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Calculations on the low-lying excited ^2S states of some members of the Li isoelectronic series

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The results of variational calculations using large Hylleraas basis sets are reported for some low-lying excited ^2S states of the Li I isoelectronic series for $3 \leq Z \leq 10$. The $3\,^2S$, $4\,^2S$, and $5\,^2S$ states are studied for Li I and Be II, and the $3\,^2S$ and $4\,^2S$ states are investigated for the other ions. The nonrelativistic energies obtained are the lowest-upper-bound estimates so far reported. In some cases the literature estimates of these energies are found to be in error, as they lie above the results of the present calculations. Hyperfine coupling constants, specific-mass shifts, transition isotope shifts, electron density at the nucleus, and the individual energy components are reported. The rates of convergence of the various expectation values are discussed.

I. INTRODUCTION

Considerable success has recently been achieved for the theoretical determination of the energy levels of excited states of various symmetry for the helium atom and members of its isoelectronic series.[1–7] Precision of the order of 1 part in 10^{10} to 1 part in 10^{17} has been achieved for various excited energy levels.[2–15] This very high level of precision has allowed an assessment of fine-structure details to be made for these systems.

For excited states of atomic three-electron systems, no calculations are available of a precision comparable to that mentioned above. A number of studies have been carried out to moderate precision on the excited states of Li I and a few excited states of some of the other members of the Li isoelectronic series.[16–34]

The present investigation has several goals. The first is to compute the nonrelativistic energy levels for several states to around the 50–100 μhartree (or better) level of accuracy. To reach a level of precision an order of magnitude beyond this would require somewhat larger basis sets, if the restrictions of fixed exponents and both spin eigenfunctions are retained. Fully optimized basis sets of about the size employed in this study would yield much higher levels of precision; however the CPU cost would be very high. Alternatively, Fock-type basis sets would be expected to have superior convergence characteristics,[1,35,36] but the matrix-element evaluations would be rather difficult.

The basis sets employed in the present investigation include both possible spin eigenfunctions. Terms involving the second spin eigenfunction are well known to lead only to a minor overall contribution to the energy, but greatly assist in the accurate calculation of hyperfine coupling constants.[37–40] Since one of the goals of the present study is the accurate calculation of the latter property, both spin eigenfunctions have been retained. If spin-dependent properties were not of interest, the present basis sets could be reduced in size by approximately 45%. The restriction to fixed exponents has been adopted for two reasons. In a recent investigation, compact analytic formulas were derived for the radial electronic density functions for the ^2S states of three-electron systems that are described by Hylleraas-type basis functions with fixed exponents.[41] Since there is very little published information that allows high-quality correlated electronic densities to be obtained for excited states, an objective of the present investigation was the construction of wave functions, a subset of which can be employed to calculate accurate electronic densities. These in turn open up an avenue to evaluate inexpensively, a number of (nondifferential, spin-independent) one-electron properties. An important advantage of fixed exponents is that it becomes feasible to store and retrieve integrals from a table held in memory (or on disk). This greatly reduces the CPU costs, as multiple evaluations of the same integral are not required.

Some recent measurements have been reported for the transition isotope shifts for various excited ^2S states of the lithium atom.[42,43] Since this is a challenging property to evaluate for the ground state, and even more so for the excited states, a goal of the present study is the accurate evaluation of these shifts.

A longer range goal is the indirect evaluation of the Lamb shifts for these states. To meet this objective, subsets of the wave functions determined in the present work will be utilized to evaluate the relativistic corrections for the energy levels of the systems studied herein.

II. THEORY

The theoretical approach employed in this study has been discussed elsewhere in the literature.[37,38,44–46] A brief statement is presented below. The trial wave function employed for each atom is

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

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

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

where the exponents i_μ, j_μ, k_μ, l_μ, m_μ, and n_μ are each ≥ 0. In Eq. (1) χ_μ 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.

Since a sequence of members of the Li I series is under investigation, it is appropriate to consider the possibilities of carrying out a Z-dependent scale change. If the exponents of the basis orbitals of Eq. (2) are expressed in the form

$$\alpha_\mu = Za_\mu, \quad \beta_\mu = Zb_\mu, \quad \text{and} \quad \gamma_\mu = Zc_\mu \ , \quad (5)$$

then the scale change

$$r_i' = Zr_i, \quad r_{ij}' = Zr_{ij} \quad (6)$$

can be used to transform Eq. (4) to the form (on dropping the prime)[30]

$$Z^{-2}H = \sum_{i=1}^{3} \left[-\frac{1}{2}\nabla_i^2 - \frac{1}{r_i} \right] + \sum_{i=1}^{3} \sum_{j>i}^{3} \frac{1}{Zr_{ij}} \ . \quad (7)$$

If fixed exponents are employed, that is $a_\mu = a$, $b_\mu = b$, and $c_\mu = c$ (for all μ), and if the a, b, and c values adequately describe the same state for several members of the series, a very considerable reduction in computational time can be achieved. Unfortunately, for the states of interest in this work, a suitable fixed set of exponents is not available. From the results of an extensive number of calculations using small trial basis sets, the scaled exponent a for the core electrons is (not surprisingly) little changed for several excited states of a particular Z, and for changes in Z in the range $3 \leq Z \leq 10$. The value of a ranged from ~ 0.92 to 0.997. The scaled exponent c describing the valence electron varied widely, depending on both the excited state for a fixed Z, and on the value of Z for a fixed excited state. This behavior is, of course, to be expected. The c values ranged from ~ 0.04 to ~ 0.43. If the restriction to fixed exponents is dropped, and several repetitions of the important basis functions are included with exponents appropriate to the members of the Li I series of interest, then the scaled approach could be effectively implemented, provided care is taken to avoid possible linear dependence problems. This approach was not adopted because of our objective for the electronic density determination mentioned in Sec. I.

Atomic units 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). Details on the evaluation of the required matrix elements have been given elsewhere.[37,44,45,47]

III. COMPUTATIONAL DETAILS

A. Choice of basis functions

The exponents for each state were determined by optimizing the exponents for a small-term wave function containing 36 basis functions. The restriction $\alpha_\mu = \beta_\mu = \alpha$ and $\gamma_\mu = \gamma$ (all μ) has been adopted. The trial basis functions employed for the different states are available from the Physics Auxiliary Publication Service.[48] The final set of exponents employed is collected in Table I. Not unexpectedly, the exponents for the core electrons for each atomic species change only slightly from one excited state to the next, nor do they change very much with respect to the values obtained for the ground states (see Ref. 40 for the ground-state exponents). Four different sized basis sets were employed. For the $3S$ state 447 basis functions were employed for Li I and Be II, and 442 basis functions were employed for the other members of the Li I series to $Z=10$. The only difference between the two sets is the deletion of five terms having factors of $i=5$ (2 terms), $l=5$ (2 terms) and $n=5$ (1 term). These terms were deleted to improve the computational speed. To describe the $4S$ states, 501 terms were employed with additional emphasis on terms of the form $(i,j,3,l,m,n)$. For the $5S$ states of Li I and Be II 522 terms were employed with the further addition of terms of the form $(i,j,4,l,m,n)$. The final results presented for the $5\,^2S$ state of Li I were based on the first 450 terms of the 522-term wave function reported.[48] If ω denotes the sum $i+j+k+l+m+n$, then the core of each wave function includes all possible terms to $\omega=4$, a total of 210 terms. After the first 210 terms, an extensive selection of terms was made to ensure that the more diffuse character of the

TABLE I. Orbital exponents employed for the excited-state wave functions for members of the Li I series.

