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Hylleraas-type calculations of the relativistic corrections for the ground state of the lithium atom

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Calculations of the principal Breit-Pauli relativistic corrections for the ground-state energy of the lithium atom have been carried out. The corrections have been determined using first-order perturbation theory. Only the non-fine-structure components of the Breit-Pauli Hamiltonian in the infinite nuclear mass approximation are considered. The wave function employed is an extensively optimized large-scale Hylleraas-type expansion. Comparisons are made with the few available relativistic corrections for the lithium atom that are available in the literature. A reevaluation of the first ionization potential for the ground state of Li is presented. [S1050-2947(98)05911-3]

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I. INTRODUCTION

The purpose of this work is to report high-precision estimates of the principal relativistic corrections to the ground-state energy of the lithium atom. There has been considerable recent interest in the high-precision determination of various properties of the ground and excited states of the lithium atom and members of its isoelectronic series (see [1,2] for recent reviews). The principal (non-fine-structure) Breit-Pauli relativistic corrections to the energy levels are a notable omission from the long list of properties that have been calculated to high precision.

A knowledge of precise values of these corrections is important for several reasons. A valuable check on the quality of *ab initio* calculations on three-electron atoms can be made by evaluating the first ionization potential of the system. The experimental first ionization potential for the lithium atom is available for comparison with a relative accuracy of 0.11 ppm. To obtain a match between theory and experiment at this level of accuracy requires rather precise estimates of the relativistic corrections to the ground-state energies of both Li and Li^+. The availability of precise estimates for the Breit-Pauli corrections would also be of value as benchmarks for other types of relativistic calculations, such as multiconfiguration Dirac-Fock and relativistic many-body perturbation theory methods. In addition, if high-precision values for the relativistic corrections to the energy levels are available, then it is possible to assess indirectly, in a semiempirical fashion, the expected size of the QED contributions to the various ionization potentials.

For the doublet states of three-electron atomic systems, almost all the available published work on precise relativistic calculations has been carried out by Chung and co-workers [3–6] using the configuration-interaction (CI) technique. For the lithium atom, Chung [3] has carried out calculations of the relativistic corrections for the ground-state energies of both Li and Li^+. For Li^+ he was able to compare his CI results with the earlier high-precision Hylleraas calculations of Pekeris [7,8]. The difference between the CI and the Hylleraas results for Li^+ was adopted as a core-correction contribution for each of the calculated Breit-Pauli contributions. These corrections were then incorporated into the calculations for the ground state of Li. While this procedure is somewhat *ad hoc*, a validation of the approach, at least for the relativistic kinetic-energy mass contribution, is given in [1]. There it is pointed out that Chung's core-corrected value for this contribution is in relatively close agreement with the result from more precise calculations. The results of the calculations reported herein will validate Chung's approach for the other Breit-Pauli relativistic corrections.

Other than Chung's calculations [3], no works are known to the authors where all the principal Breit-Pauli energy corrections are evaluated with reasonable precision for the ground state of the lithium atom. High-precision estimates of some of the individual Breit-Pauli relativistic corrections to the energy can be found in the literature [9–15]. The main reason that all the contributions have received very little attention can be traced to the rather recalcitrant integration problems that emerge. This facet of the problem will be discussed below in detail.

II. THEORY

The Breit-Pauli Hamiltonian discussed in this work is

$$H_{\mathrm{rel}}=H_{\mathrm{mass}}+H_{\mathrm{END}}+H_{\mathrm{EED}}+H_{\mathrm{SSC}}+H_{\mathrm{oo}}, \qquad (1)$$

where the various terms in Eq. (1) are given in atomic units (a.u.) by

$$H_{\mathrm{mass}}=-\frac{\alpha^2}{8}\sum_{i=1}^{3}\nabla_i^4, \qquad (2)$$

$$H_{\mathrm{END}}=\tfrac{1}{2}\alpha^2 Z\pi\sum_{i=1}^{3}\delta(\mathbf{r}_i), \qquad (3)$$

$$H_{\mathrm{EED}}=-\pi\alpha^2\sum_{i=1}^{3}\sum_{j>i}^{3}\delta(\mathbf{r}_{ij}), \qquad (4)$$

$$H_{\mathrm{SSC}}=-\frac{8\pi\alpha^2}{3}\sum_{i=1}^{3}\sum_{j>i}^{3}\mathbf{s}_i\cdot\mathbf{s}_j\,\delta(\mathbf{r}_{ij}), \qquad (5)$$

$$H_{\mathrm{oo}}=\frac{1}{2}\,\alpha^2\sum_{i=1}^{3}\sum_{j>i}^{3}\left(\frac{\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j}{r_{ij}}+\frac{\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j}{r_{ij}^3}\right). \tag{6}$$

