High precision calculations on the ^2S ground state of the lithium atom

Frederick W. King and Michael P. Bergsbaken
Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin 54702

(Received 29 March 1990; accepted 30 April 1990)

The results of a detailed variational calculation on the ^2S ground state of the lithium atom are reported. The wave function was constructed using Hylleraas-type functions with extensive exponent optimization being employed. The calculated nonrelativistic ground state energy obtained was $-7.478\,059\,53$ a.u., which is the lowest upper bound estimate for this quantity obtained to date. The discrepancy with semi-empirical estimates of this quality is discussed. The hyperfine coupling constant for ^{7}Li is calculated to be 401.795 MHz, which compares favorably with the experimental result of 401.752 043 3 MHz. Expectation values are reported for the individual energy components, as well as the electron density at the nucleus, and the specific mass shift operator. The transition isotope shift is also evaluated. The convergence characteristics of the calculations are discussed, along with the effect of retaining only one of the two possible spin eigenfunctions in the basis set.

I. INTRODUCTION

The lithium atom has long served as an attractive target for different computational techniques. This is the simplest species in which one must deal with core and valence–core correlation effects. During the past few years a number of calculations of rather high precision have been carried out on the ^2S ground state of the lithium atom.[1-11] A good deal of attention has focused on the theoretical determination of the hyperfine coupling constant.[4,5,7-9]

The motivation for the present investigation is twofold. Recent variational calculations by one of the authors[7] on the ground state of Li, using a large basis set of Hylleraas-type functions, gave a result for the nonrelativistic ground state energy of $E_{NR} = -7.478\,059$ a.u. The literature estimates for this quantity are $-7.478\,068$ a.u. (Ref. 12) $-7.478\,069$ a.u. (Ref. 13) $-7.478\,073$ a.u. (Ref. 14) and $-7.478\,071(5)$ a.u. (Ref. 15), with an error bound enclosed in brackets for the latter value. As remarked in Ref. 7, if any of these estimates of E_{NR} are accepted, the apparent convergence of E_{NR} in the Hylleraas-type calculation was rather slow. This did not appear to be realistic, considering both the size of the basis set (602 terms), and the extensive selection of basis functions depending explicitly on factors of the interelectronic separation r_{ij} that were employed in the calculation. The present calculation was undertaken to try and resolve the apparent discrepancy existing between the calculated and the semi-empirical literature estimates of E_{NR}.

Resolving this issue is of some importance because of its impact on our understanding of facets of the convergence characteristics of variational calculations with Hylleraas-type basis functions. Additionally, a knowledge of E_{NR} to high accuracy is necessary for the indirect assessment of certain fine structure shifts, such as the Lamb shift.

A second goal of the project was to examine the convergence of a couple of different expectation values, with special emphasis on the Fermi contact interaction. Our previous calculations with fixed orbital exponents required the presence of both spin eigenfunctions in the basis set, in order to yield an accurate hyperfine coupling constant.[5,7] In the present study the basis set employed includes only a single spin eigenfunction. This affords the opportunity to examine the effect of neglecting the second spin eigenfunction on the convergence of a spin dependent property. The idea being tested is that carefully optimized basis functions will offset the omission of the second spin eigenfunction.

II. THEORY

The theoretical approach employed is sketched briefly below, details can be found elsewhere in the literature.[16-19] The trial wave function employed is

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

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

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

where the exponents $i_\mu, j_\mu, k_\mu, l_\mu, m_\mu$, and n_μ are each $\geqslant 0$. In Eq. (1), χ_μ denotes the doublet spin eigenfunction, which takes the form

$$\chi_\mu = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3). \tag{3}$$

A second spin eigenfunction given by

$$\chi_\mu = 2\alpha(1)\alpha(2)\beta(3) - \beta(1)\alpha(2)\alpha(3) - \alpha(1)\beta(2)\alpha(3) \tag{4}$$

is also possible, but this has been excluded from the present calculations.