	$3\,^2S$		$4\,^2S$		$5\,^2S$	
Z	α	γ	α	γ	α	γ
3	2.85	0.32	2.83	0.188	2.79	0.115
4	3.85	0.60	3.84	0.445	3.78	0.423
5	4.84	0.88	4.85	0.70		
6	5.85	1.18	5.84	1.03		
7	6.86	1.49	6.83	1.30		
8	7.88	1.81	7.82	1.56		
9	8.90	2.13	8.82	1.82		
10	9.91	2.46	9.82	2.07		

$3\,^2S$, $4\,^2S$, and $5\,^2S$ states are adequately described. The final four sets of basis functions are available from the Physics Auxiliary Publication Service.[48]

B. Accuracy controls

A discussion of the accuracy controls underlying this work have been given elsewhere.[38–40] The matrix elements for the $3\,^2S$ level for $Z=4$ to 9 were evaluated on a Cray X-MP/48 at the National Center for Supercomputer Applications (NCSA) at the University of Illinois at Urbana-Champaign. The remaining matrix elements were evaluated on a Honeywell DPS8/49 mainframe at the University of Wisconsin-Eau Claire. The bulk of the diagonalization work was done at NCSA using the

TABLE II. Expectation values for the low-lying excited ^2S states of Li I.

State	Expectation value	Number of terms					
		40	100	200	300	400	447,[b] 501,[c] 450[d]
$3\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.340 145	7.352 740	7.353 252	7.353 976	7.354 063	7.354 076
	$\left\langle -\frac{3}{r_i} \right\rangle$	−1.650 578 0(1)[a]	−1.652 999 4(1)	−1.652 748 2(1)	−1.653 456 7(1)	−1.653 527 0(1)	−1.653 536 4(1)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	1.825 489	1.824 514	1.820 978	1.826 615	1.827 143	1.827 212
	$\langle \delta(\mathbf{r}_i) \rangle$	1.301 478(1)	1.369 305(1)	1.369 696(1)	1.373 339(1)	1.373 336(1)	1.373 110(1)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	0.298 178	0.292 939	0.552 771	0.657 042	0.668 807	0.670 256
	$\langle \nabla_i \cdot \nabla_j \rangle$	−0.390 437	−0.295 226	−0.294 347	−0.292 510	−0.292 176	−0.292 120
	η	1.000 448 2	1.000 454 4	1.000 343 7	1.000 078 0	1.000 022 4	1.000 013 2
	energy	−7.340 145	−7.352 740	−7.353 252	−7.353 976	−7.354 063	−7.354 076
$4\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.300 718	7.304 731	7.313 826	7.317 261	7.318 017	7.318 315
	$\left\langle -\frac{3}{r_i} \right\rangle$	−1.632 804 5(1)	−1.633 116 6(1)	−1.631 386 9(1)	−1.633 230 2(1)	−1.633 905 8(1)	−1.634 267 7(1)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	1.726 608	1.721 704	1.686 216	1.697 779	1.703 023	1.706 048
	$\langle \delta(\mathbf{r}_i) \rangle$	1.292 738(1)	1.304 458(1)	1.369 664(1)	1.369 209(1)	1.370 990(1)	1.370 690(1)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	1.216 854	0.238 525	2.958 133(−2)	1.407 965(−1)	1.960 425(−1)	0.230 652
	$\langle \nabla_i \cdot \nabla_j \rangle$	−0.401 240	−0.379 530	−0.291 027	−0.291 903	−0.290 924	−0.290 328
	η	1.002 650 2	0.998 968 7	1.000 463 1	1.000 429 4	1.000 249 1	1.000 123 2
	energy	−7.300 718	−7.304 731	−7.313 826	−7.317 261	−7.318 017	−7.318 315
$5\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.242 995	7.285 995	7.291 723	7.300 763	7.301 555	−7.301 943
	$\left\langle -\frac{3}{r_i} \right\rangle$	−1.626 270 8(1)	−1.622 686 5(1)	−1.623 628 0(1)	−1.624 500 2(1)	−1.624 564 0(1)	−1.624 819 9(1)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	1.776 718	1.654 874	1.652 835	1.643 476	1.642 531	1.644 313
	$\langle \delta(\mathbf{r}_i) \rangle$	1.235 507(1)	1.294 793(1)	1.324 866(1)	1.368 498(1)	1.369 661(1)	1.370 807(1)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	0.491 158	0.291 116	0.222 236	2.938 082(−2)	3.355 962(−2)	4.677 767(−2)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−9.054 543(−3)	−0.373 578	−0.366 305	−0.292 254	−0.291 109	−0.289 691
	η	0.964 851 5	1.008 146 6	1.000 238 2	1.000 314 2	1.000 409 0	1.000 387 7
	energy	−7.242 995	−7.285 995	−7.291 723	−7.300 763	−7.301 555	−7.301 943

[a] The notation (n) signifies $\times 10^n$.
[b] Final number of terms for the $3\,^2S$ state.
[c] Final number of terms for the $4\,^2S$ state.
[d] Final number of terms for the $5\,^2S$ state.

EISPACK system. All calculations were carried out in double precision.

IV. RESULTS

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

$$\langle O_i \rangle \equiv \left\langle \psi \left| \sum_{i=1}^{3} O_i \right| \psi \right\rangle , \tag{8a}$$

$$\langle O_{ij} \rangle \equiv \left\langle \psi \left| \sum_{i=1}^{3} \sum_{j>i}^{3} O_{ij} \right| \psi \right\rangle , \tag{8b}$$

TABLE III. Expectation values for the low-lying excited ^2S states of Be II.

