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

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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. 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 is 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. This work has been driven in part by the long standing existence of several incorrect empirical estimates of this energy. 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 Weinstein (Eq. (1)), Temple (Eq. (2)), and Stevenson (Eq. (3)) results:

In Eqs. (1)–(4) $\psi$ 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

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

The Temple bound requires

$$ \langle \psi | H | \psi \rangle < E_1, $$

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

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

Equations (1) and (2) can be shown to be special cases of Eq. (3) with an appropriate choice of $\alpha$. These three bounds have been discussed extensively in the literature. 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 solved for this technique to be applied in a routine manner to many-electron systems.

The lower bound problem for the lithium atom has received some attention over the past 20 years, but progress has been very limited. 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. Conroy’s formula 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 $-7.614$ 13 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 Luchow 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

\[ \psi = \sum_{\mu} C_{\mu} \phi_{\mu} \chi_{\mu}, \]

(8)

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

\[ \phi_{\mu}(r_1, r_2, r_3, r_{23}, r_{31}, r_{12}) = \prod_{i=1}^{N} \phi_{\mu_i}(r_i)^{n_{\mu_i}} \exp(-\alpha_{\mu} r_1 - \beta_{\mu} r_2 - \gamma_{\mu} r_3), \]

(9)

where the exponents \( i_\mu \), \( j_\mu \), \( m_\mu \), \( n_\mu \), and \( l_\mu \) are each \( \geq 0 \). In Eq. (8) \( \chi_{\mu} \) denotes the spin eigenfunction

\[ \chi_{\mu} = \alpha(1) \beta(2) \alpha(3) - \beta(1) \alpha(2) \alpha(3). \]

(10)

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

The nonrelativistic Hamiltonian employed is

\[ H = \sum_{i=1}^{N} -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{1}{r_{ij}}, \]

(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:

\[ I(i, j, k, l, m, n, \alpha, \beta, \gamma) = \int r_1^{i-1} r_2^{l-1} r_3^{m-1} r_{12}^{n-1} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \, dr_1 \, dr_2 \, dr_3. \]

(12)

The reduction of the matrix elements to integrals of the form indicated in Eq. (12) is most conveniently obtained 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 \( l, m, \text{ or } n \geq -2 \) or cases where two of the \( l, m, n \) set \( = -2 \). These cases lead to formidable integration problems, which have only recently been solved.81-85 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 \( r_{23}^{-2} r_{31}^{-2} r_{12}^{-2} \) with \( m \text{ and } n \text{ both odd. Such integrals can be evaluated by truncation of a rather slowly converging infinite series,}^{82,83,84} \text{ or by using convergence acceleration techniques.}

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.66 A more detailed account of these algebraic manipulations will be discussed elsewhere.85 The evaluation of \( \langle T^2 \rangle \) involves matrix elements like \( \langle \phi_{\mu}|\nabla_i^2|\phi_{\nu} \rangle \) 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 \( \langle \nabla_i^2\phi_{\mu}|\nabla_j^2|\phi_{\nu} \rangle \) 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 \( \langle \phi_{\mu}|\nabla_i^2|\phi_{\nu} \rangle \) 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 \( \mu \), 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

\[ \omega = i_\mu + j_\mu + k_\mu + l_\mu + m_\mu + n_\mu, \]

(13)

then all terms leading to particular values of \( \omega \) are included with values of \( \omega \) taken as 0, 1, 2, ..., \( \omega_{\text{max}} \). 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 \( \omega \) and then systematically increasing \( \omega \) 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,63,84 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 \( \omega \). 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. This 273 term function yields an energy of $-7.478$ a.u. which is just $1 \mu$hartree from the expected ground state energy. 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 indices) are really time consuming to evaluate. 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 $C_i C_j$ where $C_i$ and $C_j$ are the expectation values) 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 $\langle \phi_i \vert \hat{O} \vert \phi_j \rangle$ 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 $\langle \psi \vert H \vert \psi \rangle$ and $\langle \phi \vert H^2 \vert \phi \rangle$ 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:

$$\langle O \rangle = \langle \psi \vert \sum_{i=1}^{3} O_i \vert \psi \rangle,$$

$$(14)$$

$$\langle O_{ij} \rangle = \langle \psi \vert \sum_{i=1}^{3} \sum_{j>i}^{3} O_{ij} \vert \psi \rangle,$$

$$(15)$$

$$\langle O_{ijk} \rangle = \langle \psi \vert \sum_{i=1}^{3} \sum_{j>i}^{3} \sum_{k=1}^{3} O_{ijk} \vert \psi \rangle,$$

$$(16)$$

$$\langle O_{ijkl} \rangle = \frac{1}{2} \langle \psi \vert \sum_{i=1}^{3} \sum_{j>i}^{3} \sum_{k=1}^{3} \sum_{l>i}^{3} O_{ijkl} \vert \psi \rangle.$$  

$$(17)$$

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

$$\langle T \rangle = -\frac{1}{2} \nabla_i^2,$$

$$(18)$$

$$\langle V_{ee} \rangle = -\frac{1}{r_{ij}},$$

$$(19)$$

$$\langle V_{en} \rangle = -\frac{Z}{r_i},$$

$$(20)$$

and for $\langle \psi \vert H^2 \vert \psi \rangle$ the following contributions are tabulated:

