

Progress on high precision calculations for the ground state of atomic lithium

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Abstract

Progress on high precision calculations for the ground state of atomic lithium is reviewed. The following properties are considered: upper and lower bounds to the nonrelativistic ground state energy, the specific mass shift, the transition isotope shift, relativistic corrections to the ground state energy, the Lamb shift, the ionization potential, the electron affinity, the hyperfine coupling constant, the nuclear magnetic shielding constant, the diamagnetic susceptibility, several polarizability factors, shielding constants, oscillator strength sums, the electron density and spin density, intracule functions, moments $\langle r_i^n \rangle$ and $\langle r_{ij}^n \rangle$ and form factors. A discussion is also given on some convergence considerations as they apply to high precision calculations on the lithium atom. © 1997 Elsevier Science B.V.

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1. Introduction

The lithium atom has long served as a test system for various theoretical developments aimed at the accurate determination of atomic and molecular properties. As far as atomic systems are concerned, it can be regarded as a few-electron system, so one might hope to achieve results of high precision for a variety of properties. The lithium atom is the simplest system that offers the possibility of studying core, valence, and valence–core interactions.

The levels of precision that have been obtained for various properties of Li generally do not rival those obtained for the corresponding properties of the helium atom and its isoelectronic series [1–15]. However, recent theoretical progress has been

significant, as the results presented below will demonstrate.

In this review, a distinction is drawn between the terms accuracy and precision. Accuracy refers to the number of correct significant digits while precision refers simply to the number of significant digits in the calculation. The term high precision, at least as far as the energy is concerned, usually signifies a calculation that has converged to a spectroscopic level of accuracy, i.e. around 1 μ hartree (or better). For most of the properties discussed below, the tag accurate does not apply. The fact that a theoretical result agrees with an experimental estimate, while always gratifying, is not proof of an accurate calculation. The theoretical result obtained may be fortuitous for several reasons, such as a lucky cancellation of errors, or the result of a false convergence of the calculation. A handle on the accuracy of a theoretical calculation

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can be established when the property of interest can be bounded from above and below. Unfortunately, for almost all properties, bound formulas as they currently exist are not easily exploited. For the nonrelativistic energy, the variation method guarantees a strict upper bound estimate. This advantage does not transfer to other properties.

The layout of this review is as follows. After some brief discussion of two issues that are important for an understanding and interpretation of high precision calculations, the properties of the ground state are discussed. The order of topics is:

2. Convergence considerations
3. Extrapolation procedures
4. Integral problems
5. Nonrelativistic ground state energy
 - 5.1. Upper bound estimates for E_{NR}
 - 5.2. Lower bound for E_{NR}
 - 5.3. Correlation energy
 - 5.4. The radial lithium atom
6. Specific mass shift
 - 6.1. Transition isotope shift
7. Relativistic corrections to the ground state energy
8. Lamb shift
9. Ionization potential
10. Electron affinity
11. The Hyperfine coupling constant
 - 11.1. Determination of the experimental f
 - 11.2. The Hiller–Sucher–Feinberg (HSF) approach
 - 11.3. The hyperfine anomaly
 - 11.4. Hyperfine pressure shift
 - 11.5. Calculation of g_J
12. Nuclear magnetic shielding constant
 - 12.1. Connection with X-ray scattering
13. Diamagnetic susceptibility
14. Polarizability and hyperpolarizability
15. Shielding constants
16. Oscillator strength sums
 - 16.1. 2^{ℓ} -pole oscillator strength sums
 - 16.2. Log-weighted oscillator strength sums
17. Electron density and spin density
 - 17.1. The Hiller–Sucher–Feinberg approach
18. Intracule functions
19. Moments $\langle r_i^n \rangle$
20. Moments $\langle r_{ij}^n \rangle$

21. Electron correlation studies
22. Momentum space properties
23. Form factors
 - 23.1. Magnetic form factors
24. Some miscellaneous results
25. Some future directions

For most of the aforementioned properties, with the principal exception of the nonrelativistic ground state energy, a selection of what are believed to be the best calculations to date are tabulated, with sufficient references for the interested reader to trace some of the earlier key calculations of each property. Some representative values obtained by more approximate theoretical approaches are also included, so the reader can appreciate just how much of an improvement is obtained with the more sophisticated treatments. For the nonrelativistic ground state energy, a sample of the results from earlier studies is also presented to give a historical view of the progress that has been made for this key property.