State	Expectation value	Number of terms					
		40	100	200	300	400	447,[a] 501,[b] 522[c]
$3\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	1.390 574 1(1)	1.392 120 4(1)	1.392 204 7(1)	1.392 268 1(1)	1.392 275 4(1)	1.392 276 4(1)
	$\left\langle -\frac{4}{r_i} \right\rangle$	−3.045 647 0(1)	−3.049 434 6(1)	−3.049 613 5(1)	−3.049 992 4(1)	−3.050 015 6(1)	−3.050 018 4(1)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	2.644 988	2.651 938	2.652 040	2.654 562	2.654 648	2.654 656
	$\langle \delta(\mathbf{r}_{ij}) \rangle$	3.331 230(1)	3.447 555(1)	3.450 423(1)	3.457 119(1)	3.457 154(1)	3.456 738(1)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	1.728 938	2.190 844	2.981 008	3.156 058	3.170 733	3.172 531
	$\langle \boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j \rangle$	−5.423 269(−1)	−4.322 451(−1)	−4.322 979(−1)	−4.298 809(−1)	−4.293 262(−1)	−4.292 522(−1)
	η	1.001 507 8	1.000 542 6	1.000 225 2	1.000 036 3	1.000 010 7	1.000 007 0
	energy	−13.905 741	−13.921 204	−13.922 047	−13.922 681	−13.922 754	−13.922 764
$4\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	1.376 154 0(1)	1.378 306 1(1)	1.379 417 0(1)	1.379 842 6(1)	1.379 862 6(1)	1.379 866 2(1)
	$\left\langle \frac{-4}{r_i} \right\rangle$	−3.002 457 2(1)	−3.001 088 6(1)	−3.002 297 0(1)	−3.004 541 7(1)	−3.004 675 5(1)	−3.004 686 4(1)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	2.501 492	2.444 764	2.434 631	2.448 566	2.449 503	2.449 541
	$\langle \delta(\mathbf{r}_i) \rangle$	3.277 900(1)	3.323 657(1)	3.441 985(1)	3.442 090(1)	3.445 514(1)	3.445 040(1)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	6.812 107	0.440 869	0.312 140	1.197 041	1.243 384	1.252 294
	$\langle \boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j \rangle$	−0.585 364	−0.540 070	−0.425 252	−0.425 504	−0.424 432	−0.424 287
	η	0.994 071 5	1.001 203 6	1.000 558 4	1.000 111 6	1.000 027 4	1.000 016 0
	energy	−13.761 540	−13.783 061	−13.794 170	−13.798 426	−13.798 626	−13.798 662
$5\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	1.343 057 9(1)	1.368 856 2(1)	1.371 724 4(1)	1.374 411 6(1)	1.374 448 9(1)	1.374 457 7(1)
	$\left\langle -\frac{4}{r_i} \right\rangle$	−2.981 975 8(1)	−2.987 319 0(1)	−2.986 513 8(1)	−2.984 453 0(1)	−2.984 471 9(1)	−2.984 472 5(1)
	$\left\langle \frac{1}{r_i} \right\rangle$	2.958 599	2.496 066	2.430 649	2.356 299	2.355 742	2.355 572
	$\langle \delta(\mathbf{r}_i) \rangle$	2.818 425(1)	3.211 325(1)	3.265 597	3.440 371(1)	3.438 805(1)	3.441 119(1)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	2.932 681(1)	4.876 172	−1.170 379	0.622 638	0.611 473	0.618 002
	$\langle \boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j \rangle$	7.762 301(−2)	−0.412 458	−0.422 353	−0.426 263	−0.423 422	−0.422 668
	η	0.913 601 9	0.996 527 9	0.994 114 7	1.000 090 6	1.000 031 7	1.000 011 9
	energy	−13.430 579	−13.688 562	−13.717 244	−13.744 116	−13.744 489	−13.744 577

[a] Final number of terms for the $3\,^2S$ state.
[b] Final number of terms for the $4\,^2S$ state.
[c] Final number of terms for the $5\,^2S$ state.

and ψ is normalized. In addition to the energy components, Tables II–IX also contain values of the electronic density at the nucleus $\rho(0)$,

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

the Fermi contact interaction

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

the expectation value required to obtain the specific-mass shift (mass polarization correction) $\langle\nabla_i\cdot\nabla_j\rangle$, and the 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 presented in the tables.

Of particular concern during this study was the consideration that the energy obtained for a particular state might be significantly less than optimal (for the given basis set with fixed exponents), because of an inadequate selection of terms for the trial basis sets used to determine the exponents. A feeling for both the sensitivity of the computed energies on the exponents and the adequacy of the exponents can be obtained by examining the excited-state energies from each wave function. If ψ_1, ψ_2, and ψ_3 designate wave functions for the $3\,^2S$, $4\,^2S$, and $5\,^2S$ states, respectively, how do the energies E_1 ($3\,^2S$), E_2 ($4\,^2S$), and E_3 ($5\,^2S$) evaluated from ψ_1 compare with the corresponding values evaluated from ψ_2 and ψ_3? Could very accurate excited-state energies be obtained from a wave function specifically constructed to describe the ground state? To address the latter question, the excited-state energies were evaluated from a 296-term wave function for Li I, which yields a nonrelativistic ground-state energy believed to be in error by less than 1 μhartree.[49] All the excited-state energies were inferior to the final values reported in Table II. The 296-term wave function had variable exponents and a number of terms describing the diffuse part of the electronic charge cloud. The preceding calculation clearly establishes, if indeed the point needed to be proved, that a wave function care-

TABLE IV. Expectation values for the low-lying excited ^2S states of B III.

State	Expectation value	Number of terms					
		40	100	200	300	400	442,[a] 501 [b]
$3\,^2S$	$\langle -\frac{1}{2}\nabla_i^2\rangle$	2.258 270 6(1)	2.260 192 7(1)	2.260 308 3(1)	2.260 364 2(1)	2.260 371 3(1)	2.260 372 4(1)
	$\left\langle -\frac{5}{r_i}\right\rangle$	−4.862 582 4(1)	−4.867 736 4(1)	−4.868 119 9(1)	−4.868 369 6(1)	−4.868 381 7(1)	−4.868 383 0(1)
	$\left\langle \frac{1}{r_{ij}}\right\rangle$	3.460 412	3.473 510	3.475 033	3.476 412	3.476 390	3.476 382
	$\langle\delta(\mathbf{r}_i)\rangle$	6.808 660(1)	6.984 144(1)	6.991 876(1)	7.002 394(1)	7.003 523(1)	7.001 869(1)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi}\rangle$	5.179 056	6.542 717	8.073 462	8.305 090	8.324 816	8.328 058
	$\langle\nabla_i\cdot\nabla_j\rangle$	−6.862 099(−1)	−5.703 232(−1)	−5.716 630(−1)	−5.686 097(−1)	−5.678 142(−1)	−5.677 375(−1)
	η	1.002 253 4	1.000 554 1	1.000 152 3	1.000 021 3	1.000 007 0	1.000 004 9
	energy	−22.582 706	−22.601 927	−22.603 083	−22.603 642	−22.603 713	−22.603 724
$4\,^2S$	$\langle -\frac{1}{2}\nabla_i^2\rangle$	2.227 390 1(1)	2.232 628 4(1)	2.233 834 1(1)	2.234 164 1(1)	2.234 174 5(1)	2.234 177 9(1)
	$\left\langle -\frac{5}{r_i}\right\rangle$	−4.781 003 0(1)	−4.783 560 7(1)	−4.785 929 7(1)	−4.787 187 5(1)	−4.787 223 5(1)	−4.787 218 8(1)
	$\left\langle \frac{1}{r_{ij}}\right\rangle$	3.262 229	3.183 039	3.182 614	3.188 593	3.188 745	3.188 629
	$\langle\delta(\mathbf{r}_i)\rangle$	6.661 801(1)	6.779 292(1)	6.958 845(1)	6.965 312(1)	6.970 934(1)	6.969 827(1)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi}\rangle$	1.673 076(1)	1.842 568	2.055 139	3.313 595	3.337 061	3.341 481
	$\langle\nabla_i\cdot\nabla_j\rangle$	−0.795 736	−0.700 812	−0.570 396	−0.560 583	−0.559 499	−0.559 242
	η	0.990 089 0	1.001 425 9	1.000 344 0	1.000 040 2	1.000 011 1	1.000 009 2
	energy	−22.273 901	−22.326 284	−22.338 341	−22.341 641	−22.341 745	−22.341 779

[a] Final number of terms for the $3\,^2S$ state.

