

Lower bound for the nonrelativistic ground state energy of the lithium atom

Frederick W. King

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

(Received 30 January 1995; accepted 21 February 1995)

A Temple lower bound for the nonrelativistic ground state energy of the lithium atom is determined using large scale Hylleraas-type wave functions. Weinstein lower bounds for the three lowest nonrelativistic energy levels are also reported. All the component expectation values necessary to construct the lower bounds are given. Detailed information is given to assess the convergence of the calculations. © 1995 American Institute of Physics.

I. INTRODUCTION

There has been a long history of efforts focused on the determination of lower bounds for the energy levels of atomic and molecular systems. Almost all the published work has dealt with one- and two-electron systems.¹⁻¹⁷ The determination of accurate lower bounds for the energy levels of systems with three or more electrons represents one of the current significant challenges in computational quantum chemistry. In the present work this challenge is addressed for the ground state energy of the lithium atom.

The standard variational technique provides an upper bound estimate for the nonrelativistic energy E_{NR} of a system. Various extrapolation procedures are often employed to improve the computed energy. Since there is no direct experimental comparison possible for E_{NR} , estimation of uncertainties in the computed energy are very difficult, if not impossible to determine. Knowledge of the lower bounds for E_{NR} solves this problem.

There has been renewed interest in the determination of an accurate estimate of E_{NR} for the ground state of the lithium atom.¹⁸⁻²⁶ This work has been driven in part by the long standing existence of several incorrect empirical estimates of this energy.²⁷⁻²⁹ All the accurate calculations published so far utilize the variational approach, with some authors relying on substantial extrapolations to arrive at E_{NR} . To complete the solution of this problem a lower bound estimate of E_{NR} is required.

Three classical lower bound formulas that have been discussed in the literature are the Weinstein³⁰ (E_W), Temple³¹ (E_T), and Stevenson^{32,33} (E_S) results:

$$E_0 \geq E_W = \langle \psi | H | \psi \rangle - \sigma^{1/2}, \quad (1)$$

$$E_0 \geq E_T = \langle \psi | H | \psi \rangle - \frac{\sigma}{E_1 - \langle \psi | H | \psi \rangle}, \quad (2)$$

$$E_0 \geq E_S = \alpha - (\alpha^2 - 2\alpha \langle \psi | H | \psi \rangle + \langle \psi | H^2 | \psi \rangle)^{1/2} \\ = \alpha - [\sigma + (\alpha - \langle \psi | H | \psi \rangle)^2]^{1/2}, \quad (3)$$

where

$$\sigma = \langle \psi | H^2 | \psi \rangle - \langle \psi | H | \psi \rangle^2. \quad (4)$$

In Eqs. (1)–(4) ψ denotes a normalized trial wave function, E_0 is the exact nonrelativistic ground energy, and E_1 is the energy of the first excited state having the same symmetry as the ground state.

The Weinstein bound requires

$$\langle \psi | H | \psi \rangle \leq \frac{1}{2}(E_0 + E_1). \quad (5)$$

The Temple bound requires

$$\langle \psi | H | \psi \rangle < E_1, \quad (6)$$

and for practical applications, since E_1 is not known exactly, a lower bound estimate for E_1 (E_1^L) is employed with $E_1^L > \langle \psi | H | \psi \rangle$. The Stevenson bound requires

$$\alpha \leq \frac{1}{2}(E_0 + E_1). \quad (7)$$

Equations (1) and (2) can be shown to be special cases of Eq. (3) with an appropriate choice of α . These three bounds have been discussed extensively in the literature.³⁴⁻⁴⁵ Most of the applications of these formulas have been restricted to few-electron atoms and molecular systems. The principal reason for this is the considerable mathematical difficulty associated with the evaluation of $\langle \psi | H^2 | \psi \rangle$.

A number of additional lower bound formulas for the energy have been proposed. Those based on intermediate Hamiltonian methods appear to have shown the most promise in practical applications, although major problems have yet to be resolved for this technique to be applied in a routine manner to many-electron systems.⁴⁶⁻⁶⁰

The lower bound problem for the lithium atom has received some attention over the past 20 years, but progress has been very limited.^{3,61-67} This is to be contrasted with the situation for atomic two-electron systems where the error in the lower bound is approximately 10^{-4} cm⁻¹ or less.¹⁷

Conroy³ appears to be the first to have obtained a lower bound for E_{NR} for the Li atom. Using Temple's formula he found a lower bound of -7.61413 a.u. Conroy's calculation was based on a wave function with 17 terms. The level of precision of this calculation is rather surprising, since the lowest eigenvalue is determined to only three digits of precision, and matrix elements of H^2 tend not to converge very quickly. Unfortunately, minimal details are reported for the wave function that Conroy employed. The only other determination of a lower bound based on the use of the classical

formulas given in Eqs. (1)–(3) that is known to the author, is a recent work of Lüchow and Kleindienst⁶⁸ based on a large scale Hylleraas wave function.