The specific mass shift operator (mass polarization contribution) is not included with the standard nonrelativistic Hamiltonian. Atomic units are employed throughout, except for the hyperfine coupling constant and the isotope shift.

III. COMPUTATIONAL PROCEDURE

The final size of the basis set and the extremely intensive CPU requirements preclude a direct optimization of the exponents for the total wave function. The wave function was

 0021-9606/90/162570-05$03.00

constructed term by term. Optimization was carried out only on the orbital exponents of each new term added. This approach offers both advantages and well-known disadvantages. The principal advantage is that a major block of the matrix elements are computed once, only those matrix elements dependent on the last added basis function as the wave function is built up, are recomputed as the orbital exponents change. For a wave function with N terms, the fraction of matrix elements computed only once is $(N-1)/(N+1)$, which becomes increasingly favorable as the basis set expands. Without this savings, the computation is simply not feasible. The disadvantage of the approach is that the exponents that have been previously optimized are less than optimal after each additional basis function is included in the basis set. In principle, the latter drawback can be overcome by systematically recycling through each term of the basis set and reoptimizing the exponents until no further energy lowering is obtained. The aforementioned procedure can be repeated as many times as necessary to obtain a fully optimized wave function.

One important and obvious factor needs to be kept in mind. The actual choice of basis functions $\{i\,j\,k\,l\,m\,n\}$ is a matter of trial and error. Some terms such as $\{0\,0\,1\,0\,0\,0\}$, $\{0\,0\,1\,0\,0\,1\}$, etc., are fairly obvious selections, but beyond these, a good deal of trial and error enters. We have been guided by both the detailed calculations of Larsson[17] and by prior experience with Hylleraas-type variational calculations.[5,7,10,20]

In order to avoid any preconceived bias as to the importance of particular terms, a good selection of basis functions with explicit dependence on low powers of r_{ij}^n have been incorporated. Also, several repetitions of key terms, such as $\{0\,0\,1\,0\,0\,0\}$, $\{0\,0\,1\,0\,0\,1\}$, etc., were included with different exponents. This latter possibility is a definite advantage over a wave function employing the restriction $\alpha_\mu=\alpha, \beta_\mu=\beta$, $\gamma_\mu=\gamma$ for all μ. A minimal number of basis functions with factors $r_{23}^l r_{31}^m r_{12}^n$ for which l, m, and n are each nonzero were included in the basis set. These terms add greatly to the computational time, particularly those with l, m, n, each odd, and based on past experience[5,7] have rather small impact on the energy when a large basis set is employed. A large number of terms were included that describe core and valence–core interactions.

The first few basis functions were selected after carrying out trial calculations with 2-term and 3-term wave functions. Up to term 65 the "optimal" exponents for each added basis function were determined by a grid search with a grid size of 0.004 or finer. After term 65, a coarser search grid was employed. At the point where 296 terms had been added, efforts were made to refine the exponents of the first five basis functions, one term at a time. The change in the exponents was minor and the improvement in the energy was negligible, being 34 $n$hartrees. For this reason it did not appear warranted to continue this reoptimization phase. The final table of basis functions and exponents is available.[21]

All calculations during the optimization phase were carried out in single precision on a Cray 1S, which yields approximately 14 decimal digits. For the final evaluation of the matrix elements, the calculations were carried out on a Cray 1S and Cray 1M in double precision (approximately 28 decimal digits). The matrix diagonalizations were carried out on a Honeywell DPS/49 computer in double precision, which represents about 18 decimal digits of precision. Two different diagonalization algorithms were employed (the EISPACK system and NESBET). The effect of tolerance parameters in both these algorithms were carefully tested.