$$\langle r_{ij}^{-2} \rangle, \langle (r_{ij} r_{jk})^{-1} \rangle, \langle r_{ij}^{-2} \rangle, \langle (r_{ij} r_{jk})^{-1} \rangle,$$

and

$$V^2 = Z^2 \langle r_{ij}^{-2} \rangle + 2 \langle (r_{ij} r_{jk})^{-1} \rangle,$$

$$(21)$$

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

$$(22)$$

$$\nabla_i^2 \nabla_j^2 = \sum_{i=1}^{3} \langle \nabla_i^2 \psi \nabla_j^2 \phi \rangle,$$

$$(24)$$

$$\nabla_i^2 \nabla_j^2 = \sum_{i=1}^{3} \sum_{j>i}^{3} \langle \nabla_i^2 \psi \nabla_j^2 \phi \rangle,$$

$$(25)$$

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

$$\eta = \frac{\langle V \rangle}{2\langle T \rangle}$$

$$(26)$$

as well as the variance, defined in Eq. (4), are also reported in Table I. Both $\eta^{-1}$ and $\sigma$ should approach 0 for a wave function of improving quality. All expectation values have been appropriately scaled using the values of $\eta$ 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 and $\langle r_{ij}^{-2} \rangle$ appears in a number of formulas bounding the electronic density.
TABLE I. Expectation values employed in the evaluation of the lower bounds. All values are in a.u. The notation \([m]\) signifies \(\times 10^m\).

<table>
<thead>
<tr>
<th>Expectation value</th>
<th>Number of terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle T \rangle)</td>
<td>50</td>
</tr>
<tr>
<td>(\langle V_{\text{ee}} \rangle)</td>
<td>2.198 378</td>
</tr>
<tr>
<td>(\langle V_{\text{en}} \rangle)</td>
<td>-17.154 273</td>
</tr>
</tbody>
</table>

\(\sigma\) signifies \(\times 10^m\) in most cases. 

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

\[\langle V_{\text{ee}}^2 \rangle = 628.441 \pm 0.003,\]
\[\langle V_{\text{en}}^2 \rangle = 51.7829 \pm 0.0002,\]
\[\langle V_{\text{en}}^2 \rangle = 430.3792 \pm 0.0001,\]
\[\langle V_{\text{en}} \rangle = -43.097 23 \pm 0.000 01,\]
\[\langle r_{ij}^{-2} \rangle = 4.3812 \pm 0.0001,\]
\[\langle (r_{ij} r_{jk})^{-1} \rangle = 1.101 687 \pm 0.000 002,\]
\[\langle V_{\text{en}} T \rangle = -259.0006 \pm 0.0008,\]
\[\langle V_{\text{ee}} T \rangle = 20.076 \pm 0.002,\]
\[\langle V_{\text{ee}} \rangle = 6.5846 \pm 0.0001,\]
\[\langle V \rangle = 350.7693 \pm 0.0004,\]
\[\langle J \rangle = 183.001 \pm 0.002, \quad \langle H^2 \rangle = 55.9214 \pm 0.0001.\]

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 \( \langle \Sigma_1^n, r^n \rangle \). All values are in a.u. The notation \([m]\) signifies \(10^m\).

<table>
<thead>
<tr>
<th>Number of terms</th>
<th>(\langle r_1^2 \rangle)</th>
<th>(\langle r_2^2 \rangle)</th>
<th>(\langle r_3^2 \rangle)</th>
<th>(\langle r_4^2 \rangle)</th>
<th>(\langle r_5^2 \rangle)</th>
</tr>
</thead>
</table>

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 \(\langle r^n \rangle\) for different values of \(n\). Table II shows the values of the \(\langle r^n \rangle\) for \(n = -2\) see Table I, and for \(n = -1\), examine \(-\frac{1}{2}\langle V_{en} \rangle\) (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 \(E_T^1\) obtained from the Weinstein formula. Unfortunately, Temple lower bounds could not be obtained for the 3 \(^2S\) and 4 \(^2S\) states because values of \(E_T^2\) and \(E_T^3\), 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 \(\langle H \rangle\) 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 \(\mu\)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 consistent with many other calculations in the literature (mostly on two-electron atomic systems). In the present case, it is 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 \(\pm 1 \mu\)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 \(\langle r^2 \rangle^2\). 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

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

<table>
<thead>
<tr>
<th>State</th>
<th>Number of terms</th>
<th>Weinstein lower bound ([Eeq. (1)])</th>
<th>Temple lower bound ([Eeq. (2)])</th>
<th>Lowest upper bound ([Eeq. (3)])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^2S)</td>
<td>600</td>
<td>-7.4828</td>
<td>-7.478 30</td>
<td>-7.478 060</td>
</tr>
<tr>
<td>(^2S)</td>
<td>450</td>
<td>-7.3860</td>
<td>-7.354 095</td>
<td></td>
</tr>
<tr>
<td>(^2S)</td>
<td>500</td>
<td>-7.3858</td>
<td>-7.318 445</td>
<td></td>
</tr>
</tbody>
</table>

*These energies are obtained from the wave function with 760 terms.