II. COMPUTATIONAL PROCEDURE

A. Theory

A sketch of the procedure employed is presented below, additional details may be found in the literature.^{18,19,69} The trial wave function employed is

$$\psi = \mathcal{A} \sum_{\mu=1}^N C_{\mu} \phi_{\mu} \chi_{\mu}, \quad (8)$$

where \mathcal{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

$$\begin{aligned} \phi_{\mu} &\equiv \phi_{\mu}(r_1, r_2, r_3, r_{23}, r_{31}, r_{12}) \\ &= r_1^{i_{\mu}} r_2^{j_{\mu}} r_3^{k_{\mu}} r_{23}^{l_{\mu}} r_{31}^{m_{\mu}} r_{12}^{n_{\mu}} \exp(-\alpha_{\mu} r_1 - \beta_{\mu} r_2 - \gamma_{\mu} r_3), \end{aligned} \quad (9)$$

where the exponents i_{μ} , j_{μ} , k_{μ} , l_{μ} , m_{μ} , and n_{μ} are each ≥ 0 . In Eq. (8) χ_{μ} denotes the spin eigenfunction

$$\chi_{\mu} = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3). \quad (10)$$

A second doublet spin eigenfunction exists, but has not been employed in the calculations.

The nonrelativistic Hamiltonian employed is

$$H = \sum_{i=1}^3 \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}}, \quad (11)$$

with $Z=3$. The mass polarization contribution to H is ignored. Evaluation of the matrix elements $\langle \phi_{\mu} | H | \phi_{\nu} \rangle$ or $\langle \phi_{\mu} | H^2 | \phi_{\nu} \rangle$ can be shown to reduce to integrals of the following type:

$I(i, j, k, l, m, n, \alpha, \beta, \gamma)$

$$= \int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_3} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (12)$$

The reduction of the matrix elements to integrals of the form indicated in Eq. (12) is most conveniently carried out by taking advantage of the symmetry of the system and working directly with the coordinate variables $(r_1, r_2, r_3, r_{23}, r_{31}, r_{12})$. Evaluation of $\langle \phi_{\mu} | H | \phi_{\nu} \rangle$ requires I integrals with $l \geq -1$, $m \geq -1$, and $n \geq -1$. These I integrals have been extensively discussed in the literature.^{69–80} Evaluation of $\langle \phi_{\mu} | H^2 | \phi_{\nu} \rangle$ is the real bottleneck in the calculation and is the reason why very little progress has been made on this problem. I integrals required may have l, m , or $n = -2$ or cases where two of the l, m, n set $= -2$. These cases lead to formidable integration problems, which have only recently been solved.^{81–84} At first glance the shift from factors of r_{ij}^{-1} to r_{ij}^{-2} may not appear to lead to a substantial increase in complexity for the integrals that must be solved. However, the expansion of r_{ij}^{-2} contains lead-off terms containing factors of $\ln(r_i + r_j)/(r_i - r_j)$, which greatly complicate the solution of the integrals. The most difficult integral cases that arise in the present calculations have factors like $r_{23}^{-2} r_{31}^m r_{12}^n$

with m and n both odd. Such integrals can be evaluated by truncation of a rather slowly converging infinite series,⁸² or by using convergence acceleration techniques.^{83,84}

Formidable algebraic operations are involved for the determination of the square of the kinetic energy operator T^2 . Part of the algebra was done by hand,⁸⁵ and later reworked using the symbolic algebra capabilities of MATHEMATICA.⁸⁶ A more detailed account of these algebraic manipulations will be discussed elsewhere.⁸⁵ The evaluation of $\langle T^2 \rangle$ involves matrix elements like $\langle \phi_{\mu} | \nabla_i^4 | \phi_{\nu} \rangle$ and $\langle \phi_{\mu} | \nabla_i^2 \nabla_j^2 | \phi_{\nu} \rangle$ with $i \neq j$ [see Eqs. (14) and (15) below]. These were evaluated using the mathematically equivalent forms $\langle \nabla_i^2 \phi_{\mu} | \nabla_i^2 \phi_{\nu} \rangle$ and $\langle \nabla_i^2 \phi_{\mu} | \nabla_j^2 \phi_{\nu} \rangle$, respectively. This represents a considerable reduction in computational effort. The reason is that the matrix element $\langle \phi_{\mu} | \nabla_i^4 | \phi_{\nu} \rangle$ leads to additional integrals that cannot be expressed in the form of Eq. (12), and which are particularly difficult to evaluate. These integrals will be discussed elsewhere.⁸⁵

B. Choice of basis functions

There are several approaches to select the basis set. For the orbital exponents two extreme choices are fixed exponents: $\alpha_{\mu} = \beta_{\mu} = \alpha$, $\gamma_{\mu} = \gamma$ all μ , or variable exponents. The orbital indices $(i_{\mu}, j_{\mu}, k_{\mu}, l_{\mu}, m_{\mu}, n_{\mu})$ can be selected in two major ways. If

$$\omega = i_{\mu} + j_{\mu} + k_{\mu} + l_{\mu} + m_{\mu} + n_{\mu}, \quad (13)$$

then all terms leading to particular values of ω are included with values of ω taken as 0, 1, 2, ..., ω_{\max} . Alternatively the indices can be selected based on experience and with the idea of minimizing the mathematical complexities of the calculation. The approach involving taking all indices for a particular ω and then systematically increasing ω , will most likely lead to the best convergence behavior. Unfortunately this approach is not feasible without modification. If no restriction on the set $(i_{\mu}, j_{\mu}, k_{\mu}, l_{\mu}, m_{\mu}, n_{\mu})$ is made, then some I integrals with a factor $r_{ij}^{-2} r_{jk}^{-2}$ arise. Methods to deal with I integrals having such factors are available,^{83,84} but the solutions involve limited precision, which would not be easy to extend. If integrals of limited precision are employed, the resulting matrix elements would be of limited precision, which would seriously limit the computations, particularly for large basis sets. The best strategy at this time appears to be one whereby basis set members leading to such integrals are deleted from the wave function.