IV. RESULTS

The principal results of this study are presented in Tables I and II. The following shorthand notation for expectation values is employed:

$$\langle O_i\rangle \equiv \left\langle \psi \left| \sum_{i=1}^{3} O_i \right| \psi \right\rangle, \tag{5}$$

$$\langle O_{ij}\rangle \equiv \left\langle \psi \left| \sum_{i=1}^{3}\sum_{j>i}^{3} O_{ij} \right| \psi \right\rangle, \tag{6}$$

and ψ is normalized. The energy components are presented in Table I along with the scale factor η, defined in terms of the potential energy $\langle V\rangle$ and the kinetic energy $\langle T\rangle$ by

$$\eta = \frac{-\frac{1}{2}\langle V\rangle}{\langle T\rangle}. \tag{7}$$

All expectation values reported in Tables I and II have been appropriately scaled using the values of η given in Table I. The number of digits reported for the entries in Tables I and II is intended to show the convergence pattern, and does not imply convergence to a particular number of significant fig-

TABLE I. Expectation values for the energy components and scale factors for the ^2S ground state of the lithium atom.

Number of terms	$(\eta-1)\times 10^6$	$\langle -\frac{1}{2}\nabla_i^2\rangle$	$\left\langle \frac{-3}{r_i}\right\rangle$	$\left\langle \frac{1}{r_{ij}}\right\rangle$	Energy
10	1008	7.475 964 736	−17.146 831 782	2.194 902 310	−7.475 964 736
50	108	7.477 935 472	−17.154 397 259	2.198 526 315	−7.477 935 472
100	31.8	7.478 025 801	−17.154 268 352	2.198 216 750	−7.478 025 801
150	5.88	7.478 050 471	−17.154 297 255	2.198 196 314	−7.478 050 471
200	1.96	7.478 057 188	−17.154 316 690	2.198 202 314	−7.478 057 188
242	0.402	7.478 059 008	−17.154 331 343	2.198 213 327	−7.478 059 008
275	0.196	7.478 059 447	−17.154 331 417	2.198 212 523	−7.478 059 447
296	0.215	7.478 059 528	−17.154 330 780	2.198 211 724	−7.478 059 528

TABLE II. Expectation values for the ^2S ground state of the lithium atom.

Number of terms	Expectation Value $\langle\delta(\mathbf{r}_i)\rangle$	$\langle\nabla_i\cdot\nabla_j\rangle$	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi}\rangle$
10	$1.360\,710\times10^{1}$	$-3.225\,663\times10^{-1}$	2.802 774
50	$1.380\,446\times10^{1}$	$-3.025\,238\times10^{-1}$	3.012 214
100	$1.383\,492\times10^{1}$	$-3.019\,527\times10^{-1}$	2.878 842
150	$1.384\,339\times10^{1}$	$-3.019\,053\times10^{-1}$	2.903 361
200	$1.384\,142\times10^{1}$	$-3.018\,485\times10^{-1}$	2.896 161
242	$1.384\,296\times10^{1}$	$-3.018\,423\times10^{-1}$	2.899 069
275	$1.384\,256\times10^{1}$	$-3.018\,437\times10^{-1}$	2.905 763
296	$1.384\,269\times10^{1}$	$-3.018\,436\times10^{-1}$	2.907 051

ures. In Table II we report values for the electron density at the nucleus

$$\rho(0)=\langle\delta(\mathbf{r}_i)\rangle, \tag{8}$$

the Fermi contact interaction

$$f=4\pi\langle\delta(\mathbf{r}_i)\sigma_{zi}\rangle, \tag{9}$$

and the expectation value $\langle\nabla_i\cdot\nabla_j\rangle$, which is proportional to the specific mass shift. The most convenient manner to evaluate this latter expectation value is to work in terms of the coordinate set $\{r_i, r_{ij}\}$, which utilizes the inherent symmetry of the ^2S state. The form for the operator in this coordinate system is discussed elsewhere.[22]

A. The nonrelativistic energy

The first result of interest is the final value obtained for E_{NR}. This is the lowest upper bound estimate of E_{NR} reported to date. The present value is less than 1 μhartree below a previous 602-term calculation for Li. It is to be noted that the last 54 basis functions added in the present calculation gave an energy lowering of ~0.53 μhartree. Considering that each term was optimized, it is very unlikely that the correct value of E_{NR} lies a further 10–14 μhartrees below our final result. The results of the present calculation are of course not a proof of this assertion, but merely very suggestive. Based on the convergence patterns of the energy components, it is proposed that the published literature estimates of E_{NR} for the ^2S ground state of Li are in error by $\sim$10–14 μhartrees.