[b] Final number of terms for the $4\,^2S$ state.

fully tailored to the state in question, even with the restriction to fixed exponents, will with sufficient terms, yield superior energies, than those likely to be obtained with an excellent ground-state wave function.

To answer the first question posed above, a detailed comparison of the energies E_j ($j=1$–3) for each-excited state wave function ψ_i was made. For higher Z values, the best E_j was always obtained from ψ_j. For $Z=6$ to $Z=10$ the previous observation was found to be satisfied for each number of terms reported in the tables. For B III the 100-term ψ_1 gave a better E_2 than was obtained from ψ_2 ($-22.327\,852$ versus $-22.326\,284$). The other entries for B III followed the previous stated observation. These results do provide some support for the adequacy of the exponents employed for $Z=5$ to 10. For Be II and particularly Li I, the results were not as well behaved. For Be II ψ_1 always gave the best E_1 (for each of the number of terms reported in Table III), in fact the E_1 value from ψ_1 (447 terms) was lower than E_1 from ψ_2 (501 terms) and from ψ_3 (522 terms). For E_2, the lowest energy was obtained with the following wave functions: ψ_3 (40 terms), ψ_1 (100 and 200 terms), ψ_2 (300 and 400 terms). E_2 for the final ψ_2 (501 terms) was 2 μhartree above the result from both ψ_1 (447 terms) and ψ_3 (522 terms). ψ_3 yielded the best E_3 at 40, 100, and 200 terms. At 300 and 400 terms, the best E_3 was obtained with ψ_2. The best E_3 was obtained with ψ_3 at 522 terms. It is probably safe to conclude from our results for Be II that at least for the largest basis sets employed, the exponents for ψ_i are likely to be in error by only a small amount.

For Li I, ψ_1 gave the best E_1 for each number of terms given in Table II, and E_1 from ψ_1 final (447 terms) was lower than E_1 from ψ_2 final (501 terms) by ~0.5 mHartrees. For E_2 and E_3 there were a number of cases where the best E_i was not obtained from ψ_i. The best calculated E_2 was obtained from ψ_1 (447 terms), which is lower than the Table II entry (based on ψ_2) by 176 μhartrees. The best E_3 was obtained with ψ_2 (501 terms), which is lower than the Table II entry (based on ψ_3) by 1.496 mhartrees. Since the latter two results represent significant improvements in the energy, it is of interest to

TABLE V. Expectation values for the low-lying excited ^2S states of C IV.

State	Expectation value	Number of terms					
		40	100	200	300	400	442,[a] 501 [b]
$3\,^2S$	$\langle -\frac{1}{2}\nabla_i^2\rangle$	3.337 214 8(1)	3.339 440 8(1)	3.339 566 9(1)	3.339 611 0(1)	3.339 617 7(1)	3.339 618 8(1)
	$\left\langle -\frac{6}{r_i}\right\rangle$	−7.102 024 7(1)	−7.108 344 6(1)	−7.108 719 8(1)	−7.108 867 5(1)	−7.108 873 8(1)	−7.108 874 5(1)
	$\left\langle \frac{1}{r_{ij}}\right\rangle$	4.275 952	4.294 631	4.295 859	5.296 455	4.296 383	4.296 369
	$\langle \delta(\mathbf{r}_i)\rangle$	1.212 191(2)	1.236 946(2)	1.238 284(2)	1.239 836(2)	1.239 995(2)	1.239 754(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi}\rangle$	1.120 236(1)	1.459 785(1)	1.676 794(1)	1.698 686(1)	1.701 228(1)	1.701 778(1)
	$\langle \nabla_i\cdot\nabla_j\rangle$	−8.320 014(−1)	−7.121 058(−1)	−7.117 655(−1)	−7.079 060(−1)	−7.069 374(−1)	−7.068 479(−1)
	η	1.002 398 7	1.000 396 6	1.000 088 6	1.000 012 8	1.000 004 7	1.000 003 4
	energy	−33.372 148	−33.394 408	−33.395 669	−33.396 110	−33.396 177	−33.396 188
$4\,^2S$	$\langle -\frac{1}{2}\nabla_i^2\rangle$	3.279 817 9(1)	3.293 590 6(1)	3.294 497 8(1)	3.294 740 5(1)	3.294 746 8(1)	3.294 752 4(1)
	$\left\langle -\frac{6}{r_i}\right\rangle$	−6.968 183 1(1)	−6.981 364 8(1)	−6.982 468 5(1)	−6.982 207 5(1)	−6.982 214 2(1)	−6.982 209 1(1)
	$\left\langle \frac{1}{r_{ij}}\right\rangle$	4.085 473	3.941 837	3.934 729	3.927 266	3.927 206	3.927 043
	$\langle \delta(\mathbf{r}_i)\rangle$	1.166 646(2)	1.203 460(2)	1.227 341(2)	1.232 366(2)	1.233 234(2)	1.232 983(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi}\rangle$	3.500 496(1)	7.359 520	6.660 147	6.887 601	6.888 974	6.894 434
	$\langle \nabla_i\cdot\nabla_j\rangle$	−0.962 215	−0.876 407	−0.747 955	−0.696 257	−0.695 155	−0.694 603
	η	0.985 745 4	1.000 623 5	0.999 957 3	1.000 016 6	1.000 007 7	1.000 005 7
	energy	−32.798 179	−32.935 906	−32.944 978	−32.947 405	−32.947 468	−32.947 524

[a] Final number of terms for the $3\,^2S$ state.

[b] Final number of terms for the $4\,^2S$ state.

report the other properties evaluated with these wave functions. These have been tabulated in Table X. For the $4\,^2S$ state the expectation values presented in Table X are close to the corresponding entries in Table II, with the exception of the Fermi contact interaction. For the $5\,^2S$ state a similar observation can be made. The value of f reported in Table X is probably superior to the corresponding value in Table II, based on the somewhat smoother convergence of this property using ψ_1, though there are well-known traps to this type of inference, particularly for the hyperfine coupling. The values of f reported in Table II appear to be converging to a higher value, which would support the previous assertion.

For the $5\,^2S$ state of Li, the expectation values reported in Table X are expected to be superior to those reported in Table II, with the probable exception being the value for $\langle \nabla_i \cdot \nabla_j \rangle$. Part of the improvement is due to the additional 51 basis functions in the final ψ_2. The values of f reported in Table II appear to be converging rather slowly, if one assumes the f value for the $5\,^2S$ state in Table X is more reliable. For the results reported in later tables (Tables XI–XIV), entries from Table X have been employed for the $4\,^2S$ and $5\,^2S$ states of Li, except $\langle \nabla_i \cdot \nabla_j \rangle$ is taken from Table II for both states.

A. Nuclear magnetic shielding constant

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

$$\sigma = \tfrac{1}{3}\alpha^2 \left\langle \psi \left| \sum_{i=1}^{3} \frac{1}{r_i} \right| \psi \right\rangle , \tag{12}$$

where α is the fine-structure constant, whose value is taken as[52] $7.297\,353\,08 \times 10^{-3}$. Values of σ are tabulated in Table XII.