It is possible to entirely avoid all I integrals with r_{ij}^{-2} factors by appropriate selection of the indices $(i_{\mu}, j_{\mu}, k_{\mu}, l_{\mu}, m_{\mu}, n_{\mu})$. A trial calculation along these lines was done as a first attempt, with the initial focus centered on the expectation value of H . Fixed exponents (selected on the basis of past experience) were employed and terms were added in order of increasing values of ω . The results were rather disappointing, although not entirely unexpected. With 680 terms an energy of $-7.477\,000$ a.u. was obtained. Simply too many basis functions that are important for a good energy determination had to be deleted to avoid the integral problems. While this approach could have been extended, the rate of convergence of the calculation would have been rather poor.

The second basis set employed started with a stripped down version of a previously constructed wave function which had involved extensive optimization of the nonlinear parameters.²¹ This 273 term function yields an energy of $-7.478\,059$ a.u. which is just $1\ \mu\text{hartree}$ from the expected ground state energy.^{24,25} An additional 487 terms were added, in large part based on their expected impact on the energy.

With hindsight, a feasible alternative to the construction of the basis set may have been more cost effective. If fixed exponents had been employed a store and retrieve strategy becomes effective for the I integrals. This approach does however have some limitations. The most serious is that the low lying excited states would be obtained with lower precision. A good description of these states is necessary to apply the Temple formula. With the integral evaluation methods recently introduced only the cases $l = -2$, m and n both odd (or any permutation of these three exponent indicies) are really time consuming to evaluate.⁸¹⁻⁸⁴ A store and retrieve strategy for just this group of integrals would lead to a significant reduction in required CPU resources. This savings would have to be balanced against the much larger basis set that would be required, caused in part by the fact that repeats of key terms such as (001001) with different exponent scales would be excluded in the fixed exponent approach.

C. Accuracy controls

Careful attention was paid to accuracy controls for both the integral evaluations and the matrix element calculations. The I integrals were all determined with around 20 (or better) digits of precision, except for the cases $l = -2$, m and n both odd, which were evaluated with approximately 16–17 digits of precision. These levels were checked by computing a large number of test cases by independent methods.

The individual expectation values were calculated by separately combining all the positive contributions (i.e., positive factors of the form $C_i C_j \langle \phi_i | \hat{O} | \phi_j \rangle$) and all the negative contributions. With this procedure it is possible to demonstrate that there is a potential for a loss of up to 12 digits of precision for the determination of a final expectation value. This procedure points to the necessity of computing the basic integrals [Eq. (12)] to a fairly high level of precision, so the matrix elements $\langle \phi_i | \hat{O} | \phi_j \rangle$ are determined with the highest possible precision. This problem is likely to be more significant with larger basis sets.

The loss of precision that occurs for the evaluation of an individual matrix element is not a significant factor in determining the precision of a particular expectation value. This has been carefully checked in prior calculations.

The calculations were carried out in either double precision on a Cray YMP or quadruple precision on a RISC/6000 workstation.

D. Convergence considerations

In order to get some idea of the convergence of the calculations the various expectation values were determined using basis sets of varying size up to the maximum size of the final basis set. Since both $\langle \psi | H | \psi \rangle$ and $\langle \psi | H^2 | \psi \rangle$ are a combination of contributions of opposite sign, it is extremely

desirable to examine the convergence of the individual components. This provides a check for any possible cancellation of errors.

The following notation is employed for reporting expectation values:

$$\langle O_i \rangle \equiv \langle \psi | \sum_{i=1}^3 O_i | \psi \rangle, \quad (14)$$

$$\langle O_{ij} \rangle \equiv \langle \psi | \sum_{i=1}^3 \sum_{j>i}^3 O_{ij} | \psi \rangle, \quad (15)$$

$$\langle O_{ijk} \rangle \equiv \langle \psi | \sum_{i=1}^3 \sum_{j>i}^3 \sum_{k=1}^3 O_{ijk} | \psi \rangle, \quad (16)$$

$$\langle O_{ijkl} \rangle = \frac{1}{2} \langle \psi | \sum_{i=1}^3 \sum_{j>i}^3 \sum_{k=1}^3 \sum_{l>i}^3 O_{ijkl} | \psi \rangle. \quad (17)$$

($k=i, l=j$ excluded)