A possible criticism of previous calculations of E_{NR} using fixed exponents is that the more distant region of configuration space is not adequately described. For calculations with fixed exponents, the diffuse orbitals have less than optimal exponents, since the exponents are fixed for orbitals describing the near-nuclear region. This is not a limitation of the present calculation. A good number of diffuse basis functions, including those with explicit r_{ij} dependence, are included in the basis set. The repetition of certain key terms that emphasize the near-nuclear region of configuration space, also minimizes possible problems in the construction of the basis set for this region.

As is evident from Table I, the individual components contributing to the energy appear to have converged to about 1 μhartree (or better). On this point a cautionary note is in order; the convergence of both $\langle 1/r_{ij}\rangle$ and $\langle -3/r_i\rangle$ is not monotonic nor could the convergence of the energy be considered smooth. These observations make attempts at estimating an extrapolated value for E_{NR} of doubtful validity.

B. Hyperfine coupling constant

The hyperfine coupling constant, $A_{1/2}$ (in MHz), and the expectation value f are related by

$$A_{1/2}=95.410\,67(7)\left(\frac{g_e\mu_I}{3I}\right)f, \tag{10}$$

where g_e is the electronic g-factor (including bound state effects), μ_I is the magnetic moment, and I is the nuclear spin. The error estimate for the collection of fundamental constants represented numerically in Eq. (10) is shown in parentheses. Using the known literature values[23–25] for ^{7}Li, $g_e=2.0023\,019$, μ_I^0 (the unshielded moment in nuclear magnetons, nm) $=3.256\,416$ nm and $A_{1/2}=401.7520\,433$ MHz yields f (experimental) $=2.906\,058$ a.u. The final f value reported in Table II needs to be corrected for the effects of finite nuclear mass using the factor

$$\left(1+\frac{m_e}{M_{^7\mathrm{Li}}}\right)^{-3}\approx0.999\,765,$$

where m_e is the electron mass and $M_{^7\mathrm{Li}}$ is the nuclear mass of ^{7}Li. The corrected f value is 2.906 37 a.u. which corresponds to a hyperfine coupling constant of 401.795 MHz. This value is in very good agreement with the experimental value reported above. Relativistic corrections to the calculated value of f are expected to be small. There are two points that deserve special note with regard to the present calculation of f as a function of the size of the basis set. f may have converged to approximately four significant digits, although it is far from certain that this is the case based on the convergence behavior exhibited in Table II. Results from a previous calculation[7] using fixed exponents also showed nonmonotonic convergence for f, but interestingly, the observed fluctuation in f over the last 300 terms was small in comparison to what is observed in Table II. The final result for f obtained in that study was $f=2.906\,359$ (not mass corrected), which is in close agreement with the result of the present study.

The second point is that subject to the constraint that the value of f has stabilized in Table II (to at least four decimal digits of precision), the present calculation does show that the absence of the second spin eigenfunction in the basis set does not preclude an accurate calculation of f. The minimal fluctuations observed in our previous calculation[7] of f are due, at least in part, to the presence of both spin eigenfunctions in the basis set. When the basis terms involving the second spin eigenfunction were stripped from the wave function, the resulting change in the energy was very minor, however, the calculated f showed increased fluctuation and the final value obtained with 332 basis functions was 2.928 674 a.u. This value is slightly poorer than that reported for the 602-term wave function[7] or the result from the present study.