B. Specific-mass shift

The nonrelativistic form of the specific-mass shift is given by

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

where μ is the reduced electron mass,

TABLE VI. Expectation values for the low-lying excited ^2S states of N v.

State	Expectation value	Number of terms					
		40	100	200	300	400	442,[a] 501[b]
$3\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	4.627 349 4(1)	4.629 821 9(1)	4.629 950 1(1)	4.629 986 0(1)	4.629 992 6(1)	4.629 993 6(1)
	$\left\langle -\frac{7}{r_i} \right\rangle$	−9.763 882 3(1)	−9.771 133 8(1)	−9.771 456 4(1)	−9.771 545 3(1)	−9.771 549 1(1)	−9.771 549 6(1)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	5.091 834	5.114 901	5.115 562	5.115 734	5.115 639	5.115 623
	$\langle \delta(\mathbf{r}_i) \rangle$	1.966 124(2)	1.999 159(2)	2.001 252(2)	2.003 398(2)	2.003 611(2)	2.003 280(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	2.076 521(1)	2.719 830(1)	2.989 645(1)	3.008 623(1)	3.011 893(1)	3.012 749(1)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−9.771 255(−1)	−8.556 530(−1)	−8.521 669(−1)	−8.475 488(−1)	−8.464 141(−1)	−8.463 092(−1)
	η	1.002 382 6	1.000 275 9	1.000 052 9	1.000 008 6	1.000 003 3	1.000 002 4
	energy	−46.273 494	−46.298 219	−46.299 501	−46.299 860	−46.299 926	−46.299 936
$4\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	4.538 100 2(1)	4.560 447 4(1)	4.561 311 9(1)	4.561 568 2(1)	4.561 574 6(1)	4.561 580 9(1)
	$\left\langle -\frac{7}{r_i} \right\rangle$	−9.562 570 6(1)	−9.589 487 6(1)	−9.590 024 3(1)	−9.589 682 6(1)	−9.589 686 9(1)	−9.589 682 7(1)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	4.863 701	4.685 928	4.674 005	4.665 463	4.665 377	4.665 210
	$\langle \delta(\mathbf{r}_i) \rangle$	1.881 067(2)	1.949 950(2)	1.982 130(2)	1.990 113(2)	1.991 360(2)	1.990 998(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	6.192 748(1)	1.437 941(1)	1.217 237(1)	1.228 287(1)	1.228 209(1)	1.229 126(1)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−1.189 347	−1.037 854	−0.900 493	−0.832 453	−0.831 059	−0.830 316
	η	0.985 191 1	1.000 465 6	0.999 923 7	1.000 012 2	1.000 006 1	1.000 004 2
	energy	−45.381 002	−45.604 474	−45.613 119	−45.615 682	−45.615 746	−45.615 809

[a] Final number of terms for the $3\,^2S$ state.

[b] Final number of terms for the $4\,^2S$ state.

$$\mu = \frac{m_e M}{m_e + M} , \tag{14}$$

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,[53] and have been corrected for the mass of the appropriate number of electrons for each species. The specific-mass shifts are collected in Table XIII.

C. Isotope shift

The quantity defined in Sec. IV B leads to the *absolute* specific-mass shift for a given level. Of greater interest to experimentalists is the transition isotope shift, which represents the difference between the transition frequencies for a pair of isotopes undergoing the same change of state. Interest in this study focuses on the ionization limit, so the transition isotope shift (TIS) for a pair of isotopes ${}^{A_1}X$ and ${}^{A_2}X$ (with mass numbers $A_1 > A_2$) is calculated as

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

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 XIV, along with the transition isotope shift defined by Eq. (15). The results for the two-electron shifts reported in Table XIV have been evaluated using the values of $\langle \nabla_1 \cdot \nabla_2 \rangle$ calculated by Pekeris.[10,54]

D. Hyperfine coupling constant

The Fermi contact operator evaluated in this work is

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

TABLE VII. Expectation values for the low-lying excited ${}^2S$ states of O VI.

State	Expectation value	Number of terms 40	100	200	300	400	442,[a] 501[b]
$3\,{}^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	6.128 698 2(1)	6.131 326 9(1)	6.131 450 9(1)	6.131 481 0(1)	6.131 487 6(1)	6.131 488 6(1)
	$\left\langle -\frac{8}{r_i} \right\rangle$	−1.284 8232 7(2)	−1.285 612 89(2)	−1.285 637 17(2)	−1.285 642 51(2)	−1.285 642 76(2)	−1.285 642 79(2)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	5.908 363	5.934 752	5.934 699	5.934 631	5.934 524	5.934 506
	$\langle \delta(\mathbf{r}_i) \rangle$	2.981 407(2)	3.024 115(2)	3.027 014(2)	3.029 833(2)	3.030 107(2)	3.029 675(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	3.465 763(1)	4.537 424(1)	4.834 807(1)	4.849 128(1)	4.853 297(1)	4.854 534(1)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−1.129 654	−1.001 000	−9.926 755(−1)	−9.873 900(−1)	−9.861 025(−1)	−9.859 812(−1)
	η	1.002 142 7	1.000 172 2	1.000 031 9	1.000 006 1	1.000 002 4	1.000 001 8
	energy	−61.286 982	−61.313 269	−61.314 509	−61.314 810	−61.314 876	−61.314 886
$4\,{}^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	6.001 280 4(1)	6.033 529 1(1)	6.034 385 9(1)	6.034 648 1(1)	6.034 654 8(1)	6.034 661 4(1)
	$\left\langle -\frac{8}{r_i} \right\rangle$	−1.256 598 89(2)	−1.260 975 36(2)	−1.260 996 86(2)	−1.260 964 94(2)	−1.260 965 227(2)	−1.260 964 92(2)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	5.634 280	5.426 954	5.411 968	5.403 533	5.403 432	5.403 263
	$\langle \delta(\mathbf{r}_i) \rangle$	2.842 734(2)	2.955 327(2)	2.997 481(2)	3.008 318(2)	3.010 012(2)	3.009 531(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	9.968 197(1)	2.386 319(1)	1.977 955(1)	1.988 969(1)	1.988 922(1)	1.990 327(1)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−1.446 713	−1.195 693	−1.049 175	−0.968 841	−0.967 138	−0.966 217
	η	0.985 110 6	1.000 458 9	0.999 929 8	1.000 009 5	1.000 004 8	1.000 003 3
	energy	−60.012 804	−60.335 291	−60.343 859	−60.346 481	−60.346 548	−60.346 614

[a] Final number of terms for the $3\,{}^2S$ state.

[b] Final number of terms for the $4\,{}^2S$ state.

which can be rewritten as an effective operator

$$H_F \equiv h A_J \mathbf{I}\cdot\mathbf{J} \,, \tag{17}$$

where μ_0 is the vacuum permeability, g_e is the electronic g factor (incorporating bound-state corrections), g_I is the nuclear g factor, μ_B and μ_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 δ 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, of Eq. (10) is (using a conventional grouping of terms)

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

Using the most recent[52] values of μ_B, μ_N, h, and a_0, Eq. (18) simplifies to

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

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 XV.