For $\langle \psi | H | \psi \rangle$ the following three components are reported:

$$\langle T \rangle = \langle -\frac{1}{2} \nabla_i^2 \rangle, \quad (18)$$

$$\langle V_{ee} \rangle = \left\langle \frac{1}{r_{ij}} \right\rangle, \quad (19)$$

$$\langle V_{en} \rangle = \left\langle -\frac{Z}{r_i} \right\rangle \quad (20)$$

and for $\langle \psi | H^2 | \psi \rangle$ the following contributions are tabulated: $\langle r_i^{-2} \rangle$, $\langle (r_i r_j)^{-1} \rangle$, $\langle r_{ij}^{-2} \rangle$, $\langle (r_{ij} r_{ik})^{-1} \rangle$, and

$$\langle V_{en}^2 \rangle = Z^2 \{ \langle r_i^{-2} \rangle + 2 \langle (r_i r_j)^{-1} \rangle \}, \quad (21)$$

$$\langle V_{ee}^2 \rangle = \langle r_{ij}^{-2} \rangle + 2 \langle (r_{ij} r_{kl})^{-1} \rangle, \quad (22)$$

$$\langle V_{ee} V_{en} \rangle = -Z \langle (r_{ij} r_k)^{-1} \rangle, \quad (23)$$

$$\langle \nabla_i^2 | \nabla_i^2 \rangle = \sum_{i=1}^3 \langle \nabla_i^2 \psi | \nabla_i^2 \psi \rangle, \quad (24)$$

$$\langle \nabla_i^2 | \nabla_j^2 \rangle = \sum_{i=1}^3 \sum_{j>i}^3 \langle \nabla_i^2 \psi | \nabla_j^2 \psi \rangle \quad (25)$$

as well as $\langle V^2 \rangle$, $\langle V_{en} T \rangle$, $\langle V_{ee} T \rangle$, $\langle VT \rangle$, $\langle T^2 \rangle$, and $\langle H^2 \rangle$. The scale factor η defined by

$$\eta = -\frac{\langle V \rangle}{2 \langle T \rangle} \quad (26)$$

as well as the variance, defined in Eq. (4), are also reported in Table I. Both $\eta - 1$ and σ should approach 0 for a wave function of improving quality. All expectation values have been appropriately scaled using the values of η indicated in Table I.

Some of the above components may be of interest for other applications. For example, the expectation value in Eq. (24) is required to evaluate one of the principal relativistic corrections. The expectation value $\langle r_{ij}^{-2} \rangle$ appears in a formula for a lower bound to the atomic electronic density at the nucleus,⁸⁷ and $\langle r_i^{-2} \rangle$ appears in a number of formulas bounding the electronic density.^{87,88}

TABLE I. Expectation values employed in the evaluation of the lower bounds. All values are in a.u. The notation $[m]$ signifies $\times 10^m$.

Expectation value	Number of terms								
	50	100	200	300	404	521	600	695	760
$\langle T \rangle$	7.477 948	7.478 020	7.478 057	7.478 0592	7.478 0595	7.478 0598	7.478 059 86	7.478 059 97	7.478 060 0
$\langle V_{ee} \rangle$	2.198 378	2.198 172	2.198 215	2.198 212	2.198 2119	2.198 2123	2.198 212 25	2.198 212 32	2.198 212 32
$\langle V_{en} \rangle$	-17.154 273	-17.154 212	-17.154 328	-17.154 330	-17.154 3309	-17.154 3319	-17.154 331 98	-17.154 332 27	-17.154 332 33
E	-7.477 948	-7.478 020	-7.478 057	-7.478 0592	-7.478 0595	-7.478 0598	-7.478 059 86	-7.478 059 97	-7.478 060 0
$\eta-1$	5.65[-5]	3.47[-5]	5.24[-7]	3.16[-7]	2.39[-7]	1.69[-7]	1.58[-7]	1.30[-7]	1.19[-7]
$\left\langle \frac{1}{r_i^2} \right\rangle$	30.226 155	30.236 252	30.240 595	30.240 910	30.241 002	30.240 958	30.240 963	30.240 969	30.240 959
$\left\langle \frac{1}{r_i r_j} \right\rangle$	8.788 448	8.788 686	8.789 450	8.789 470	8.789 474	8.789 4771	8.789 4773	8.789 4776	8.789 477 5
$\langle V_{en}^2 \rangle$	430.227 46	430.322 62	430.375 46	430.378 64	430.379 54	430.379 21	430.379 26	430.379 32	430.379 22
$\left\langle \frac{1}{r_{ij}^2} \right\rangle$	4.382 870	4.381 848	4.381 284	4.381 271	4.381 290	4.381 223	4.381 161	4.380 695	4.382 075
$\left\langle \frac{1}{r_{ij} r_{jk}} \right\rangle$	1.101 566	1.101 488	1.101 676	1.101 683	1.101 6848	1.101 6863	1.101 6864	1.101 6874	1.101 687 5
$\langle V_{ee}^2 \rangle$	6.586 003	6.584 825	6.584 635	6.584 636	6.584 660	6.584 596	6.584 533	6.584 070	6.585 450
$\langle V_{ee} V_{en} \rangle$	-43.096 685	-43.094 341	-43.097 256	-43.097 214	-43.097 220	-43.097 237	-43.097 238	-43.097 237	-43.097 232
$\langle V^2 \rangle$	350.620 096	350.718 765	350.765 580	350.768 853	350.769 764	350.769 330	350.769 315	350.768 914	350.770 211
$\langle V_{en} T \rangle$	-258.613 68	-258.879 09	-258.984 68	-258.998 83	-259.002 58	-259.000 27	-259.000 67	-259.001 15	-259.000 60
$\langle V_{ee} T \rangle$	20.076 67	20.076 70	20.075 40	20.076 05	20.075 93	20.075 96	20.076 04	20.076 20	20.087 05
$\langle VT \rangle$	-238.537 00	-238.802 40	-238.909 28	-238.922 77	-238.926 65	-238.924 30	-238.924 62	-238.924 95	-238.913 56
$\langle \nabla_i^2 \nabla_i^2 \rangle$	626.037 2	627.722 9	628.333 4	628.428 8	628.455 5	628.437 8	628.440 4	628.444 4	628.440 9
$\langle \nabla_i^2 \nabla_j^2 \rangle$	51.742 82	51.757 67	51.782 73	51.782 12	51.782 47	51.782 60	51.782 46	51.782 64	51.782 94
$\langle T^2 \rangle$	182.380 71	182.809 56	182.974 70	182.998 26	183.005 11	183.000 74	183.001 33	183.002 42	183.001 70
$\langle H^2 \rangle$	55.926 80	55.923 53	55.921 72	55.921 56	55.921 57	55.921 47	55.921 40	55.921 44	55.944 480
σ	7.10[-3]	2.75[-3]	3.9[-4]	1.9[-4]	1.9[-4]	8.8[-5]	2.2[-5]	5.4[-5]	2.3[-2]

