4.837 689 4[1]	4.837 689 6[1]	4.837 689 6[1]
$\langle -\frac{7}{r_i} \rangle$	-1.030 857 61[2]	-1.030 857 71[2]	-1.030 885 774[2]	-1.030 857 75[2]	-1.030 857 75[2]	-1.030 857 75[2]
$\langle \frac{1}{r_{ij}} \rangle$	6.332 245 5	6.332 080 7	6.332 026 7	6.331 986 5	6.331 982 5	6.331 982 1
$\langle r_i \rangle$	1.505 328	1.505 319	1.505 320	1.505 320		
$\langle r_i^2 \rangle$	1.428 062	1.428 064	1.428 066	1.428 065		
$\langle r_i^3 \rangle$	1.842 217	1.842 313	1.842 281	1.842 276		
$\langle r_{ij} \rangle$	2.504 049	2.504 041	2.504 041	2.504 041		
$\langle r_{ij}^2 \rangle$	2.866 388	2.866 418	2.866 419	2.866 418		
$\langle \delta(\mathbf{r}_i) \rangle$	2.056 151[2]	2.056 342[2]	2.056 960[2]	2.056 734[2]	2.056 803[2]	2.056 786[2]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	1.096 367[2]	1.095 347[2]	1.094 925[2]	1.095 132[2]	1.095 084[2]	1.095 036[2]
$\langle \nabla_i \cdot \nabla_i \rangle$	-9.166 250[-1]	-9.156 208[-1]	-9.150 437[-1]	-9.148 011[-1]		
$\eta$	1.000 008 9	1.000 003 2	1.000 001 6	1.000 000 2	1.000 000 1	1.000 000 1
Energy	-48.376 758	-48.376 845	-48.376 873	-48.376 894	-48.376 896	-48.376 896

TABLE VII. Expectation values for the  $^2S$  ground state of O vi. The notation  $[n]$  signifies  $\times 10^n$ .

Expectation value	Number of terms					
	100	200	300	400	500	561
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	6.422 839 9[1]	6.422 848 8[1]	6.422 851 7[1]	6.422 853 8[1]	6.422 854 0[1]	6.422 854 0[1]
$\langle -\frac{8}{r_i} \rangle$	-1.358 138 47[2]	-1.358 138 52[2]	-1.358 138 55[2]	-1.358 138 56[2]	-1.358 138 55[2]	-1.358 138 55[2]
$\langle \frac{1}{r_{ij}} \rangle$	7.357 049 8	7.356 876 1	7.356 820 8	7.356 780 0	7.356 775 9	7.356 775 5
$\langle r_i \rangle$	1.287 829	1.287 826	1.287 826	1.287 826	1.287 826	1.287 826
$\langle r_i^2 \rangle$	1.035 548	1.035 559	1.035 559	1.035 559	1.035 560	1.035 560
$\langle r_i^3 \rangle$	1.131 001	1.131 084	1.131 064	1.131 062	1.131 064	1.131 063
$\langle r_{ij} \rangle$	2.136 022	2.136 022	2.136 022	2.136 022	2.136 023	2.136 023
$\langle r_{ij}^2 \rangle$	2.077 897	2.077 936	2.077 935	2.077 934	2.077 936	2.077 936
$\langle \delta(\mathbf{r}_i) \rangle$	3.115 804[2]	3.116 035[2]	3.116 839[2]	3.116 541[2]	3.116 629[2]	3.116 604[2]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	1.747 136[2]	1.745 775[2]	1.745 217[2]	1.745 510[2]	1.745 450[2]	1.745 382[2]
$\langle \nabla_i \cdot \nabla_i \rangle$	-1.071 879	-1.070 667	-1.069 989	-1.069 706	-1.069 681	-1.069 679
$\eta$	1.000 006 8	1.000 002 5	1.000 001 2	1.000 000 2	1.000 000 1	1.000 000 1
Energy	-64.228 399	-64.228 448	-64.228 517	-64.228 538	-64.228 540	-64.228 540

TABLE VIII. Expectation values for the  $^2S$  ground state of F VII. The notation  $[n]$  signifies  $\times 10^n$ .