V. DISCUSSION

A. The nonrelativistic energy

The convergence of the excited-state energies runs as one would expect: the higher the excited state, the less rapidly the energy converges, for the basis sets employed in this work. The final energies have probably converged to within ~10–110 μhartrees of the correct nonrelativis-

TABLE VIII. Expectation values for the low-lying excited ^2S states of F VII.

State	Expectation value	Number of terms					
		40	100	200	300	400	442,[a] 501 [b]
$3\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.841 154 6(1)	7.843 943 5(1)	7.844 065 4(1)	7.844 092 4(1)	7.844 098 9(1)	7.844 099 9(1)
	$\left\langle -\frac{9}{r_i} \right\rangle$	−1.635 478 48(2)	−1.636 328 81(2)	−1.636 348 05(2)	−1.636 351 60(2)	−1.636 351 77(2)	−1.636 351 80(2)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	6.724 757	6.754 010	6.753 498	6.753 313	6.753 200	6.753 181
	$\langle \delta(\mathbf{r}_i) \rangle$	4.297 019(2)	4.350 697(2)	4.354 481(2)	4.358 040(2)	4.358 385(2)	4.357 837(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	5.353 981(1)	6.977 660(1)	7.298 362(1)	7.308 979(1)	7.314 152(1)	7.315 853(1)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−1.284 526	−1.146 262	−1.133 264	−1.127 387	−1.125 938	−1.125 799
	η	1.001 901 4	1.000 112 7	1.000 021 2	1.000 004 6	1.000 001 9	1.000 001 4
	energy	−78.411 546	−78.439 435	−78.440 654	−78.440 924	−78.440 989	−78.440 999
$4\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.668 945 2(1)	7.712 859 3(1)	7.713 712 6(1)	7.713 979 2(1)	7.713 986 1(1)	7.713 993 0(1)
	$\left\langle -\frac{9}{r_i} \right\rangle$	−1.597 818 13(2)	−1.604 247 21(2)	−1.604 240 74(2)	−1.604 211 24(2)	−1.604 211 51(2)	−1.604 211 20(2)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	6.402 909	6.167 534	6.149 822	6.141 539	6.141 428	6.141 259
	$\langle \delta(\mathbf{r}_i) \rangle$	4.087 014(2)	4.257 701(2)	4.311 502(2)	4.325 506(2)	4.327 700(2)	4.327 084(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	1.501 663(2)	3.635 930(1)	2.997 168(1)	3.008 392(1)	3.008 443(1)	3.010 441(1)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−1.742 964	−1.362 064	−1.197 418	−1.105 315	−1.103 315	−1.102 228
	η	0.984 216 2	1.000 252 2	0.999 934 7	1.000 007 6	1.000 003 8	1.000 002 6
	energy	−76.689 452	−77.128 593	−77.137 126	−77.139 792	−77.139 861	−77.139 930

[a] Final number of terms for the $3\,^2S$ state.

[b] Final number of terms for the $4\,^2S$ state.

TABLE IX. Expectation values for the low-lying excited ^2S states of Ne VIII.

State	Expectation value	Number of terms					
		40	100	200	300	400	442,[a] 501 [b]
$3\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	9.764 828 87(1)	9.767 674 5(1)	9.767 793 4(1)	9.767 818 0(1)	9.767 824 5(1)	9.767 825 6(1)
	$\left\langle -\frac{10}{r_i} \right\rangle$	−2.028 388 28(2)	−2.029 266 68(2)	−2.029 279 96(2)	−2.029 282 26(2)	−2.029 282 39(2)	−2.029 282 41(2)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	7.542 253	7.573 177	7.572 128	7.571 867	7.571 748	7.571 729
	$\langle \delta(\mathbf{r}_i) \rangle$	5.952 147(2)	6.017 364(2)	6.022 553(2)	6.026 922(2)	6.027 350(2)	6.026 672(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	7.934 056(1)	1.014 976(2)	1.046 975(2)	1.047 729(2)	1.048 346(2)	1.048 572(2)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−1.440 121	−1.292 667	−1.273 931	−1.267 502	−1.265 880	−1.265 721
	η	1.001 719 4	1.000 072 2	1.000 014 7	1.000 003 6	1.000 001 5	1.000 001 1
	energy	−97.648 287	−97.676 745	−97.677 934	−97.678 180	−97.678 245	−97.678 256
$4\,^2S$	$\langle -\frac{1}{2}\nabla_i^2 \rangle$	9.542 211 0(1)	9.598 443 2(1)	9.599 297 2(1)	9.599 561 1(1)	9.599 568 1(1)	9.599 575 2(1)
	$\left\langle -\frac{10}{r_i} \right\rangle$	−1.980 083 18(2)	−1.988 740 28(2)	−1.988 732 62(2)	−1.988 707 31(2)	−1.988 707 55(2)	−1.988 707 27(2)
	$\left\langle \frac{1}{r_{ij}} \right\rangle$	7.164 099	6.905 164	6.887 317	6.879 510	6.879 392	6.879 224
	$\langle \delta(\mathbf{r}_i) \rangle$	5.655 951(2)	5.896 614(2)	5.963 247(2)	5.980 154(2)	5.982 907(2)	5.982 149(2)
	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	2.145 205(2)	5.128 774(1)	4.302 619(1)	4.323 861(1)	4.324 272(1)	4.326 988(1)
	$\langle \nabla_i \cdot \nabla_j \rangle$	−2.075 210	−1.524 365	−1.343 157	−1.241 868	−1.239 568	−1.238 327
	η	0.983 861 5	1.000 212 4	0.999 949 6	1.000 006 2	1.000 003 1	1.000 002 1
	energy	−95.422 110	−95.984 432	−95.992 972	−95.995 611	−95.995 681	−95.995 752

[a] Final number of terms for the $3\,^2S$ state.
[b] Final number of terms for the $4\,^2S$ state.

TABLE X. Expectation values for the $4\,^2S$ and $5\,^2S$ states of Li I using different basis sets.

Expectation value	$4\,^2S$ [a]	$5\,^2S$ [b]
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.318 491	7.303 439
$\left\langle -\frac{3}{r_i} \right\rangle$	−1.634 541 9(1)	−1.626 155 4(1)
$\left\langle \frac{1}{r_{ij}} \right\rangle$	1.708 437	1.654 675
$\langle \delta(\mathbf{r}_i) \rangle$	1.370 712(1)	1.369 962(1)
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	2.543 974(−1)	1.131 167(−1)
$\langle \nabla_i \cdot \nabla_j \rangle$	−0.290 383	−0.289 770
η	1.000 010 1	1.000 068 0
energy	−7.318 491	−7.303 439

[a] Results obtained from 447-term ψ_1, wave function.
[b] Results obtained from 501-term ψ_2, wave function.

tic energies, with the likely exception of the $5\,^2S$ states of Li and Be$^+$. As Z increases, the absolute convergence rates for the energy of a particular state are observed to be similar. The relative increment in the energy improves by a factor of approximately 3 to 7 as Z increases from 3 to 10.