III. RESULTS

Table I summarizes the results for the individual expectation values that are required for the evaluation of $\langle H \rangle$ and $\langle H^2 \rangle$. The most apparent feature from Table I is that many of the component expectation values required for the evaluation of $\langle H^2 \rangle$ are converging at slower rates compared to what is observed for the various components needed to evaluate $\langle H \rangle$. This is not a totally unexpected behavior. Several of the expectation values involved in the calculation of $\langle H^2 \rangle$ are dependent on the quality of the wave function in the near nuclear region. This is one region of configuration space where it is more difficult to improve the accuracy of the wave function.

The second feature to be noted from Table I is the breakdown in convergence of several expectation values when the size of the basis set is very large. This convergence behavior has been explored for a number of additional wave functions not present in Table I. The most probable explanation for the observed convergence behavior is a combination of the following two factors. As the size of the basis set increases the possibility for significant figure loss in the construction of the expectation values increases, a fact that can be noted by examination of the sum of the positive and the sum of the negative contributions to a particular expectation value. This is coupled with the precision limits available for the computation of some of the most difficult integrals (the cases such as $l = -2$ and m and n both odd discussed earlier). The fact that most of the convergence problems show up for expectation values dependent on the more difficult integral cases

lends support for this argument. Because of the convergence accelerator techniques employed to compute some of the more difficult integrals, its not easy to extend the precision available for these integral cases.⁸⁴

As estimate of the converged value of several of the key expectation values along with reasonable estimates of the likely errors (based on Table I and many additional values of the expectation values not reported in this table) are

$$\langle \nabla_i^2 | \nabla_i^2 \rangle = 628.441 \pm 0.003,$$

$$\langle \nabla_i^2 | \nabla_j^2 \rangle = 51.7829 \pm 0.0002,$$

$$\langle V_{en}^2 \rangle = 430.3792 \pm 0.0001,$$

$$\langle V_{ee} V_{en} \rangle = -43.097 23 \pm 0.000 01,$$

$$\langle r_{ij}^{-2} \rangle = 4.3812 \pm 0.0001,$$

$$\langle (r_{ij} r_{jk})^{-1} \rangle = 1.101 687 \pm 0.000 002,$$

$$\langle V_{en} T \rangle = -259.0006 \pm 0.0008,$$

$$\langle V_{ee} T \rangle = 20.076 \pm 0.002,$$

$$\langle V_{ee}^2 \rangle = 6.5846 \pm 0.0001,$$

$$\langle V^2 \rangle = 350.7693 \pm 0.0004,$$

$$\langle T^2 \rangle = 183.001 \pm 0.002, \quad \langle H^2 \rangle = 55.9214 \pm 0.0001.$$

For the other expectation values the 760 term values are the most reliable, and the reader can gauge the error estimates by examination of the convergence trends.

TABLE II. Expectation values for the moments $\langle \Sigma_{i=1}^3 r_i^n \rangle$. All values are in a.u. The notation $[m]$ signifies $\times 10^m$.