Expectation value	Number of terms					
	100	200	300	400	500	561
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	8.233 019 2[1]	8.233 028 3[1]	8.233 031 3[1]	8.233 033 4[1]	8.233 033 6[1]	8.233 033 6[1]
$\langle -\frac{9}{r_i} \rangle$	-1.730 416 55[2]	-1.730 416 60[2]	-1.730 416 62[2]	-1.730 416 63[2]	-1.730 416 63[2]	-1.730 416 63[2]
$\langle \frac{1}{r_{ij}} \rangle$	8.381 271 2	8.381 093 1	8.381 036 8	8.380 995 3	8.380 991 1	8.380 990 8
$\langle r_i \rangle$	1.125 616	1.125 613	1.125 613	1.125 613	1.125 614	1.125 614
$\langle r_i^2 \rangle$	7.857 124[-1]	7.857 196[-1]	7.857 192[-1]	7.857 192[-1]	7.857 197[-1]	7.857 196[-1]
$\langle r_i^3 \rangle$	7.442 732[-1]	7.443 245[-1]	7.443 123[-1]	7.443 114[-1]	7.443 123[-1]	7.443 120[-1]
$\langle r_{ij} \rangle$	1.862 897	1.862 896	1.862 896	1.862 896	1.862 896	1.862 896
$\langle r_{ij}^2 \rangle$	1.576 161	1.576 186	1.576 184	1.576 184	1.576 185	1.576 185
$\langle \delta(\mathbf{r}_i) \rangle$	4.488 650[2]	4.488 964[2]	4.489 983[2]	4.489 603[2]	4.489 713[2]	4.489 681[2]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	2.611 352[2]	2.609 624[2]	2.608 945[2]	2.609 355[2]	2.609 276[2]	2.609 187[2]
$\langle \nabla_i \cdot \nabla_j \rangle$	-1.227 367	-1.225 924	-1.225 137	-1.224 812	-1.224 781	-1.224 779
$\eta$	1.000 005 5	1.000 002 0	1.000 001 0	1.000 000 1	1.000 000 1	1.000 000 1
Energy	-82.330 192	-82.330 283	-82.330 313	-82.330 334	-82.330 336	-82.330 336

TABLE IX. Expectation values for the  $^2S$  ground state of Ne VIII. The notation  $[n]$  signifies  $\times 10^n$ .

Expectation value	Number of terms					
	80	200	300	400	500	561
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	1.026 819 57[2]	1.026 821 76[2]	1.026 822 06[2]	1.026 822 27[2]	1.026 822 29[2]	1.026 822 29[2]
$\langle -\frac{10}{r_i} \rangle$	-2.147 693 31[2]	-2.147 693 01[2]	-2.147 693 03[2]	-2.147 693 04[2]	-2.147 693 03[2]	-2.147 693 03[2]
$\langle \frac{1}{r_{ij}} \rangle$	9.405 417 2	9.404 949 1	9.404 890 2	9.404 849 6	9.404 845 3	9.404 844 9
$\langle r_i \rangle$	9.998 627[-1]	9.998 801[-1]	9.998 800[-1]	9.998 802[-1]	9.998 804[-1]	9.998 803[-1]
$\langle r_i^2 \rangle$	6.166 657[-1]	6.167 411[-1]	6.167 405[-1]	6.167 406[-1]	6.167 409[-1]	6.167 409[-1]
$\langle r_i^3 \rangle$	5.156 644[-1]	5.158 996[-1]	5.158 915[-1]	5.158 913[-1]	5.158 918[-1]	5.158 917[-1]
$\langle r_{ij} \rangle$	1.651 957	1.651 992	1.651 992	1.651 992	1.651 992	1.651 992
$\langle r_{ij}^2 \rangle$	1.236 757	1.236 918	1.236 916	1.236 916	1.236 917	1.236 917
$\langle \delta(\mathbf{r}_i) \rangle$	6.214 685[2]	6.215 717[2]	6.216 998[2]	6.216 506[2]	6.216 640[2]	6.216 599[2]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	3.714 489[2]	3.716 940[2]	3.716 356[2]	3.716 656[2]	3.716 557[2]	3.716 443[2]
$\langle \nabla_i \cdot \nabla_i \rangle$	-1.386 319	-1.381 322	-1.380 410	-1.380 056	-1.380 020	-1.380 018
$\eta$	1.000 004 9	1.000 001 6	1.000 000 8	1.000 000 1	1.000 000 1	1.000 000 1
Energy	-102.681 957	-102.682 176	-102.682 206	-102.682 227	-102.682 229	-102.682 229

TABLE X. Nuclear magnetic shielding constants and diamagnetic susceptibilities for the  $^2S$  ground states of selected members of the Li I isoelectronic series. The notation  $[n]$  signifies  $\times 10^n$ .

Species	Nuclear magnetic shielding Constant (a.u.)	Diamagnetic susceptibility ( $\text{cm}^3 \text{mol}^{-1}$ )
Li I	1.014 990 4[-4]	-1.453 72[-6]
B III	1.815 077 2[-4]	-2.691 342[-6]
C IV	2.214 582 2[-4]	-1.662 279[-6]
N V	2.614 027 5[-4]	-1.131 049[-6]
O VI	3.013 447 0[-4]	-8.201 794[-7]
F VII	3.412 853 4[-4]	-6.223 019[-7]
Ne VIII	3.812 252 6[-4]	-4.884 682[-7]

### C. Specific mass shift

The nonrelativistic form of the specific mass shift is given by

$$\Delta E_{\text{SMS}} = -\frac{\mu}{M} \left\langle \psi \left| \sum_{i < j}^3 \nabla_i \cdot \nabla_j \right| \psi \right\rangle, \quad (13)$$

where  $\mu$  is the reduced electron mass,

$$\mu = \frac{m_e M}{m_e + M}, \quad (14)$$

and  $m_e$  and  $M$  are the mass of the electron and the mass of the nucleus, respectively. The values of  $M$  for the atomic systems studied are taken from the most recent atomic mass tables of Wapstra and Audi,<sup>28</sup> and have been corrected for the mass of the appropriate number of electrons for each species. The specific mass shifts are collected in Table XI.