H_{mass} represents the kinetic-energy mass correction, H_{END} is the electron-nuclear Darwin term, H_{EED} denotes the electron-electron Darwin term, H_{SSC} is the spin-spin contact interaction, and H_{oo} designates the electron-electron orbit interaction. In Eqs. (2)–(6), the fine-structure constant is denoted by α. $\delta(\mathbf{r})$ is a Dirac delta function, $\mathbf{s}_i$ is an electron spin operator, and Z is the nuclear charge. Only the non-fine-structure contributions have been shown in Eq. (1). In addition to these terms, there are fine-structure contributions that include spin-orbit, spin-other-orbit, and spin-spin interactions.

The individual contributions are evaluated using first-order perturbation theory. The wave function employed is based on the Hylleraas expansion

$$\psi=\mathcal{A}\sum_{\mu=1}^{N}C_\mu\phi_\mu\chi_\mu, \tag{7}$$

where $\mathcal{A}$ is the three-electron antisymmetrizer, C_μ are the variationally determined expansion coefficients, and N designates the number of basis functions employed. The Hylleraas-type basis terms ϕ_μ are functions of the electron-nuclear (r_i) and electron-electron (r_{ij}) separations and are defined by

$$\phi_\mu(r_1,r_2,r_3,r_{23},r_{31},r_{12}) = r_1^{i_\mu}r_2^{j_\mu}r_3^{k_\mu}r_{23}^{l_\mu}r_{31}^{m_\mu}r_{12}^{n_\mu}e^{-\alpha_\mu r_1-\beta_\mu r_2-\gamma_\mu r_3}. \tag{8}$$

The Hylleraas approach that we employed is described in Refs. [9–13].

Integration problems

Using the form of the nonrelativistic Hamiltonian written in Hylleraas coordinates, it is not difficult to show that the matrix elements needed for the eigenvalue and eigenfunction determination all simplify to sets of integrals of the form

$$I(i,j,k,l,m,n,a,b,c) = \int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n e^{-ar_1-br_2-cr_3}d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \tag{9}$$

with the conditions $l,m,n \geqslant -1$. These integrals, the auxiliary functions on which they depend, and some related generalizations have been extensively investigated in the literature [16–40]. Effective numerical methods for the evaluation of these integrals are well known. For an energy evaluation, only I integrals with *one* of the indices l,m,n equal to -1 are required. These integrals can be conveniently evaluated using available algorithms [18,35,40]. When two of the l,m,n indices are equal to -1 (a situation that arises for the evaluation of the relativistic corrections), a much more effective approach to evaluate these I integrals is by the use of convergence accelerator techniques, using a transformation procedure given by Pelzl and King [40].

The integral problems become extremely severe when the expectation values of two of the Breit-Pauli operators H_{mass} and H_{oo} are evaluated using Hylleraas-type wave functions. The electron-nuclear Darwin term, the electron-electron Darwin term, and the spin-spin contact interaction present no special difficulties. These latter three contributions all simplify to the integrals given in Eq. (9) with the condition $l,m,n \geqslant -1$. The matrix elements of the kinetic-energy mass operator can all be reduced to integrals of the form given in Eq. (9), but the constraint $l,m,n \geqslant -1$ no longer applies. The required integrals for the kinetic-energy mass correction and the electron-electron orbit interaction include I integrals having at least one of the factors $l,m,n=-2$. On the surface, this might seem like a relatively minor change from the previous cases, but the difficulties introduced can be appreciated by noting the form for the expansion of r_{12}^{-2} [41–44]. The appearance of a logarithm factor in the expansion of r_{12}^{-2} greatly complicates the integral evaluations.