The following two standard conventions are employed in this review. Error estimates are reported in parentheses; for example, $3.672 \pm 0.021 \times 10^{-2}$ will be given as $3.672(21) \times 10^{-2}$. For expectation values, an implied summation convention is employed, so that $\langle r_i^2 \rangle$ and $\langle r_{ij}^2 \rangle$ refer respectively to

$$\langle r_i^2 \rangle = \left\langle \psi \left| \sum_{i=1}^3 r_i^2 \right| \psi \right\rangle \quad (1)$$

and

$$\langle r_{ij}^2 \rangle = \left\langle \psi \left| \sum_{i=1}^3 \sum_{j>i}^3 r_{ij}^2 \right| \psi \right\rangle \quad (2)$$

where ψ is a normalized wave function. The following abbreviations are employed in various sections: CCPPA, coupled cluster polarization propagator approximation; CCSD, coupled cluster with single and double excitations; CCSD(T), triple excitations also included in CCSD; CEA, complex eigenvalue approach; CEPA, coupled electron pair approximation; CI, configuration interaction; HF, Hartree–Fock; HY, Hylleraas-type calculations; MBPT, many-body perturbation theory; MCEP, multi-configuration electron propagator method; MCHF, multiconfiguration Hartree Fock; MCLR, multi-configuration linear response theory; MP, modified

potential method; PNO, pseudonatural orbital; PP, pseudopotential method; PT, perturbation theory; PV, perturbation–variational method; SCC, superposition of correlation configurations; SD, single determinant; SEHF, spin extended Hartree–Fock; SOC, superposition of configurations; ST, scattering theory; and UHF, unrestricted Hartree–Fock. Relativistic versions of some techniques will be preceded by the prefix REL-

2. Convergence considerations

A particularly difficult feature of the area of high precision calculations is assessment of the convergence of the calculation of a particular property. It is well known that the calculation of a precise value for the energy is no guarantee that all other properties will be equally precise. A few issues should be kept in mind. A standard result from quantum theory is that a first-order error in the wave function manifests itself as a second-order error in the energy [16]. This favorable circumstance underlies much of the success of early calculations of nonrelativistic energies. Such an advantageous reduction in error does not carry over to general properties. Since the energy is the sum of the potential energy and kinetic energy contributions, it is possible, and in practice not uncommon, to observe a cancellation of errors between the two energy contributions; this leads to a precision in the energy determination that may not be justified when the precisions of the separate contributions are examined.

For properties other than the energy, the rough rule of thumb is that the precision of the calculated quantity will be comparable to the precision obtained for the energy, if the property depends essentially on the same region of configuration space that determines the energy. This notion often breaks down when the property of interest depends on a difference of terms close in magnitude, as for example in a transition isotope shift, or when the property depends on a sum over excited states. When the required property depends on some region of configuration space not emphasized in the energy determination, reliable assessment of the precision of the calculated quantity is often very difficult. Calibration using known experimental results is very useful but, as mentioned

above, not a guarantee that a particular precision level has been reached.

The principal approaches that have been employed for high precision calculations on the lithium atom include many-body perturbation theory, configuration interaction calculations of various sorts, Hylleraas-type calculations, and the hybrid CI-Hylleraas technique. The chief advantage of the first two approaches are their applicability to multielectron systems; in contrast, the Hylleraas technique is essentially restricted to systems with four electrons or less. Also, the Hylleraas technique, when applied with a general expansion for the basis set, yields mathematically intractable integration problems. This is the primary reason why the technique has not been pushed beyond four-electron systems. As far as the speed of convergence of the nonrelativistic energy is concerned, the Hylleraas approach is far superior for few-electron systems. This has been amply demonstrated in high precision calculations on two- and three-electron systems, where results with an improvement ranging from a few to several orders of magnitude in precision level have been obtained using the Hylleraas technique. The slow convergence of the CI technique and issues related to the convergence of the Rayleigh–Ritz method have been the subject of a number of papers [17–27]. The hybrid CI-HY technique [28] has shown considerable recent promise for both three- and four-electron systems [29,30], and an approach based on explicitly correlated gaussian functions [31] has yielded high precision results for the ground state of Be. Both of these methods can probably be extended to larger electronic systems.

For some properties of few-electron systems, the current level of precision of the best experimental results may only be a few digits. For such properties, the CI technique, despite its slow convergence, will be adequate for the computation of most properties at these lower levels of precision.