TABLE XI. Specific mass shifts  $\Delta E_{\text{SMS}}$  for the  $^2S$  ground states of selected members of the Li I isoelectronic series.

Species	Number of basis functions for wave function	$\Delta E_{\text{SMS}}$ (a.u.)
<sup>6</sup> Li I	602	$2.7533 \times 10^{-5}$
<sup>7</sup> Li I	602	$2.3605 \times 10^{-5}$
<sup>10</sup> B III	503	$3.3213 \times 10^{-5}$
<sup>11</sup> B III	503	$3.0207 \times 10^{-5}$
<sup>12</sup> C IV	561	$3.4760 \times 10^{-5}$
<sup>13</sup> C IV	561	$3.2077 \times 10^{-5}$
<sup>14</sup> N V	400	$3.5846 \times 10^{-5}$
<sup>15</sup> N V	400	$3.3463 \times 10^{-5}$
<sup>16</sup> O VI	561	$3.6696 \times 10^{-5}$
<sup>17</sup> O VI	561	$3.4527 \times 10^{-5}$
<sup>18</sup> O VI	561	$3.2609 \times 10^{-5}$
<sup>19</sup> F VII	561	$3.5374 \times 10^{-5}$
<sup>20</sup> Ne VIII	561	$3.7876 \times 10^{-5}$
<sup>21</sup> Ne VIII	561	$3.6069 \times 10^{-5}$
<sup>22</sup> Ne VIII	561	$3.4433 \times 10^{-5}$

### D. Transition isotope shift

The transition isotope shift for a pair of isotopes  $^{A_1}X$  and  $^{A_2}X$  (with mass numbers  $A_1 > A_2$ ) is calculated as

$$\begin{aligned} \Delta E_{\text{TIS}} &\equiv (\Delta E_{\text{SMS}}^{A_1 X^+} - \Delta E_{\text{SMS}}^{A_1 X}) - (\Delta E_{\text{SMS}}^{A_2 X^+} - \Delta E_{\text{SMS}}^{A_2 X}) \\ &\equiv (\Delta E_{\text{SMS}}^{A_2 X} - \Delta E_{\text{SMS}}^{A_1 X}) - (\Delta E_{\text{SMS}}^{A_2 X^+} - \Delta E_{\text{SMS}}^{A_1 X^+}), \end{aligned} \quad (15)$$

where + signifies the ionization limit of the species. In the second line of Eq. (15), the terms in parentheses represent, respectively, the isotope shifts for the three-electron and two-electron atomic systems. These individual isotope shifts are tabulated in Table XII, along with the transition isotope shift defined by Eq. (15). The results for the two-electron shift reported in Table XII have been evaluated using the values of  $\langle \nabla_1 \cdot \nabla_2 \rangle$  calculated by Pekeris.<sup>1,4</sup>

### E. Hyperfine coupling constant

The Fermi contact operator evaluated in this work is

$$H_F = \frac{2}{3} \mu_0 g_e g_I \mu_B \mu_N \mathbf{I} \cdot \sum_{i=1}^3 \delta(\mathbf{r}_i) \mathbf{S}_i, \quad (16)$$

which can be rewritten as an effective operator

$$H_F \equiv h A_J \mathbf{I} \cdot \mathbf{J}, \quad (17)$$

where  $\mu_0$  is the vacuum permeability,  $g_e$  is the electronic  $g$  factor (incorporating bound-state corrections),  $g_I$  is the nuclear  $g$  factor,  $\mu_B$  and  $\mu_N$  are the Bohr and nuclear magneton, respectively,  $\mathbf{I}$  is the nuclear spin operator,  $\mathbf{S}_i$  is the electron spin operator for electron  $i$ ,  $\delta(\mathbf{r}_i)$  is the Dirac  $\delta$  function,  $h$  is Planck's constant,  $\mathbf{J}$  is the total electronic angular momentum operator, and  $A_J$  is the hyperfine coupling constant. The connection between the coupling constant (expressed in MHz) and the expectation value  $f$ , Eq. (8), is (using a conventional grouping of terms)

$$A_{1/2} = \left[ \frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} \right] \frac{g_e \mu_I f}{3I}. \quad (18)$$

Using the most recent<sup>27</sup> values of  $\mu_B$ ,  $\mu_N$ ,  $h$ , and  $a_0$ , Eq. (18) simplifies to

$$A_{1/2} = 95.410\,67(7) \left[ \frac{g_e \mu_I}{3I} \right] f, \quad (19)$$

and the error estimate for the collection of fundamental constants is shown in parentheses. The values of the hyperfine coupling constant obtained using Eq. (19) are collected in Table XIII.

TABLE XII. Transition isotope shifts  $\Delta E_{\text{TIS}}$  for the  $^2S$  ground states of selected members of the Li I isoelectronic series.