Number of terms	Expectation value				
	$\langle r_i^2 \rangle$	$\langle r_i^4 \rangle$	$\langle r_i^6 \rangle$	$\langle r_i^8 \rangle$	$\langle r_i^{10} \rangle$
50	1.837 472[1]	5.516 864[2]	2.783 37[4]	2.0795[6]	2.178[8]
100	1.836 830[1]	5.520 525[2]	2.814 66[4]	2.2293[6]	3.102[8]
200	1.835 439[1]	5.500 872[2]	2.775 75[4]	2.0880[6]	2.262[8]
300	1.835 477[1]	5.500 799[2]	2.772 71[4]	2.0718[6]	2.163[8]
404	1.835 471[1]	5.500 814[2]	2.773 16[4]	2.0755[6]	2.206[8]
521	1.835 465[1]	5.500 749[2]	2.772 90[4]	2.0725[6]	2.163[8]
636	1.835 4630[1]	5.500 732[2]	2.772 91[4]	2.0734[6]	2.187[8]
695	1.835 4623[1]	5.500 728[2]	2.772 89[4]	2.0730[6]	2.177[8]
760	1.835 4627[1]	5.500 736[2]	2.772 89[4]	2.0726[6]	2.164[8]

One measure of the improving quality of the wave function in different regions of configuration space can be obtained by an examination of the convergence of the moments $\langle r_i^n \rangle$ for different values of n . Table II shows the values of the $\langle r_i^n \rangle$ for positive n , for $n = -2$ see Table I, and for $n = -1$, examine $-\frac{1}{3}\langle V_{en} \rangle$ (from Table I). The moments for small n are generally converging fairly satisfactorily though not monotonically. The higher moments ($n = 8, 10$) are converging much more slowly. This behavior for the higher values of n is not unexpected, since the 760 term wave function employed does not have a large number of basis functions emphasizing the diffuse regions of configuration space.

The lower bound results obtained in this work are summarized in Table III. For the ground state of Li the Temple lower bound is as expected better than the Weinstein lower bound. The Temple bound for the ground state employed the value E_1^L obtained from the Weinstein formula. Unfortunately, Temple lower bounds could not be obtained for the 3^2S and 4^2S states because values of E_2^L and E_3^L , lower bounds for the energies of the 4^2S and 5^2S states, respectively, were not obtained with sufficiently high accuracy to meet the generalization of the constraint given in Eq. (6). For both these excited states there is a fairly rapid breakdown in the convergence of the expectation values required for the calculation of $\langle H^2 \rangle$. For the components required for the evaluation of $\langle H \rangle$ for the excited states, the convergence of the expectation values is well behaved. In fact the value of E_{NR} for the 3^2S state obtained from the 760 term wave function is within $2.3 \mu\text{hartree}$ of the lowest upperbound estimate of this quantity published to date.²⁶

A key observation from Table III is that the upper bound estimate for E_{NR} is obtained to a much higher level of precision than the lower bound estimate. This finding is consis-

TABLE III. Lower bound estimates for E_{NR} . All values are in a.u.

State	Number of terms	Weinstein	Temple	Lowest
		lower bound [Eq. (1)]	lower bound [Eq. (2)]	upper bound ^a
2^2S	600	-7.4828	-7.478 30	-7.478 060
3^2S	450	-7.3860		-7.354 095
4^2S	500	-7.3858		-7.318 445

^aThese energies are obtained from the wave function with 760 terms.

tent with many other calculations in the literature (mostly on two-electron atomic systems). In the present case, its clear from the values presented in Table I why this observation is to be expected. Simply focus on the convergence of some of the key components of $\langle H^2 \rangle$.

The final values of $\langle H^2 \rangle$ reported in Table I appear to have convergence to more digits of precision than is justified by the component expectation values. That is, there is some fortuitous cancellation of errors in the construction of $\langle H^2 \rangle$. Its obviously going to take a very carefully constructed wave function to produce values of all the separate expectation values converged to better than $\pm 1 \mu\text{hartree}$.

IV. CONCLUDING REMARKS

Several issues obviously need additional attention if highly accurate lower bounds are to be obtained. Probably the pressing (and the most difficult) problem is to find superior methods to evaluate the integrals that have factors such as r_{ij}^{-2} . Such new methods should offer the possibility to compute the integrals to high precision, but at the same time be cost effective in terms of CPU resources. The second issue to resolve is how to build better wave functions that are highly accurate in the near nuclear region, without using basis functions that lead to intractable integration problems. Finally, there would be considerable interest if new lower bound formulas could be found which totally avoid the problem of working with $\langle H^2 \rangle$.

It might be possible to improve the quality of the lower bounds by a variance minimization technique. This topic is under investigation by the author.

ACKNOWLEDGMENTS

Support from the National Science Foundation (Grant Nos. PHY-9004899 and PHY-9300863), the Camille and Henry Dreyfus Foundation, and the Petroleum Research Fund of the American Chemical Society are greatly appreciated. The author thanks Paul Dressel for some helpful comments and Professor Kleindienst for an advance preprint of Ref. 68. A grant of computer time at the National Center for Supercomputing Applications, Illinois and a generous grant of supercomputer time from Cray Research, Inc. are acknowledged with thanks.