It is a very common practice for authors of high precision calculations to display in part the convergence pattern for the property under investigation. In some cases, this pattern can be deceptive in terms of what is displayed. Two works are selected for illustrative purposes. The first example is taken from an early excellent Hylleraas-type calculation of the Fermi contact parameter f , defined later in Eq. (102)

Table 1
Convergence of the Fermi contact term (from Ref. [32]) for the ground state of the lithium atom

Number of basis functions	Fermi contact term (u)
14	2.882
27	2.870
45	2.887
64	2.894
82	2.903
90	2.904
94	2.907
100	2.906

[32]. Table 1 shows a partial set of results for f as a function of the size of the basis set. The experimentally estimated value of f used for comparison was 2.9062 u, which is observed to be in excellent agreement with the final result reported in Table 1. The convergence pattern for these results has been labeled erratic [33]. A better characterization might be that the convergence of f is simply nonmonotonic. Two points need to be made with respect to the example illustrated in Table 1. The calculation has definitely not yet converged. Adding more basis terms actually alters the final value reported in Table 1. So, the agreement with experiment is not as close as it first appears. The second issue concerns the relatively small number of terms being used to monitor the convergence pattern. Finally, the basis terms were selected for their impact on the energy, and this is not expected to be an optional choice for obtaining smooth convergence for a property such as the Fermi contact term.

A second illustrative example is taken from a

Table 2
Convergence pattern for the moment $\langle r_i^{-2} \rangle$ (from Ref. [34]) for the ground state of the lithium atom

Wave function ^a	(u)
[8s]	30.764 068
[8s, 6p]	30.242 285
[8s, 6p, 6d]	30.242 411
[8s, 6p, 6d, 4f]	30.242 646
[8s, 6p, 6d, 4f, 4g]	30.242 740
[8s, 6p, 6d, 4f, 4g, 2h]	30.242 713
[8s, 6p, 6d, 4f, 4g, 2h, 2i]	30.242 718

^a The numbers of each Slater-type orbital in the basis set are indicated by the numerical prefixes.

quality calculation on the lithium ground state [34]. Table 2 shows the convergence pattern for the moment $\langle r_i^{-2} \rangle$. To what value of $\langle r_i^{-2} \rangle$ does the reader think the calculation is converging? The final (extrapolated) value reported is 30.242 52 u. The convergence pattern in this example is deceptive. An older literature value for this expectation value is 30.2407 u [35], and two more recent calculations yield the values 30.240 959 u [36] and 30.240 965 15(25) u [37]. So, for the expectation value $\langle r_i^{-2} \rangle$ given in Table 2, the CI results are observed to converge relatively quickly to four digits of precision, but do not converge to five digits. The extrapolated value reported is only reliable to four digits of precision.

It is useful to note that for the two examples just selected, the properties of interest are not that easy to calculate to high precision. There is a long history of efforts to calculate precise (and accurate) Fermi contact terms. This is discussed later in Section 11 for the ground state of Li. The expectation value $\langle r_i^{-2} \rangle$ depends in a sensitive manner on the region of configuration space close to the nucleus, which is usually more difficult to describe via standard variational techniques.

3. Extrapolation procedures

It is a rather common practice by many workers to attempt to extrapolate the results obtained with a finite basis set to an expected value for an infinite basis set. With reference to work on the lithium atom, examples can be found where extrapolations are rather conservative, i.e. one, or perhaps two, digits of precision beyond the yield of the finite basis set is/are obtained by extrapolation. Other less conservative extrapolations have been employed, where several digits of precision are estimated. The reader needs to be aware of several important points in connection with extrapolated results. For the calculation of the nonrelativistic energy, the extrapolated estimates are no longer guaranteed to be a rigorous upper bound estimate. Calculations of any desired property need not converge monotonically. This becomes a problematic issue for extrapolation procedures. Even when the calculation of a particular property is monotonically converging to the point where the calculation is terminated, there is no guarantee for a

general property that the convergence would continue to remain monotonic in the region where an extrapolation is attempted. It is of course always easier to make an extrapolation when the results of other high precision calculations are available for comparison.