Isotope pair	$\Delta E_{\text{shift}}$ (three-electron species) (GHz)	$\Delta E_{\text{shift}}$ (two-electron ion) (GHz) <sup>a</sup>	$\Delta E_{\text{TIS}}$ (GHz)
$^6\text{Li}, ^7\text{Li}$	25.8436	24.7416	1.1020
$^{10}\text{B}, ^{11}\text{B}$	19.7796	18.0390	1.7406
$^{12}\text{C}, ^{13}\text{C}$	17.6496	15.9118	1.7378
$^{14}\text{N}, ^{15}\text{N}$	15.6794	14.0223	1.6571
$^{16}\text{O}, ^{17}\text{O}$	14.2656	12.6833	1.5823
$^{16}\text{O}, ^{18}\text{O}$	26.8896	23.9070	2.9826
$^{17}\text{O}, ^{18}\text{O}$	12.6240	11.2237	1.4003
$^{20}\text{Ne}, ^{21}\text{Ne}$	11.8896	10.4859	1.4037
$^{20}\text{Ne}, ^{22}\text{Ne}$	22.6566	19.9816	2.6750
$^{21}\text{Ne}, ^{22}\text{Ne}$	10.7670	9.4957	1.2713

<sup>a</sup>Computed from the values of  $\langle \psi | \nabla_1 \cdot \nabla_2 | \psi \rangle$  given in Refs. 1 and 4.

## V. DISCUSSION

### A. The nonrelativistic ground-state energy

A number of extended basis set calculations have been carried out on members of the Li I isoelectronic series, but none has reached the accuracy obtained in this study.<sup>18,19,29–33</sup> Table XIV lists the percentage of the correlation energy obtained using the wave functions constructed in this study. Only four significant figures have been retained for the calculated correlation energies, in part, because of difficulties in deciding the reliability of the next decimal digit for the calculated nonrelativistic energies. Only accurate lower-bound calculations will resolve this issue satisfactorily. The Hartree-Fock values for  $E_{\text{NR}}$  are taken from Refs. 32 and 34 and the semiempirical estimates of the “exact”  $E_{\text{NR}}$  are taken from Refs. 31 and 35–37. For all systems in this investigation, over 99% of the correlation energy is obtained. This should make these wave functions particularly suited for the calculation of accurate values of the specific mass shifts and transition isotope shifts, properties which are known to be particularly sensitive to electron correlation effects. The present calculations yield energies ranging

TABLE XIII. Hyperfine coupling constants for the  $^2S$  ground states of selected members of the Li I isoelectronic series.

Species	Magnetic moment	Hyperfine coupling constant (MHz)
$^7\text{Li I}$	3.256 416	$4.0179 \times 10^2$
$^6\text{Li I}$	0.822 045	$1.5214 \times 10^2$
$^{10}\text{B III}$	1.8007	$1.2032 \times 10^3$
$^{11}\text{B III}$	2.6880	$3.5921 \times 10^3$
$^{13}\text{C IV}$	0.702 199	$5.6178 \times 10^3$
$^{14}\text{N V}$	0.403 47	$2.8135 \times 10^3$
$^{15}\text{N V}$	−0.282 98	$−3.9466 \times 10^3$
$^{17}\text{O VI}$	−1.8930	$−8.4161 \times 10^3$
$^{19}\text{F VII}$	2.627 27	$8.7307 \times 10^4$
$^{21}\text{Ne VIII}$	−0.661 40	$−1.0435 \times 10^4$

from  $\sim 14$  microhartrees for Li I to  $\sim 480$  microhartrees for Ne VIII above the literature estimates for  $E_{\text{NR}}$ . Unfortunately, the literature estimates may well be in error by several microhartrees (or more), since there is a lack of accurate values for the relativistic contributions, and there are uncertainties associated with estimating the Lamb shifts. For example, two common estimates of  $E_{\text{NR}}$  for Li I differ by 5 microhartrees from each other.<sup>31,36</sup> There is a clear need to have lower-bound estimates for  $E_{\text{NR}}$ , which will greatly assist in attaching limits on the accuracy of the present variational calculations. Such calculations are very difficult to make with Hylleraas-type wave functions for systems with more than two electrons, because of the rather obdurate integrals that arise. Extensions of the Fromm-Hill<sup>38</sup> work on the analytic evaluation of three-electron atomic integrals, to treat the cases needed for the lower-bound calculations, would be a valuable piece of work.

### B. Basis set selection

The basis set employed for each atom studied is very much biased towards a description of the energy-important region of configuration space, that is, the near-nuclear region. Since the size of the basis set is not the same for all species studied, it is not possible to comment on any trends in the accuracy of  $E_{\text{NR}}$  versus the nuclear charge. For the cases where the same selection of  $\{i, j, k, l, m, n\}$  terms is made (C IV, N V, O VI, F VII, and Ne VIII), the relative errors for  $E_{\text{NR}}$  are determined to be  $6.7 \times 10^{-4} \%$ ,  $7.9 \times 10^{-4} \%$ ,  $6.4 \times 10^{-4} \%$ ,  $5.4 \times 10^{-4} \%$ , and  $4.7 \times 10^{-4} \%$ , respectively. This might suggest that the basis set is more effective as the electronic charge cloud becomes increasingly contracted around the nucleus. Two cautionary notes, however, must be mentioned. The relative errors given depend on the quality of the semiempirical estimates of  $E_{\text{NR}}$ . It is also possible that the orbital exponents employed for these five cases are not equally optimal in terms of their impact on the computed  $E_{\text{NR}}$ .