Three-electron integrals with r_{12}^{-2} factors [42,44–49] have received far less study than the other cases mentioned above. The additional I integrals that must be evaluated can be divided into three cases: (i) those having $l=-2$ and $m,n \geqslant -1$ and not *both* odd, (ii) I integrals having $l=-2$ and $m,n \geqslant -1$ and *both* odd, and (iii) $l=-2$ and $m=-2$. All other I integrals can be reduced to one of these three cases by using the symmetry implicit in Eq. (9). For case (i), effective methods were developed by King [42] to deal with these integrals several years ago. A large number of integrals of this type can be reduced to integrals that arise in the relativistic problem for two-electron systems. The latter integrals are much easier to evaluate and have been well studied. The case (ii) integrals, which are significantly more difficult to evaluate than the case (i) integrals, were considered in [42]. Several different approaches have now been developed to deal with these integrals [43–49], but these methods do not yield the precision levels that can be obtained for the case (i) I integrals. Case (iii) integrals are the most difficult to resolve. Although methods to evaluate case (iii) have been discussed in the literature [44,46], the precision available is somewhat limited. Cases (ii) and (iii) in particular have been a major bottleneck to carrying out relativistic calculations with Hylleraas-type expansions. If the most general Hylleraas expansion is employed, then both case (ii) and case (iii) integrals arise.

The obvious question to pose is: Is it possible, by judicious selection of the basis functions, to avoid these difficult integral cases entirely? Deleting a number of basis functions that have two or three odd entries for $\{l_\mu,m_\mu,n_\mu\}$ allows the case (ii) and case (iii) I integrals to be avoided. The omission of basis functions having three odd entries for $\{l_\mu,m_\mu,n_\mu\}$ has an insignificant effect on the determination of a precise energy estimate or the calculation of a number of other properties. The omission of basis functions with two odd entries for $\{l_\mu,m_\mu,n_\mu\}$ is more problematic, but it is still possible to obtain reasonable levels of precision when a large basis set is employed. It is possible to select the basis terms such that cases (i)–(iii) I integrals do not arise; however, the energy obtained with a basis set of this design, even with several hundred terms included, is relatively poor. A compromise was selected in the present work, namely, that basis functions with two and three odd values for the indices

$\{l_\mu, m_\mu, n_\mu\}$ were excluded. This simplifies the integral evaluations for the relativistic kinetic-energy mass correction and the electron orbit-orbit correction since only case (i) I integrals need to be evaluated.

For the evaluation of the electron-electron orbit interaction, in addition to the I integral cases having one of $\{l_\mu, m_\mu, n_\mu\}=-2$, some integrals of the following form arise:

$$I_1(i,j,k,l,m,n,a,b,c)=\int r_1^i r_2^j r_3^k (r_1^2-r_2^2) r_{23}^l r_{31}^m r_{12}^{-3} \times e^{-ar_1-br_2-cr_3} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \tag{10}$$

and

$$I_2(i,j,k,l,m,n,a,b,c)=\int r_1^i r_2^j r_3^k (r_{23}^2-r_{31}^2) r_{23}^l r_{31}^m r_{12}^{-3} \times e^{-ar_1-br_2-cr_3} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 . \tag{11}$$

The integrals defined in Eqs. (10) and (11) look at first glance like they might be simple extensions of the I integrals defined in Eq. (9). This turns out not to be the case; the integrals I_1 and I_2 cannot be split into two parts, as the separate integrals diverge. Different approaches to deal with these more singular-looking integrals were investigated. An effective approach to evaluate these integrals involves working directly with the expansions of the factors $(r_1^2-r_2^2)r_{12}^{-3}$ and $(r_{23}^2-r_{31}^2)r_{12}^{-3}$. The integrals I_1 and I_2 may both be evaluated rapidly and to high precision. A detailed discussion of the evaluation of these integrals is given by Feldmann, Pelzl, and King [49].

There are still several unresolved problems connected to the evaluation of some of the more difficult integrals. The principal issue to resolve is the current inability to obtain high-precision results without significantly increasing the CPU time required for evaluation. Efforts in this direction are in progress on some of the more obdurate integrals.

III. COMPUTATIONAL PROCEDURE

The wave function employed was constructed in the following manner. An index ω is defined by