Table XI presents a summary of some accurate literature values for several of the states studied in this work. In each case, the present results represent the lowest upper-bound estimates to the energies of the states tabulated. The agreement with the empirical estimates of the nonrelativistic energies is generally fairly satisfactory. The largest discrepancy occurs, not unexpectedly, for the $5\,^2S$ state of Li. The literature estimates of the nonrelativistic energies given in Table XI depend upon a couple of factors that may not be known with high accuracy, namely, the Lamb shifts and relativistic corrections for the states in question. So some caution is needed in comparison with these estimates. This is illustrated in particular for the $3\,^2S$ states for $Z=7$, 8, and 9, where the literature estimates[51] for the nonrelativistic energies lie *above* the results of the present calculations. The literature estimates are clearly in error for these three cases.

TABLE XI. Upper bounds to the low-lying excited nonrelativistic energies of the ^2S states of some members of the Li I series.

Species	Wave function	Type	Number of terms	Energy
Li $3\,^2S$	Perkins[a]	Hylleraas	18	−7.317 5
	Larsson[b]	Hylleraas	57	−7.353 92
	Sims and Hagstrom[c]	Combined CI-Hylleraas	150	−7.354 013
	Hijikata, Matsubara, and Maruyama[d]	Hylleraas	100	−7.354 023
	Pipin and Woznicki[e]	Combined CI-Hylleraas	170	−7.354 030
	Present work	Hylleraas	447	−7.354 076
	Empirical estimate[b,c,d]			−7.354 099
Li $4\,^2S$	Larsson[b]	Hylleraas	57	−7.318 37
	Sims and Hagstrom[c]	Combined CI-Hylleraas	150	−7.318 404
	Present work	Hylleraas	447	−7.318 491
	Empirical estimate[b,c]			−7.318 530
Li $5\,^2S$	Larsson[b]	Hylleraas	57	−7.303 39
	Sims and Hagstrom[c]	Combined CI-Hylleraas	150	−7.303 402
	Present work	Hylleraas	501	−7.303 439
	Empirical estimate[b,c]			−7.303 550
Be II $3\,^2S$	Pipin and Woznicki[e]	Combined CI-Hylleraas	170	−13.922 72
	Present work	Hylleraas	447	−13.922 764
	Empirical estimate[e]			−13.922 80
B III $3\,^2S$	Pipin and Woznicki[e]	Combined CI-Hylleraas	170	−22.603 61
	Present work	Hylleraas	442	−22.603 724
	Empirical estimate[e]			−22.603 79
C IV $3\,^2S$	Present work	Hylleraas	442	−33.396 188
	Empirical estimate[f]			−33.396 22
N V $3\,^2S$	Present work	Hylleraas	442	−46.299 936
	Empirical estimate[f]			−46.299 79
O VI $3\,^2S$	Present work	Hylleraas	442	−61.314 886
	Empirical estimate[f]			−61.314 51
F VII $3\,^2S$	Present work	Hylleraas	442	−78.440 999
	Empirical estimate[f]			−78.440 20

[a] Reference 16.
[b] Reference 17.
[c] Reference 19.
[d] Reference 50.
[e] Reference 31.
[f] Reference 51.

B. Basis-set selection

The systematic selection of all terms to $\omega=4$ should provide a good description of the core electrons. The real difficulty arises with the description of the valence electron. Once the restriction to fixed exponents is imposed, it is not realistic to expect the exponents to be close to optimal for a wide selection of diffuse orbitals. Even

TABLE XII. Nuclear magnetic shielding constants (in a.u.) for some low-lying ^2S states of the Li I isoelectronic series for $Z \leq 10$.

Z	$3\,^2S$	$4\,^2S$	$5\,^2S$
3	9.783 67(−5)	9.671 3(−5)	9.621 7(−5)
4	1.353 480(−4)	1.333 36(−4)	1.324 39(−4)
5	1.728 320(−4)	1.699 51(−4)	
6	2.103 096(−4)	2.065 62(−4)	
7	2.477 849(−4)	2.431 73(−4)	
8	2.852 593(−4)	2.797 84(−4)	
9	3.227 332(−4)	3.163 94(−4)	
10	3.602 068(−4)	3.530 046(−4)	

TABLE XIII. Specific-mass shifts ΔE_{SMS} for some low-lying ^2S states of the Li I isoelectronic series for $Z \leq 10$.

Species		ΔE_{SMS} (a.u.)[a]	
	$3\,^2S$	$4\,^2S$	$5\,^2S$
^{6}Li I	26.646	26.483	26.425
^{7}Li I	22.844	22.704	22.654
^{9}Be II	26.134	25.831	25.733
^{10}B III	31.112	30.646	
^{11}B III	28.295	27.872	
^{12}C IV	32.321	31.761	
^{13}C IV	29.826	29.309	
^{14}N V	33.163	32.536	
^{15}N V	30.958	30.373	
^{16}O VI	33.824	33.146	
^{17}O VI	31.826	31.188	
^{18}O VI	30.057	29.455	
^{19}F VII	32.515	31.834	
^{20}Ne VIII	34.739	33.987	
^{21}Ne VIII	33.082	32.366	
^{22}Ne VIII	31.581	30.897	

[a] Each entry must be multiplied by 10^{-6}.

TABLE XIV. Transition isotope shifts ΔE_{TIS} for some low-lying ^2S states of the Li I isoelectronic series for $Z \leq 10$.

Isotope pair	State (three-electron species)	Absolute $\Delta E_{\mathrm{shift}}$ (three-electron species) (GHz)	Absolute $\Delta E_{\mathrm{shift}}$ (two-electron species, ^1S ground state) (GHz)	ΔE_{TIS}
^{6}Li,^{7}Li	$3\,^2S$	25.011	24.7416	0.269
^{6}LI,^{7}Li	$4\,^2S$	24.85_7		0.11_5
^{6}Li,^{7}Li	$5\,^2S$	24.80_3		0.06_1
^{10}B,^{11}B	$3\,^2S$	18.528	18.0390	0.489
^{10}B,^{11}B	$4\,^2S$	18.25_1		0.21_2
^{12}C,^{13}C	$3\,^2S$	16.411	15.9118	0.499
^{12}C,^{13}C	$4\,^2S$	16.12_7		0.21_5
^{14}N,^{15}N	$3\,^2S$	14.505	14.0223	0.483
^{14}N,^{15}N	$4\,^2S$	14.23_1		0.20_9
^{16}O,^{17}O	$3\,^2S$	13.149	12.6833	0.466
^{16}O,^{17}O	$4\,^2S$	12.88_6		0.20_3
^{16}O,^{18}O	$3\,^2S$	24.786	23.9070	0.879
^{16}O,^{18}O	$4\,^2S$	24.28_9		0.38_2
^{17}O,^{18}O	$3\,^2S$	11.636	11.2237	0.412
^{17}O,^{18}O	$4\,^2S$	11.40_3		0.17_9
^{20}Ne,^{21}Ne	$3\,^2S$	10.905	10.4859	0.419
^{20}Ne,^{21}Ne	$4\,^2S$	10.66_9		0.18_3
^{20}Ne,^{22}Ne	$3\,^2S$	20.780	19.9816	0.799
^{20}Ne,^{22}Ne	$4\,^2S$	20.33_0		0.34_8
^{21}Ne,^{22}Ne	$3\,^2S$	9.8752	9.4957	0.380
^{21}Ne,^{22}Ne	$4\,^2S$	9.661_5		0.16_6

TABLE XV. Hyperfine coupling constants for some low-lying ^2S states for members of the Li I isoelectronic series for $Z \leq 10$.