The purpose of the present investigation was not solely

TABLE XIV. Calculated correlation energies using the wave functions of the present study.

Species	Correlation energy		Percentage of correlation energy for wave functions in this study
	Calculated in this study	Semiempirical estimate <sup>a</sup>	
Li I	0.045 33	0.045 35	99.96
B III	0.048 62	0.048 75	99.73
C IV	0.049 45	0.049 69	99.52
N V	0.050 05	0.050 44	99.23
O VI	0.050 50	0.050 91	99.19
F VII	0.050 85	0.051 29	99.14
Ne VIII	0.051 13	0.051 61	99.07

<sup>a</sup>Based on data taken from Refs. 31, 32, and 34–37.

the calculation of accurate  $E_{NR}$  values with the most compact basis set expansions. Since a number of different expectation values were of interest, a more balanced basis set was selected. From prior experience it was known what likely impact a particular selection of basis functions would have on the computed  $E_{NR}$ . It is, however, an extremely difficult task to estimate how a great number of the basis functions will influence the computed energy and other expectation values. The well-known difficulty is that particular basis functions that might have a very minor impact on improving the computed  $E_{NR}$  may be important for the accurate evaluation of a target expectation value. The systematic inclusion of all terms to  $\omega=4$  avoids the possibility that any important terms for a particular expectation value are omitted. A large number of terms for  $\omega=5$  have been included for most atoms as well as a selection of terms that will have significance for describing the long-range region of the electronic charge cloud.

The most important basis functions as far as the energy expectation value is concerned are generally combinations of  $\{i, j, k\}$  sets such as  $\{0, 0, 1\}$  and  $\{i, 0, 1\}$ , with  $i \geq 1$ , coupled with  $\{l, m, n\}$  sets involving a single interelectronic function  $r_{ij}^n$ , with  $n=1$  typically being the most significant value. Basis functions with  $\{l, m, n\}$  all odd slow the calculation considerably because of the more difficult integrals that must be evaluated. From prior experience, such terms do not have much impact on the energy. This was the justification for deleting certain terms from the basis set employed for the last five members of the Li I series studied in this work.

### C. Convergence characteristics

An immediate inspection of Tables III–IX indicates the slow overall convergence of these variational calculations. If the semiempirical estimates of  $E_{NR}$  are accepted, the apparent convergence for  $E_{NR}$  in the last quoted significant figure for each atom is illusory. In each case, the last 100 or more basis functions added lead to a lowering of the energy by less than 2 microhartrees. However, the differences [ $E_{NR}$  (present study) –  $E_{NR}$  (semiempirical estimate exact)] for the series in units of microhartrees are Li I 14, B III  $1.3 \times 10^2$ , C IV  $2.3 \times 10^2$ , N V  $3.8 \times 10^2$ , O VI  $4.1 \times 10^2$ , F VII  $4.4 \times 10^2$ , and Ne VIII

$4.8 \times 10^2$ . It is therefore clear that a very much larger basis set is required if convergence of the energy to within a few microhartrees of the exact  $E_{NR}$  is desired. To sharpen the discussion of the convergence of the energy expectation values requires accurate lower-bound estimates of  $E_{NR}$ .

The slow convergence is not simply a reflection of the fixed components employed. Calculations presently underway on Li I using a Hylleraas-type basis set with optimized exponents also show rather slow convergence. Fixed exponents do suffer the obvious limitation that as the size of the basis set increases, more  $s$  orbitals with increased diffuse character are included, and for such basis functions the exponents become less optimal.

The convergence of the higher moments of  $\langle r_i^n \rangle$ , in this work  $\langle r_i^3 \rangle$ , will reflect in part how well the “tail region” of the electronic charge cloud is described. The basis set has only a modest number of terms that will describe this region. For Li I the value of  $\langle r_i^3 \rangle$  has apparently converged to approximately four to five significant figures. For the other members of the series, the apparent convergence of this particular expectation value improves roughly with increasing nuclear charge, to yield approximately seven decimal digits of precision for the last couple of members studied. With the increased concentration of electronic charge around the nucleus, the lack of a large number of more diffuse  $s$  orbitals in the basis set becomes less important for the improved convergence of matrix elements that emphasize the more distant region from the nucleus, such as  $\langle r_i^3 \rangle$ .