$$\omega=i_\mu+j_\mu+k_\mu+l_\mu+m_\mu+n_\mu . \tag{12}$$

Basis functions were then added in terms of increasing powers of ω, $\omega=0$, 1, 2, 3, and 4, except terms with $\omega=0$ and 1 were added in a nonsequential fashion at the start of the basis expansion. The number of terms included for each value of ω, N_ω, is shown in Table I. Four repetitions of each basis function were included for $\omega=0$, 1, 2, and 3; for $\omega=4$, four to five repetitions were employed. The repeats were added in clusters in a manner intended to avoid problems associated with linear dependence in the basis set. For each term added, the exponent set $\{\alpha_\mu, \beta_\mu, \gamma_\mu\}$ was determined using a global optimization approach. A stochastic procedure was used to locate the minima for a reasonably sized grid of the exponent set $\{\alpha_\mu, \beta_\mu, \gamma_\mu\}$. This approach has the advantage that there is a high confidence that the global minimum has been located, but this is at the expense of requiring significant CPU resources. The global optimization procedure also gives an indication of the plethora of false minima that occur for a number of basis functions; the difference in energies between the false minima and the global minima can often be significant. The optimization phase of the calculation was carried out in double precision (with a 32-bit word length). The final energy determination and the evaluation of the relativistic contributions were done after the matrix elements were reevaluated in quadruple precision.

TABLE I. Ground-state energy of the lithium atom (in a.u.) as a function of the basis set size.

ω [Eq. (12)]	N_ω	N	Nonrelativistic energy
0,1	28	28	−7.477 198 9
2	72	100	−7.478 007 7
		200	−7.478 055 5
3	181	281	−7.478 057 4
		400	−7.478 059 6
		500	−7.478 059 76
		600	−7.478 059 83
4	419	700	−7.478 059 89

The operators given in Eqs. (2) and (6) emphasize the near-nuclear region of configuration space. The variation method leads to the most significant improvements in the wave function in a region further (on average) from the nucleus than that emphasized by $H_{\rm mass}$ and $H_{\rm oo}$. Adding large numbers of more diffuse basis functions is likely to improve the convergence of the expectation values of the aforementioned two operators, but at a somewhat slower rate.

Alternative forms for expectation values

A considerable investment of labor and CPU resources was made in order to check the calculations. The formulas for the expectation values of the kinetic-energy mass correction and the electron-electron orbit interaction are straightforward but rather tedious to evaluate. The final expressions are too lengthy to reproduce here. The original formulas were worked out by hand and then later evaluated using the symbolic capabilities of MATHEMATICA. In order to check the results, an alternative approach was employed. For the kinetic-energy mass correction we have

$$\langle H_{\rm mass}\rangle = -\frac{\alpha^2}{8}\sum_{i=1}^{3}\langle\psi|\nabla_i^4|\psi\rangle \tag{13}$$

and this can be recast as

$$\langle H_{\rm mass}\rangle = -\frac{\alpha^2}{8}\sum_{i=1}^{3}\langle\nabla_i^2\psi|\nabla_i^2\psi\rangle . \tag{14}$$

Equations (13) and (14) should yield identical results, even for an approximate eigenfunction. It actually turns out that Eq. (14) is much easier to work with and most of the calculations were done with this form. However, a number of

TABLE II. Breit-Pauli relativistic contributions to the ground-state energy of the lithium atom (in a.u.).

Number of basis functions	$\langle H_{\rm mass}\rangle$	$\langle H_{\rm END}\rangle$	$\langle H_{\rm EED}\rangle$	$\langle H_{\rm SSC}\rangle$	$\langle H_{\rm oo}\rangle$	$\langle H_{\rm rel}\rangle$
28	$-4.171\,28\times10^{-3}$	$3.469\,12\times10^{-3}$	$-9.567\,52\times10^{-5}$	$1.913\,50\times10^{-4}$	$-2.412\,01\times10^{-5}$	$-6.306\,08\times10^{-4}$
100	$-4.183\,94\times10^{-3}$	$3.474\,48\times10^{-3}$	$-9.212\,47\times10^{-5}$	$1.842\,49\times10^{-4}$	$-2.331\,84\times10^{-5}$	$-6.406\,56\times10^{-4}$
200	$-4.182\,73\times10^{-3}$	$3.473\,50\times10^{-3}$	$-9.123\,90\times10^{-5}$	$1.824\,78\times10^{-4}$	$-2.321\,84\times10^{-5}$	$-6.412\,07\times10^{-4}$
281	$-4.183\,22\times10^{-3}$	$3.473\,74\times10^{-3}$	$-9.121\,30\times10^{-5}$	$1.824\,26\times10^{-4}$	$-2.321\,35\times10^{-5}$	$-6.414\,80\times10^{-4}$
400	$-4.183\,08\times10^{-3}$	$3.473\,65\times10^{-3}$	$-9.114\,73\times10^{-5}$	$1.822\,95\times10^{-4}$	$-2.320\,31\times10^{-5}$	$-6.414\,90\times10^{-4}$
500	$-4.183\,01\times10^{-3}$	$3.473\,61\times10^{-3}$	$-9.114\,56\times10^{-5}$	$1.822\,91\times10^{-4}$	$-2.320\,27\times10^{-5}$	$-6.414\,54\times10^{-4}$
600	$-4.183\,05\times10^{-3}$	$3.473\,63\times10^{-3}$	$-9.114\,39\times10^{-5}$	$1.822\,88\times10^{-4}$	$-2.320\,24\times10^{-5}$	$-6.414\,79\times10^{-4}$
700	$-4.183\,08\times10^{-3}$	$3.473\,64\times10^{-3}$	$-9.113\,61\times10^{-5}$	$1.822\,72\times10^{-4}$	$-2.320\,18\times10^{-5}$	$-6.415\,04\times10^{-4}$