¹T. Kinoshita, Phys. Rev. **115**, 366 (1959).²C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).³H. Conroy, J. Chem. Phys. **41**, 1336 (1964).⁴J. Goodisman and D. Secrest, J. Chem. Phys. **41**, 3610 (1964).⁵J. Goodisman and D. Secrest, J. Chem. Phys. **45**, 1515 (1966).⁶M. Walmsley and C. A. Coulson, Proc. Philos. Soc. **62**, 769 (1966).⁷M. Walmsley, Proc. Cambridge Philos. Soc. **63**, 451 (1967).⁸J. Goodisman, J. Chem. Phys. **47**, 5247 (1967).⁹M. E. Schwartz, Proc. Phys. Soc. **90**, 51 (1967).¹⁰I. T. Keaveny and R. E. Christoffersen, J. Chem. Phys. **50**, 80 (1969).¹¹J. O. Eaves, B. C. Walsh, and E. Steiner, J. Phys. B **7**, 1451 (1974).¹²B. E. Ley, T. Thorpe, and S. M. Rothstein, Int. J. Quantum Chem. **8**, 971 (1974).¹³G. F. Thomas, F. Javor, and S. M. Rothstein, J. Chem. Phys. **64**, 1574 (1975).¹⁴M. A. Abdel-Raouf, Physica C **97**, 103 (1979).¹⁵H. Kleindienst and W. Müller, Theor. Chim. Acta **56**, 183 (1980).¹⁶H. Kleindienst and D. Hoppe, Theor. Chim. Acta **70**, 221 (1986).¹⁷H. Kleindienst and R. Emrich, Int. J. Quantum Chem. **37**, 257 (1990).