Inspection of Tables III–IX indicates that the convergence of a number of expectation values shows nonmonotonic behavior for the basis sets employed in this work. The kinetic energy and  $\langle \nabla_i \cdot \nabla_j \rangle$  converge monotonically for each species; the electron-nuclear and electron-electron potential-energy matrix elements generally converge monotonically, or are very close to monotonic. The electron density at the nucleus and the Fermi-contact interaction both show nonmonotonic convergence for each atom studied. Both of these properties depend sensitively on the charge cloud at the nucleus, a region which is rather difficult to adequately describe with even a rather substantial number of Hylleraas functions. Basis functions that better mimic the expected near-nuclear structure of the wave function,<sup>39</sup> e.g., those hav-

ing certain logarithmic coordinate dependency, would probably lead to enhanced convergence of  $\rho(0)$  and  $f$ , as well as other expectation values. For two-electron systems, improved convergence of the energy has been observed with logarithmic-dependent terms in the basis set.<sup>8-10</sup> Rather recalcitrant integrals emerge for the three-electron problem using logarithmic terms. For the other expectation values listed in Tables III-IX, there do not appear to be any clear trends in predicting monotonic versus nonmonotonic convergence as a function of increased nuclear charge for the basis sets employed. The lack of monotonic behavior makes attempts at determining extrapolated estimates rather error prone.

#### D. Effects of one versus two spin eigenfunctions

A number of papers have discussed the situation of including more than one spin eigenfunction in the basis set in order to obtain accurate expectation values.<sup>16,19,40-44</sup> Much of the available numerical information is derived from wave functions of limited size. Larsson has presented detailed results specifically for the effect of the second spin function on the energy and Fermi contact interaction.<sup>19</sup> In that work, the energy was found to be relatively insensitive to the presence of the second spin function in the basis set, but it had a substantial impact on the accuracy of the Fermi contact interaction. Since the wave functions of the present study are considerably larger than the basis set employed by Larsson, which had 60 terms with the first spin eigenfunction [Eq. (3a)] and 40 with the second spin eigenfunction, an investigation of how the second spin eigenfunction alters the expectation values was undertaken.

The results of the calculations when only one spin eigenfunction is included can be obtained from the Physics Auxiliary Publication Service.<sup>26</sup> For Li I, the Fermi contact interaction for the final 332-term wave function is approximately 0.8% too high, compared with the result from the 602-term wave function (Table III). A similar situation was found in a previous calculation using a somewhat smaller basis set.<sup>16</sup> Since the size of the Hylleraas wave function for Li I having only the first spin eigenfunction is quite large (332 terms), it is apparent that a great many terms would be needed for a high-accuracy calculation of  $f$  using only the first spin eigenfunction in the basis set. As the nuclear charge increases, the correspondence between the values of  $f$  calculated with the different wave functions (one spin eigenfunction versus both spin eigenfunctions included) improves substantially, the relative errors dropping from  $\sim 0.06\%$  for B III to less than  $0.02\%$  for Ne VIII. These small differences are still typically larger than the differences observed for other expectation values, and are thus not attributable entirely to size effects in the two basis sets.

For all the other expectation values evaluated, the correspondence between the final results for the two different wave functions is generally excellent. It is clear that the expectation values of the spin-independent operators can be accurately evaluated using only the first spin eigenfunction in the basis set; however, the spin-dependent Fermi contact interaction requires both spin

eigenfunctions in the basis set, even for wave function of considerable size.

The convergence characteristics for the single spin eigenfunction calculations are similar to those reported above for the wave functions that include both spin eigenfunctions in the basis set. A number of expectation values computed using single spin eigenfunction wave functions show nonmonotonic convergence. The interested reader can consult the results available from PAPS for further details.

#### E. Some comparisons with experiment

For the more highly charged members of the Li I isoelectronic series there is generally a shortage of experimental results. Hyperfine coupling constants are available for the  $^2S$  ground states of Li I,<sup>45</sup> Be II,<sup>46</sup> and F VII.<sup>47</sup> The transition isotope shift has been measured<sup>48,49</sup> for the  $^2S$  ground state of Li I but no measurements appear to have been reported for other members of the series.<sup>50</sup>

The "experimental" value of  $f$  can be computed using Eq. (19) and the values of  $g_e$ ,  $I$ ,  $\mu_I$ , and  $A_{1/2}$  for the species of interest. For  $^7\text{Li}$  I the values<sup>45,51</sup>  $g_e = 2.002\,301\,9$ ,  $\mu_I^0$  (the unshielded moment) =  $3.256\,416$ , and  $A_{1/2} = 401.752\,0433$  MHz were employed, which leads to  $f$  (experimental) =  $2.906\,06$  a.u. This value is slightly smaller than a value of  $2.9096$  a.u. which can be found in several references. The source of the difference is that the latter value arises when the electron magnetic moment anomaly is neglected. This value may also possibly arise when different choices for the experimental parameters are employed in Eq. (18). The value of  $f$  reported in Table III needs to be slightly adjusted for the effects of finite nuclear mass. The correction factor is

$$\left[1 + \frac{m_e}{M_{^7\text{Li}}}\right]^{-3} \approx \left[1 - \frac{3m_e}{M_{^7\text{Li}}}\right] \sim 0.999\,765.$$

This lowers the calculated  $f$  to yield  $f = 2.9057$ , which is in excellent agreement with the experimental value of  $f$ . Relativistic corrections are expected to be fairly small for Li I.<sup>52</sup> A great number of calculations have been carried out to determine  $f$  for the  $^2S$  ground state of Li I. One extensive summary can be found in Ref. 53.