Species	State	Magnetic moment (in nuclear magnetons)	Hyperfine coupling constant (MHz)
^{6}Li I	$3\,^2S$	0.822 047 28	3.51×10^1
^{6}Li I	$4\,^2S$		1.3×10^1
^{6}Li I	$5\,^2S$		5.9
^{7}Li I	$3\,^2S$	3.256 416	9.27×10^1
^{7}Li I	$4\,^2S$		3.5×10^1
^{7}Li I	$5\,^2S$		1.6×10^1
^{9}Be II	$3\,^2S$	$-1.177\,432$	-1.586×10^2
^{9}Be II	$4\,^2S$		-6.260×10^1
^{9}Be II	$5\,^2S$		-3.09×10^1
^{10}B III	$3\,^2S$	1.800 644 75	3.183×10^2
^{10}B III	$4\,^2S$		1.277×10^2
^{11}B III	$3\,^2S$	2.688 648 9	9.506×10^2
^{11}B III	$4\,^2S$		3.814×10^2
^{13}C IV	$3\,^2S$	0.702 411 8	1.522×10^3
^{13}C IV	$4\,^2S$		6.168×10^2
^{14}N V	$3\,^2S$	0.403 761 00	7.746×10^2
^{14}N V	$4\,^2S$		3.160×10^2
^{15}N V	$3\,^2S$	$-0.283\,188\,842$	-1.087×10^3
^{15}N V	$4\,^2S$		-4.433×10^2
^{17}O VI	$3\,^2S$	$-1.893\,79$	-2.342×10^3
^{17}O VI	$4\,^2S$		-9.601×10^2
^{19}F VII	$3\,^2S$	2.628 868	2.449×10^4
^{19}F VII	$4\,^2S$		1.008×10^4
^{21}Ne VIII	$3\,^2S$	$-0.661\,797$	-2.946×10^3
^{21}Ne VIII	$4\,^2S$		-1.216×10^3

though these exponents were optimized for trial wave functions having a variety of diffuse functions, the final basis sets include a number of terms having even more diffuse character than appears in the trial sets of functions.

The basis sets include a large number of terms with explicit r_{ij} dependence. The sets are fairly well balanced for a description of core-core and core-valence electron interactions. There are also a number of terms of a linked variety, $r_{ij}r_{jk}$ $(k \neq i)$, incorporated in the basis sets.

C. Convergence characteristics

The worse convergence is observed for the Fermi contact term. This comes as no surprise, based on the convergence of this quantity for the ^2S ground states observed previously in the literature.[37,38–40] For the $4\,^2S$ and $5\,^2S$ states of Li I, it is not at all clear from the results presented in Table II to what value the Fermi contact term is converging. Because of this particularly poor convergence, the hyperfine coupling constants reported for ^{6,7}Li for the $4\,^2S$ and $5\,^2S$ states in Table XV probably have a considerable uncertainty associated with them. It appears that the accurate calculation of hyperfine coupling constants for the low-lying excited ^2S states is going to provide a significant theoretical challenge, at least for the Li atom. Since the basis sets employed in this study were taylored in part (by the inclusion of the second spin eigenfunction) so an accurate hyperfine constant would be obtained, it appears that an alternative approach may be necessary. Two possibilities are worth exploring. A better description of the electronic density near the nucleus would be expected to accelerate the convergence of the Fermi contact term. An expansion employing Fock-type basis orbitals with logarithmic functions of the coordinates present, could achieve this goal. Unfortunately, the use of such basis functions leads to rather difficult integration problems. A second possible approach is to replace the δ function by a more global operator. For example, $\rho(0)$ may be evaluated from the expectation value of the derivative of the potential.[55–57] For a detailed discussion of global operators for δ functions, the papers by Hiller, Sucher, and Feinberg[58] and Sucher and Drachman[59] should be consulted. The use of such alternative operators for the calculation of the hyperfine coupling constant should reduce the sensitivity of the calculation on the electron density at the nucleus. A configuration-interaction calculation of f for the ^2S ground state of Li using an identity of Hiller-Sucher-Feinberg[58] did find improved convergence using this strategy.[60]

For the higher Z members of the series the Fermi contact term appears to have converged to 3 to 4 digits of precision. Unfortunately, there is a lack of experimental data to get an idea as to whether this might be a reasonable assertion. It is to be noted that agreement with experiment is *not* a guarantee that convergence to a particular number of digits has been achieved, particularly for an expectation value such as the Fermi contact term.

With a couple of exceptions, it is the electron-electron potential energy which is converging least slowly (in absolute magnitude) of the three energy components. For all states studied there are cancellations in the individual energy components which lead to a more quickly convergent energy.

The convergence of $\rho(0)$ seems well behaved. Generally four to five digits of precision appear to be obtained for this quantity. The expectation value $\langle \nabla_i \cdot \nabla_j \rangle$ also converges in a well-behaved manner, and in a number of cases the convergence is monotonic. About three to five digits of precision are obtained for this quantity.

D. Isotope shift

For the transition (to the ionization limit) isotope shift, some experimental data is available for the $3\,^2S$ and $4\,^2S$ states of Li I, and an experimentally extrapolated value is available for the $5\,^2S$ state of Li I. This data is summarized in Table XVI along with the results of the present calculations.

The agreement between the present calculations and experiment is fairly good. ΔE_{TIS} is a rather good measure of the extent to which electron correlation is accounted for by the wave function. This quantity is zero when evaluated using a Hartree-Fock wave function.

VI. CONCLUSIONS

The principal results of this investigation are the lowest upper-bound estimates for the energies of the $3\,^2S$ and $4\,^2S$ states of the Li I series for $3 \leq Z \leq 10$ and for the $5\,^2S$ states of Li I and Be II. Some of these results point to erroneous estimates for the nonrelativistic energies given in the literature, for a few of the states investigated.

Several properties have been reported, including the hyperfine coupling constant and the transition isotope shift. It is hoped that the present results may provide further stimulation for experimentalists to examine these systems. Perhaps measurements of the hyperfine coupling constants for the low-lying excited ^2S states of Be$^+$ using ion-trap techniques would be an interesting experimental challenge.

In order to improve (in the energetic sense) upon the results of the present study, the restriction to fixed exponents must be dropped. It may in fact be feasible to reduce the overall computational labor by utilizing a scaling approach. Preliminary explorations on this are being investigated by the author.

TABLE XVI. Comparison of experimental and theoretical transition isotope shifts for ^{6,7}Li I.

	ΔE_{TIS} (MHz)	
State	Experiment[a]	Theory
$3\,^2S$	276(26) 273(71)	230[b], 269[c]
$4\,^2S$	111(12)	88[b], $1.1_5\times10^2$ [c]
$5\,^2S$	53	42[b], 6×10^1 [c]

[a] Data from Refs. 42 and 43. Error bounds indicated in parentheses.

[b] Values from Ref. 61.

[c] Present calculations.

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