checks were made using Eq. (13). The set of integrals that arise when the expectation value of $H_{\rm mass}$ is evaluated is quite different for the two forms. This is rather easy to see, for Eq. (14) involves no δ-function evaluations, but the expansion of ∇_i^4 does lead to such terms. Much more singular-looking integrals can also arise when Eq. (13) is employed.

For the electron-electron orbit interaction, the expectation value can be written as the expectation value of $H_{\rm oo}$ given in Eq. (6), or as the alternative form

$$\langle H_{\rm oo}\rangle = \tfrac{1}{2}\alpha^2\sum_{i=1}^{3}\sum_{j>i}^{3}[\langle\psi|r_{ij}^{-1}\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j|\psi\rangle - \langle r_{ij}^{-3}(1+\mathbf{r}_{ij}\cdot\boldsymbol{\nabla}_i)\psi|\mathbf{r}_{ij}\cdot\boldsymbol{\nabla}_j\psi\rangle]. \qquad (15)$$

For an application of this identity to the corresponding problem for the ground state of the helium atom see [50]. Both the expectation value shown in Eq. (15) and the expectation value of Eq. (6) were evaluated as a check on each calculation.

IV. RESULTS

The energies obtained with the different size basis sets are tabulated in Table I. The final energy is approximately 0.4 μhartree above the best previous estimate of the ground-state energy [14] (see [1] for an extensive tabulation of previous calculations of this quantity). In Table II the convergence of the five contributions determined from the operators defined in Eqs. (2)–(6) are shown as a function of the size of the basis sets employed.

The scale factor η, defined by

$$\eta = -\frac{\langle V\rangle}{2\langle T\rangle}, \qquad (16)$$

where $\langle V\rangle$ and $\langle T\rangle$ are the potential energy and kinetic energy, respectively, was also calculated for each wave function. For the final 700-term wave function employed, $\eta = 1.000\,000\,1$, which is very close to the result $\eta = 1$, expected on the basis of the virial theorem for an exact wave function.

V. DISCUSSION

A. Convergence characteristics and literature comparisons

The comments on the convergence characteristics are based on the results presented in Table II. The convergence of the expectation value of $H_{\rm END}$ is relatively smooth, but not monotonic. The final value reported in Table II is in close agreement with other high-precision estimates of this quantity [9–11,14], the most precise of which leads to the value $\langle H_{\rm END}\rangle = 3.473\,66(1)\times10^{-3}$ a.u. [14].

The convergence patterns for the expectation values of $H_{\rm EED}$ and $H_{\rm SSC}$ behave similarly, with the convergence being approximately monotonic. It is straightforward to show, using the spin eigenfunction given in Eq. (9), that

$$\left\langle \sum_{i=1}^{3}\sum_{j>i}^{3}\mathbf{s}_i\cdot\mathbf{s}_j\delta(\mathbf{r}_{ij})\right\rangle = -\tfrac{3}{4}\left\langle \sum_{i=1}^{3}\sum_{j>i}^{3}\delta(\mathbf{r}_{ij})\right\rangle, \qquad (17)$$