For the other members of the Li I series studied, less accurate values of  $\mu_I^0$  are available. Also, there is a lack of information on the electronic  $g$  factors for these ions. In computing the hyperfine coupling constants listed in Table XIII the free-electron  $g_e$  value was employed in Eq. (19), for all atoms except  $^6\text{Li}$  and  $^7\text{Li}$ .

An experimental measurement<sup>47</sup> for the 197-keV level in  $^{19}\text{F}$  VII yields a hyperfine splitting for the  $^2S$  state of  $\nu = 73.1(1.5)$  GHz. Making use of Eq. (19), the frequency is calculated to be

$$\begin{aligned} \nu &= \left[ \frac{2I+1}{2} \right] A_{1/2} \\ &= 31.804\,44(2I+1)g_I f \\ &= 71.88(15) \text{ GHz}; \end{aligned}$$

on employing for the state of  $^{19}\text{F}$  of interest:  $I = \frac{5}{2}$  and  $g_I = 1.442(3)$  and the value of  $f$  is taken from Table III. Garpman *et al.*<sup>54</sup> have estimated that relativistic effects lead to an increase of about 0.9% for the hyperfine coupling constant of F VII compared to the calculated non-relativistic value. This increment leads to closer agreement between the calculated and experimental hyperfine frequencies.

The transition isotope shift  $\Delta E_{\text{TIS}}$  is particularly sensitive to correlation effects and, as a consequence, provides one stringent test on the quality of the wave function. For the  $^2\text{S}$  ground state of Li I the computed  $\Delta E_{\text{TIS}}$  is 1.102 GHz, compared with the recent experimental values of  $1.111 \pm 0.006$  GHz given by Lorenzen and Niemax<sup>48</sup> and  $1.108 \pm 0.008$  GHz given by Vadla *et al.*<sup>49</sup> Since the matrix elements are evaluated using first-order perturbation theory, a small shift in the aforementioned theoretical value would be obtained if the entire Hamiltonian, including the specific mass shift operator, was diagonalized. This approach was carried out in a previous work<sup>22</sup> with a smaller basis set. Unfortunately, only the first-order perturbation theory results are available from the work of Pekeris<sup>4</sup> for  $\text{Li}^+$ , so a theoretically consistent calculation of the transition isotope shift cannot be performed.

## VI. CONCLUSIONS

The principal results of this study are the lowest upper-bound computational estimates for the nonrelativistic ground-state energies of Li I, B III, C IV, N V, O VI,

F VII, and Ne VIII. For the ground-state properties of the Li I series for which experimental results are available, the agreement with the computational values is quite good. Less encouraging is the apparently rather slow convergence of the calculations. The uncertainties and approximations involved in the estimation of the exact values of  $E_{\text{NR}}$  makes it particularly difficult to discuss the quality of the final computed  $E_{\text{NR}}$  values. Efforts to obtain sharp lower bounds on  $E_{\text{NR}}$  would be of considerable value.

For the higher- $Z$  members of the series studied, an adequate approach is to operate with just the first spin eigenfunction in the basis set. This, however, does not apply for Li I, if an accurate hyperfine coupling is required.

## ACKNOWLEDGMENTS

Financial assistance was provided by a University of Wisconsin-Eau Claire faculty seed grant, and acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support in the initial stages of this work. Support from the National Science Foundation (Grant No. PHY-8704125) and the Camille and Henry Dreyfus Foundation is appreciated. The calculations were made possible by a sizable allocation of computer time from the University of Wisconsin-Eau Claire Computer Center, and a grant of computer time at the National Center for Supercomputer Applications at the University of Illinois at Urbana-Champaign.

<sup>1</sup>C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

<sup>2</sup>C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

<sup>3</sup>C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).

<sup>4</sup>C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

<sup>5</sup>C. L. Pekeris, Phys. Rev. **127**, 509 (1962).

<sup>6</sup>Y. Accad, C. L. Pekeris, and B. Shift, Phys. Rev. **183**, 78 (1969).

<sup>7</sup>Y. Accad, C. L. Pekeris, and B. Shift, Phys. Rev. A **4**, 516 (1971).

<sup>8</sup>K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966).

<sup>9</sup>K. Frankowski, Phys. Rev. **160**, 1 (1967).

<sup>10</sup>D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. A **29**, 980 (1984).

<sup>11</sup>A. Kono and S. Hattori, Phys. Rev. A **34**, 1727 (1986); J. S. Sims and W. C. Martin, *ibid.* **37**, 2259 (1988).

<sup>12</sup>G. W. F. Drake, Nucl. Instrum. Methods B **31**, 7 (1988).

<sup>13</sup>W. C. Martin, Phys. Rev. A **29**, 1883 (1984).

<sup>14</sup>W. C. Martin, Phys. Rev. A **36**, 3575 (1987).

<sup>15</sup>F. W. King, Phys. Rev. A **38**, 6017 (1988).