C. The electronic density at the nucleus

As is evident from Table II, $\rho(0)$ does not exhibit monotone convergence as a function of basis set size. The final

value reported appears to have converged to at least five significant digits, which is fairly satisfactory, considering that the variational calculation emphasizes the energy important region away from the nucleus. In our previous work[7] $\rho(0)$ was calculated to be 13·8418, and the direction of change was $\rho(0)$ increasing at the end of the employed basis set. The present result is in very close agreement with the aforementioned value.

D. $\langle \nabla_i \cdot \nabla_j \rangle$

The expectation value $\langle \nabla_i \cdot \nabla_j \rangle$ is a sensitive reflection of the extent to which electron correlation is described by the wave function. This expectation value is zero in the Hartree–Fock approximation. The convergence of this quantity is observed to be nonmonotonic.

This expectation value offers one important check on the quality of the wave function, since it can be related to an experimentally measured quantity, the 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

$$\Delta E_{TIS} \equiv (\Delta E_{SMS}^{^{A_1}X^+} - \Delta E_{SMS}^{^{A_1}X}) - (\Delta E_{SMS}^{^{A_2}X^+} - \Delta E_{SMS}^{^{A_2}X}) \equiv (\Delta E_{SMS}^{^{A_2}X} - \Delta E_{SMS}^{^{A_1}X}) - (\Delta E_{SMS}^{^{A_2}X^+} - \Delta E_{SMS}^{^{A_1}X^+}), \quad (11)$$

where + signifies the ionization limit of the species. In the second line of Eq. (11), the terms in parentheses represent, respectively, the isotope shifts for the three-electron and two-electron atomic systems. The nonrelativistic form of the specific mass shift used in Eq. (11) is given by

$$\Delta E_{SMS} = -\frac{\mu}{M}\left\langle \psi \left| \sum_{i<j}^{3} \nabla_i \cdot \nabla_j \right| \psi \right\rangle, \quad (12)$$

where μ is the reduced electron mass,

$$\mu = \frac{m_e M}{m_e + M}, \quad (13)$$

and M is the mass of the nucleus.

Using the final value of $\langle \nabla_i \cdot \nabla_j \rangle$ from Table II the shift for ^{6}Li–^{7}Li is calculated to be 25·84337 GHz. Employing data from Pekeris[26,27] for $\langle \nabla_1 \cdot \nabla_2 \rangle$, the shift for $^6Li^+ - ^7Li^+$ is determined to be 24·74162 GHz. The resulting isotope shift is calculated to be 1·1018 GHz. This value is in close agreement with the most recent experimental value[28] of 1·108 ± 0·008 GHz.

V. CONCLUSION

In this study the lowest upper bound estimate so far available for E_{NR} for the ^2S ground state of the lithium atom is reported. The present result for E_{NR} is believed to be correct to the 1 μhartree level (or better). As reported in Sec. IV, this result is not in agreement with the literature estimates of this quality. If the above assertion is correct, it is interesting that erroneous estimates of E_{NR} should have prevailed so long in the literature.

A number of factors enter into the determination of E_{NR}. The most significant being the experimental ionization potentials, the relativistic corrections, the Lamb shift and the specific mass shift. The literature values of E_{NR} are probably incorrect because of inaccurate estimates of the major relativistic corrections and of the Lamb shift. The specific mass shift is known with sufficient accuracy that this particular contribution does not give rise to any significant uncertainty in E_{NR}.

The only way to convincingly demonstrate the accuracy of the present calculation is to determine a lower bound for E_{NR}. Unfortunately, evaluation of a lower bound for E_{NR} using a general Hylleraas basis set requires some formidable integration problems to be resolved. A number of the difficulties have recently been unraveled by one of the authors and efforts are now underway to determine a lower bound for E_{NR}. Calculations are also in progress to evaluate the principal relativistic corrections. The latter calculation will help resolve one of the possible sources of error in the literature estimates of E_{NR}.