which implies

$$\langle H_{\rm SSC}\rangle = -2\langle H_{\rm EED}\rangle. \qquad (18)$$

Both $\langle H_{\rm SSC}\rangle$ and $\langle H_{\rm EED}\rangle$ were computed separately to check for possible roundoff errors and to confirm that Eq. (18) was satisfied. The similarity of the observed convergence behavior for $\langle H_{\rm SSC}\rangle$ and $\langle H_{\rm EED}\rangle$ results directly from the connection given in Eq. (18). An estimate for $\langle H_{\rm SSC}\rangle$ and $\langle H_{\rm EED}\rangle$ can be determined from the high-precision result for the expectation value of $\langle\delta(\mathbf{r}_{ij})\rangle$ given by Yan and Drake [14]. The value obtained for $\langle H_{\rm EED}\rangle$ is $-9.106\,30(6)\times10^{-5}$ a.u. [14], and the final value reported in Table II is about 0.08% lower. A possible explanation for one of the contributing factors for the slower convergence observed for $\langle H_{\rm SSC}\rangle$ and $\langle H_{\rm EED}\rangle$ may be the omission of basis functions where two of the set $\{l_\mu, m_\mu, n_\mu\}$ are both odd values. Some of these terms, particularly for smaller values of ω [see Eq. (12)], would be expected to play a more important role for obtaining precise expectation values such as $\langle\delta(\mathbf{r}_{ij})\rangle$.

The expectation value of $H_{\rm mass}$ displays a convergence behavior that is clearly not monotonic, while the convergence of the expectation value of $H_{\rm oo}$ exhibits monotonic characteristics. Both of these expectation values are expected to be more sensitive to the behavior of the wave function in the region of configuration space fairly close to the nucleus. Since the wave functions were determined using the standard

TABLE III. Contributions (in absolute a.u.) to the first ionization potential of the lithium atom.

Energy contribution	$^7\mathrm{Li}^+(1s^2)$	$^7\mathrm{Li}(1s^22s)$
E_{NR}	−7.279 913 412 669 305 9[a]	−7.478 060 323(3)[d]
E_{Bohr}	0.000 569 303 94(4)[b]	0.000 584 799 43(4)[e]
E_{SMS}	0.000 022 588 912(2)[b]	0.000 023 593 74(4)[e,f]
E_{rel}	−0.000 628 865 188(57)[c]	−0.000 641 50(8)[g]
ΔE_{QED}		−0.000 001 1(1)[h]
theoretical I_1		0.198 141 9(1)
experimental I_1		0.198 142 03(2)[i]

[a] From Ref. [51].

[b] Evaluated from results in Ref. [51] using the mass information given in Sec. V B.

[c] Evaluated from results in Ref. [51] and the value of the fine-structure constant given in Ref. [55].

[d] From Ref. [14].

[e] Evaluated from results in Ref. [14] using the mass information given in Sec. V B.

[f] Evaluated from results in Ref. [52].

[g] Present work.

[h] From Refs. [53,54].

[i] From Ref. [57].

implementation of the variation method, where the important focus is the region of configuration space near but not too close to the nucleus, it should be expected that $\langle H_{\mathrm{mass}}\rangle$ and $\langle H_{\mathrm{oo}}\rangle$ would exhibit a slower rate of convergence. A superior approach would be to determine the wave function so that the variance σ, defined by

$$\sigma=\langle H_{\mathrm{NR}}^2\rangle-\langle H_{\mathrm{NR}}\rangle^2, \tag{19}$$

is optimized. As the approximate wave function approaches the exact eigenfunction, $\sigma\rightarrow 0$. An alternative strategy might be to augment the standard variation approach with the constraint that σ also be optimized. Both these approaches would lead to wave functions that provide a better description of configuration space close to the nucleus. Unfortunately, such calculations would be prohibitively expensive in terms of the CPU resources required.

Because the convergence patterns for the individual contributions to $\langle H_{\mathrm{rel}}\rangle$ are not monotonic, it is rather difficult to arrive at reliable estimates for extrapolated values of these expectation values, as the size of the basis set becomes infinite. The approximate uncertainty for the final value of $\langle H_{\mathrm{rel}}\rangle$ reported in Table II is estimated (in part) on the basis of convergence trends, to be about 2–8 in the fifth significant digit reported.

Chung [3] reports the values $\langle H_{\mathrm{mass}}\rangle+\langle H_{\mathrm{END}}\rangle=-7.0942\times10^{-4}$ a.u. (in the present work we obtain -7.0944×10^{-4}), $\langle H_{\mathrm{EED}}\rangle+\langle H_{\mathrm{SSC}}\rangle=9.1154\times10^{-5}$ a.u. (9.1136×10^{-5}), $\langle H_{\mathrm{oo}}\rangle=-2.3201\times10^{-5}$ a.u. (-2.3202×10^{-5}), and $\langle H_{\mathrm{rel}}\rangle=-6.4147\times10^{-4}$ a.u. (-6.4150×10^{-4}). The final results reported in Table II are in very close agreement with Chung's results. This comparison provides a validation of the core-correction strategy employed for the CI calculations carried out by Chung.