- ¹⁸F. W. King and V. Shoup, *Phys. Rev. A* **33**, 2940 (1986).
- ¹⁹F. W. King, *Phys. Rev. A* **40**, 1735 (1989).
- ²⁰H. Kleindienst and S. Beutner, *Chem. Phys. Lett.* **164**, 291 (1989).
- ²¹F. W. King and M. Bergsbaken, *J. Chem. Phys.* **93**, 2570 (1990).
- ²²O. Jitrik and C. F. Bunge, *Phys. Rev. A* **43**, 5804 (1991).
- ²³K. T. Chung, *Phys. Rev. A* **44**, 5421 (1991).
- ²⁴D. K. McKenzie and G. W. F. Drake, *Phys. Rev. A* **44**, R6973 (1991).
- ²⁵J. Pipin and D. M. Bishop, *Phys. Rev. A* **45**, 2736 (1992).
- ²⁶A. Lüchow and H. Kleindienst, *Chem. Phys. Lett.* **197**, 105 (1992).
- ²⁷J. Muszynska, D. Papierowska, J. Pipin, and W. Woznicki, *Int. J. Quantum Chem.* **22**, 1153 (1982).
- ²⁸C. W. Scherr, J. N. Silverman, and F. A. Matsen, *Phys. Rev.* **127**, 830 (1962).
- ²⁹C. F. Bunge, *Phys. Rev. A* **16**, 2496 (1977).
- ³⁰D. H. Weinstein, *Proc. Natl. Acad. Sci. U.S.A.* **20**, 529 (1934).
- ³¹G. Temple, *Proc. R. Soc. London Ser. A* **119**, 276 (1928).
- ³²A. F. Stevenson, *Phys. Rev.* **53**, 199 (1938).
- ³³A. F. Stevenson and M. F. Crawford, *Phys. Rev.* **54**, 375 (1938).
- ³⁴T. Kato, *J. Phys. Soc. Jpn.* **4**, 334 (1949).
- ³⁵G. L. Caldow and C. A. Coulson, *Proc. Cambridge Philos. Soc.* **57**, 341 (1961).
- ³⁶A. Fröman and G. G. Hall, *J. Mol. Spectrosc.* **7**, 410 (1961).
- ³⁷E. B. Wilson, Jr., *J. Chem. Phys.* **43**, S172 (1965).
- ³⁸E. Switkes, *J. Chem. Phys.* **47**, 869 (1967).
- ³⁹E. W. Schmid and J. Schwager, *Z. Phys.* **210**, 309 (1968).
- ⁴⁰L. M. Delves, *J. Phys. A* **5**, 1123 (1972).
- ⁴¹C. A. Coulson and P. J. Haskins, *J. Phys. B* **6**, 1741 (1973).
- ⁴²M. Cohen and T. Feldmann, *J. Phys. A* **4**, 761 (1979).
- ⁴³M. Cohen and T. Feldman, *J. Phys. A* **9**, 1617 (1976).
- ⁴⁴M. Cohen and T. Feldman, *J. Phys. B* **12**, 2771 (1979).
- ⁴⁵A. Scrinzi, *Phys. Rev. A* **45**, 7787 (1992).
- ⁴⁶N. W. Bazley, *Proc. Natl. Acad. Sci. U.S.A.* **48**, 850 (1959).
- ⁴⁷N. W. Bazley, *Phys. Rev.* **120**, 144 (1960).
- ⁴⁸N. W. Bazley and D. W. Fox, *Phys. Rev.* **124**, 483 (1961).
- ⁴⁹B. P. Johnson and C. A. Coulson, *Proc. Phys. Soc.* **84**, 263 (1964).
- ⁵⁰J. G. Kay, *Phys. Rev.* **135**, A1220 (1964).
- ⁵¹W. H. Miller, *J. Chem. Phys.* **42**, 4305 (1965).
- ⁵²P. O. Löwdin, *Phys. Rev.* **139**, A357 (1965).
- ⁵³P. O. Löwdin, *J. Chem. Phys.* **43**, S175 (1965).
- ⁵⁴T. M. Wilson, *J. Chem. Phys.* **47**, 3912 (1967).
- ⁵⁵T. M. Wilson and C. E. Reid, *J. Chem. Phys.* **47**, 3920 (1967).
- ⁵⁶T. M. Wilson, *Int. J. Quantum Chem. Symp.* **1**, 511 (1967).
- ⁵⁷P. S. C. Wang, *J. Chem. Phys.* **48**, 4131 (1968).
- ⁵⁸C. E. Reid, in *Quantum Science Methods and Structure*, edited by J.-L. Calais, O. Goscinski, J. Linderberg, and Y. Öhrn (Plenum, New York, 1976), p. 315.
- ⁵⁹W. Stenger, in *The Uncertainty Principle and Foundations of Quantum Mechanics*, edited by W. C. Price and S. S. Chissick (Wiley, New York, 1977), p. 277.
- ⁶⁰R. N. Hill, *J. Math. Phys.* **21**, 2182 (1980).
- ⁶¹C. E. Reid, *Int. J. Quantum Chem.* **6**, 793 (1972).
- ⁶²D. W. Fox and V. G. Sigillito, *Chem. Phys. Lett.* **13**, 85 (1972).
- ⁶³D. W. Fox and V. G. Sigillito, *Chem. Phys. Lett.* **14**, 583 (1972).
- ⁶⁴D. W. Fox, *SIAM J. Math. Anal.* **3**, 617 (1972).
- ⁶⁵D. W. Fox and V. G. Sigillito, *J. Appl. Math. Phys.* **23**, 392 (1972).
- ⁶⁶C. E. Reid, *Chem. Phys. Lett.* **26**, 243 (1974).
- ⁶⁷D. M. Russell and W. M. Greenlee, *Phys. Rev. Lett.* **54**, 665 (1985).
- ⁶⁸A. Lüchow and H. Kleindienst, *Int. J. Quantum Chem.* **51**, 211 (1994).
- ⁶⁹S. Larsson, *Phys. Rev.* **169**, 49 (1968).
- ⁷⁰H. M. James and A. S. Coolidge, *Phys. Rev.* **49**, 688 (1936).
- ⁷¹L. Szasz, *J. Chem. Phys.* **35**, 1072 (1961).
- ⁷²Y. Öhrn and J. Nording, *J. Chem. Phys.* **39**, 1864 (1963).
- ⁷³J. F. Perkins, *J. Chem. Phys.* **48**, 1985 (1968).
- ⁷⁴V. McKoy, *J. Chem. Phys.* **42**, 2959 (1965).
- ⁷⁵R. A. Bonham, *J. Mol. Spectrosc.* **15**, 112 (1965).
- ⁷⁶E. A. Burke, *Phys. Rev.* **130**, 1871 (1963).
- ⁷⁷Y. K. Ho and B. A. P. Page, *J. Comput. Phys.* **17**, 122 (1975).
- ⁷⁸A. Berk, A. K. Bhatia, B. R. Junker, and A. Temkin, *Phys. Rev. A* **34**, 4591 (1986).
- ⁷⁹E. Remiddi, *Phys. Rev. A* **44**, 5492 (1991).
- ⁸⁰D. M. Fromm and R. N. Hill, *Phys. Rev. A* **36**, 1013 (1987). These authors discuss a generalization of Eq. (12).
- ⁸¹F. W. King, *Phys. Rev. A* **44**, 7108 (1991).
- ⁸²F. W. King, K. J. Dykema, and A. D. Lund, *Phys. Rev. A* **46**, 5406 (1992). An error has been detected in the first line of Eq. (28), it should read $f(t) = \epsilon^{L+2}/[(\epsilon+1)^{L+1}(L+1)(at)^{L+2}]$.
- ⁸³A. Lüchow and H. Kleindienst, *Int. J. Quantum Chem.* **45**, 445 (1993).
- ⁸⁴I. Porras and F. W. King, *Phys. Rev. A* **49**, 1637 (1994).
- ⁸⁵F. W. King, D. Ballegeer, D. Larson, S. Nelson, and T. Prosa (work in progress and to be submitted).
- ⁸⁶MATHEMATICA is a software package available from Wolfram Research, Inc. in Illinois.
- ⁸⁷F. W. King, *J. Chem. Phys.* **80**, 4317 (1984).
- ⁸⁸T. Hoffmann-Ostenhof and M. Hoffmann-Ostenhof, *J. Phys. B* **11**, 17 (1978). M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and W. Thirring, *ibid.* **11**, L571 (1978). F. W. King, *J. Math. Phys.* **24**, 1891 (1983); *J. Chem. Phys.* **78**, 2459, 3091 (1983); J. S. Dehesa, F. J. Galvez, and I. Porras, *Phys. Rev. A* **39**, 494 (1989).