<sup>16</sup>F. W. King and V. Shoup, Phys. Rev. A **33**, 2940 (1986).

<sup>17</sup>F. W. King and P. R. Dressel, J. Chem. Phys. **90**, 6449 (1989).

<sup>18</sup>E. A. Burke, Phys. Rev. **130**, 1871 (1963).

<sup>19</sup>S. Larsson, Phys. Rev. **169**, 49 (1968).

<sup>20</sup>Y. Öhrn and J. Nordling, J. Chem. Phys. **39**, 1864 (1963).

<sup>21</sup>R. A. Sack, J. Math. Phys. **5**, 245 (1964).

<sup>22</sup>F. W. King, Phys. Rev. A **34**, 4543 (1986). The value of  $\langle \nabla_1 \cdot \nabla_2 \rangle$  for  $\text{Li}^+$  quoted in this reference ( $-0.2889940$  a.u.)

should read  $-0.2889758$  a.u. This change alters the absolute shift for  $\text{Li}^+$  from 27.74318 to 24.74162 GHz and the isotope shift values reported in Table IV from 1.102 and 1.101 GHz to 1.103 and 1.102 GHz, respectively.

<sup>23</sup>J. F. Perkins, J. Chem. Phys. **48**, 1985 (1968).

<sup>24</sup>Y. K. Ho and B. A. P. Page, J. Comput. Phys. **17**, 122 (1975).

<sup>25</sup>J. F. Perkins, Phys. Rev. A **13**, 915 (1976).

<sup>26</sup>See AIP document No. PAPS PLRAA-40-1735-07 for 7 pages of tables reporting expectation values for Li I, B III, C IV, N V, O VI, F VII, and Ne VIII using only one spin eigenfunction. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The prepaid price is \$1.50 for a microfiche or \$5.00 for a photocopy. Airmail additional.

<sup>27</sup>E. R. Cohen and B. N. Taylor, Rev. Mod. Phys. **59**, 1121 (1987).

<sup>28</sup>A. H. Wapstra and G. Audi, Nucl. Phys. A **432**, 1 (1985).

<sup>29</sup>A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

<sup>30</sup>J. S. Sims and S. A. Hagstrom, Phys. Rev. A **11**, 418 (1975).

<sup>31</sup>J. Muszyńska, D. Papierowska, J. Pipin, and W. Woźnicki, Int. J. Quantum Chem. **22**, 1153 (1982).

<sup>32</sup>J. Pipin and Woźnicki, Chem. Phys. Lett. **95**, 392 (1983).

<sup>33</sup>Y. K. Ho, Int. J. Quantum Chem. **20**, 1072 (1981).

<sup>34</sup>E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

<sup>35</sup>C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev.

- 127, 830 (1962).
- <sup>36</sup>C. F. Bunge, Phys. Rev. A **16**, 2496 (1977).
- <sup>37</sup>C. F. Bunge, Phys. Rev. A **19**, 936 (1979).
- <sup>38</sup>D. M. Fromm and R. N. Hill, Phys. Rev. A **36**, 1013 (1987).
- <sup>39</sup>R. J. White and F. H. Stillinger, Phys. Rev. A **3**, 1521 (1971).
- <sup>40</sup>Z. W. Ritter, R. Paunz, and K. Appel, J. Chem. Phys. **35**, 571 (1961).
- <sup>41</sup>L. M. Delves, J. Chem. Phys. **46**, 2563 (1967).
- <sup>42</sup>U. Kaldor and F. E. Harris, Phys. Rev. **183**, 1 (1969).
- <sup>43</sup>J. C. Slater, Int. J. Quantum Chem. **4**, 561 (1970).
- <sup>44</sup>A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **15**, 2143 (1977).
- <sup>45</sup>A. Beckmann, K. D. Böklen, and D. Elke, Z. Phys. **270**, 173 (1974).
- <sup>46</sup>D. J. Wineland, J. J. Bollinger, and W. M. Itano, Phys. Rev. Lett. **50**, 628 (1983).
- <sup>47</sup>W. L. Randolph, J. Asher, J. W. Koen, P. Rowe, and E. Matthias, Hyperfine Interact. **1**, 145 (1975).
- <sup>48</sup>C.-J. Lorenzen and K. Niemax, J. Phys. B **15**, L139 (1982).
- <sup>49</sup>C. Vadla, A. Obrebski, and K. Niemax, Opt. Commun. **63**, 288 (1987).
- <sup>50</sup>W. H. King, *Isotope Shifts in Atomic Spectra* (Plenum, New York, 1984).
- <sup>51</sup>K. D. Böklen, W. Dankwort, E. Pitz, and S. Penselin, Z. Phys. **200**, 467 (1967).
- <sup>52</sup>I. Lindgren, Phys. Rev. A **31**, 1273 (1985).
- <sup>53</sup>J. E. Harriman, *Theoretical Foundations of Electron Spin Resonance* (Academic, New York, 1978), p. 271.
- <sup>54</sup>S. Garpman, I. Lindgren, J. Lindgren, and J. Morrison, Z. Phys. A **276**, 167 (1976).