B. The first ionization energy

The first ionization energy of the ground state of Li, I_1, can be determined from the result

$$I_1=E_T(\mathrm{Li}^+)-E_T(\mathrm{Li}), \tag{20}$$

where $E_T(\mathrm{Li}^+)$ and $E_T(\mathrm{Li})$ denote the total energy of the ground-state energies of Li^+ and Li, respectively. $E_T(\mathrm{Li})$ is given by

$$E_T(\mathrm{Li})=E_{\mathrm{NR}}(\mathrm{Li})+E_{\mathrm{rel}}(\mathrm{Li})+E_{\mathrm{mass}}(\mathrm{Li})+E_{\mathrm{QED}}(\mathrm{Li}), \tag{21}$$

with a similar expression for $E_T(\mathrm{Li}^+)$. The first ionization potential can therefore be written as

$$I_1=E_{\mathrm{NR}}(\mathrm{Li}^+)-E_{\mathrm{NR}}(\mathrm{Li})+\Delta E_{\mathrm{rel}}+\Delta E_{\mathrm{mass}}+\Delta E_{\mathrm{QED}}, \tag{22}$$

where the energy differences refer to ion−neutral species.

In Table III the most precise values for each energy contribution are collected, along with the available error estimates [51–54]. The value of the fine-structure constant has been taken from [55] and the nuclear mass for ^{7}Li has been taken from [56]. The specific mass shift correction has been evaluated using

$$\frac{\mu}{^7M}=7.820\,202\,2(6)\times10^{-5},$$

where μ is the reduced mass (for the isotope ^{7}Li) and ^7M is the nuclear mass for ^{7}Li [$^7M=7.014\,358\,4(5)$ amu [56]]. The calculated ionization potential is observed to be in rather close agreement with the available experimental result [57]. To convert the values of I_1 to cm^{-1}, the conversion factor is 1 a.u. (absolute)$=219\,474.631\,368\,8(62)$ cm^{-1}. Other recent high-precision theoretical evaluations of I_1 can be found in [3,14,58–61] and a summary of earlier results is given in [1]. It is clear from the results presented in Table III that a major part of the uncertainty in the theoretical determination of I_1 now resides with the QED contribution.

C. Further refinements

If some of the integration difficulties inherent in the present approach can be resolved in a more effective manner, it should be possible to improve the precision of the present results for the various Breit-Pauli relativistic contributions. The obvious starting point is to make two improvements to the basis set. The first is to add more diffuse functions (terms with $\omega > 4$). These basis functions would improve the precision of the calculations, but at an expected slow rate of convergence. The second and more important improvement would be to include those basis functions having two odds for the set $\{l,m,n\}$ for values of $\omega = 2$, 3, and 4. Inclusion of these functions is expected to improve the precision level of several parts of the calculation. This is, however, at the cost of dealing with a significant number of the most difficult integrals. Improved numerical evaluation procedures for these integrals would be of considerable value if the indicated extensions of the proposed basis set were employed.

The next most significant refinement of the calculation would be the incorporation of nuclear mass-dependent relativistic corrections (see [62]). Because of the high precision of the experimental value of I_1, the largest of the Stone corrections would be expected to play a role in determining an equally precise theoretical value of I_1.

VI. CONCLUSION

The final value of $E_{\rm rel}$ obtained is of sufficient precision to allow a theoretical determination of the first ionization potential of the lithium atom to seven digit precision. Improved calculation of the QED contribution to I_1 will be essential if the precision of the theoretical determination of the ionization potential is to approach the precision level available from experiment.

Significant refinements to the present calculations will depend on the development of improved methods to evaluate the most difficult integral cases that arise. Work is in progress attempting to improve the evaluation procedures for the most difficult integral cases.

Note added in proof. Recently the authors received unpublished work from Dr. Drake on relativistic and QED energies in lithium, which has now been published (Z.-C. Yan and G. W. F. Drake [63]). The work of Yan and Drake [63] also evaluates the relativistic correction for the ground-state energy of Li, but using a much larger basis-set expansion.

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