Should the present value of E_{NR} be in error at the 10–14 μhartree level, some rather interesting questions would emerge on the convergence characteristics of the present calculations. As the last 54 terms are added to the wave function, the change in the electron–nuclear contribution is offset in part by the changes in the electron–electron and kinetic energy contributions. In order for an error of ~10 μhartree to exist, this cancellation pattern would probably have to change, and in addition, one or more of the three energy contributions would have to show a marked rate of change in convergence behavior. It is of interest to note that the final values for the electron–nuclear and electron–electron energy components obtained in our previous calculation[7] appear to be converging towards the final values reported in Table I, but are approaching from the opposite direction. This is suggestive that the observed convergence pattern in the present study is unlikely to start exhibiting erratic behavior, at least at the 10 μhartree level.

ACKNOWLEDGMENTS

Acknowledgment is 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 are greatly appreciated. This work would not have been possible without an extremely generous grant of supercomputer time by Cray Research, Inc.

[1] J. Muszyńska, D. Papierowska, and W. Woźnicki, Chem. Phys. Lett. **76**, 136 (1980).
[2] Y. K. Ho, Int. J. Quantum Chem. **20**, 1077 (1981).
[3] J. Pipin and W. Woźnicki, Chem. Phys. Lett. **95**, 392 (1983).
[4] I. Lindgren, Phys. Rev. A **31**, 1273 (1985).
[5] F. W. King and V. Shoup, Phys. Rev. A **33**, 2940 (1986).
[6] W. R. Johnson, S. A. Blundell, and J. R. Sapirstein, Phys. Rev. A **37**, 2764 (1988).
[7] F. W. King, Phys. Rev. A **40**, 1735 (1989).
[8] S. N. Panigrahy, R. W. Dougherty, T. P. Das, and J. Andriessen, Phys. Rev. A **40**, 1765 (1989).
[9] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **40**, 2233 (1989).
[10] F. W. King and P. R. Dressel, J. Chem. Phys. **90**, 6449 (1989).
[11] H. Kleindienst and S. Beutner, Chem. Phys. Lett. **164**, 291 (1989).
[12] J. Muszyńska, D. Papierowska, J. Pipin, and W. Woznicki, Int. J. Quantum Chem. **22**, 1153 (1982).

[13] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).
[14] C. F. Bunge, Phys. Rev. A **16**, 2496 (1977).
[15] C. F. Bunge, Phys. Rev. A **19**, 936 (1979).
[16] E. A. Burke, Phys. Rev. **130**, 1871 (1963).
[17] S. Larsson, Phys. Rev. **169**, 49 (1968).
[18] Y. Öhrn and J. Nordling, J. Chem. Phys. **39**, 1864 (1963).
[19] R. A. Sack, J. Math. Phys. **5**, 245 (1964).
[20] F. W. King, Phys. Rev. A **38**, 6017 (1988).
[21] See AIP document no. PAPS JCPSA-93-2570-5 for 5 pages of one table. The table gives the basis set $\{i\,j\,k\,l\,m\,n\,\alpha\,\beta\,\gamma\}$ for the final wave function employed in the calculations. 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 price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
[22] F. W. King, Phys. Rev. A **34**, 4543 (1986).
[23] A. Beckmann, K. D. Böklen, and D. Elke, Z. Phys. **270**, 173 (1974).
[24] K. D. Böklen, W. Dankwort, E. Pitz, and S. Penselin, Z. Phys. **200**, 467 (1967).
[25] Slightly different experimental values have been reported for the nuclear moment of ^{7}Li. For a recent tabulation see: P. Raghavan, Atom. Data Nucl. Data Tables **42**, 189 (1989).
[26] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[27] C. L. Pekeris, Phys. Rev. **126**, 143 (1962).
[28] C. Vadla, A. Obrebski, and K. Niemax, Opt. Commun. **63**, 288 (1987).