For the energy, one very common approach [37] that has been employed is to estimate $E(\infty)$, the extrapolated energy for a basis set of infinite size, from the relationship

$$E(\infty) = E(N_{\max}) + \frac{E(N_{\max}) - E(N_{\max} - 1)}{R - 1} \quad (3)$$

where

$$R(N) = \frac{E(N - 1) - E(N - 2)}{E(N) - E(N - 1)} \quad (4)$$

and N denotes a measure of the size of the polynomial order of the basis set. $E(N)$ is the energy computed using all basis functions up to the given value of N . Related extrapolated procedures have been employed in the literature for a long time (see, for example, Refs. [1] and [38]).

An alternative approach [39], which has been employed when a progressively larger orbital basis set is utilized, is to compute the energy difference ΔE^ℓ :

$$\Delta E^\ell = E^\ell - E^{\ell-1} \quad (5)$$

where E^ℓ designates the limit of the ℓ partial wave. ΔE^ℓ is then fit to a functional form of the type

$$\Delta E^\ell = a_0 \left(\ell + \frac{1}{2} \right)^{-4} + a_1 \left(\ell + \frac{1}{2} \right)^{-5} + a_2 \left(\ell + \frac{1}{2} \right)^{-6} \quad (6)$$

which is based on the known ℓ^{-4} behavior [17,40] for the rate of convergence.

The wave function is of course not improved by the above type of extrapolation procedure. This in turn means that a separate extrapolation evaluation must be carried out for each property of interest.

4. Integral problems

When explicitly correlated factors are introduced into the wave function as in the Hylleraas or CI-HY techniques, a number of integration problems arise. For the 2S ground state of Li, it can be shown that

the integrals arising in the calculation of most properties reduce to the form

$$I(i, j, k, \ell, m, n, a, b, c) = \int r_1^i r_2^j r_3^k r_{23}^\ell r_{31}^m r_{12}^n e^{-ar_1 - br_2 - cr_3} dr_1 dr_2 dr_3 \quad (7)$$

where r_i denotes an electron–nuclear coordinate and r_{ij} is the electron–electron separation. For most applications ℓ, m, n are each ≥ -1 , and this case has received the most attention in the literature [32,41–62]. It is possible to reduce the I -integrals to a sum of integrals of the form

$$W(I, J, K, \alpha, \beta, \gamma) = \int_0^\infty x^I e^{-\alpha x} dx \int_x^\infty y^J e^{-\beta y} dy \int_y^\infty z^K e^{-\gamma z} dz \quad (8)$$

These W -integrals have received considerable attention in the literature [32,42,44,46,53,62]. The decomposition of the I -integrals leads to a finite sum of W -integrals, except when ℓ, m and n are all odd in Eq. (7). Even in this case, the sum of W -integrals converges sufficiently quickly that direct summation can be employed, although a faster asymptotic procedure has recently been suggested [62].

For a number of properties, such as several of the relativistic corrections, the calculation of $\langle r_{ij}^{-2} \rangle$, which is useful in certain lower bound formulas for the electronic density [63], or problems involving $\langle H^2 \rangle$ (where H is the Hamiltonian for the system), which is required to evaluate the classical lower bound formulas for the energy, I -integrals arise with one of the indices ℓ, m or $n = -2$. For a general Hylleraas expansion, integral cases with two of the indices ℓ, m or $n = -2$ arise. Limited attention has been directed towards these more difficult integral cases [56,57,60,61]. The expansion of r_{12}^{-2} [56,57,61,64,65] can be written as [56,61]

$$r_{12}^{-2} = \sum_{n=0}^{\infty} \frac{r_{12}^n}{r_{12}^{n+2}} \ell_n^1(\cos\theta_{12}) \quad (9)$$

where $\ell_n^1(\cos\theta)$ are the Gegenbauer polynomials, $r_{12<} denotes $\min(r_1, r_2)$ and $r_{12>} signifies $\max(r_1, r_2)$. This form has obvious similarities to the well-known expansion of r_{12}^{-1} in terms of Legendre polynomials; however, the complexities of the expansion are carried with the angular term. An alternative expansion for r_{12}^{-2} , which gives a better indication of some of the$$

difficulties that arise, is [56]

$$\begin{aligned} \frac{1}{r_{12}^2} = & \sum_{l=0}^{\infty} \left(\frac{2l+1}{2} \right) 4^{-l} \left[\ell n \left| \frac{r_1+r_2}{r_1-r_2} \right| \sum_{\kappa=0}^l r_1^{2\kappa-l-1} r_2^{l-2\kappa-1} \right. \\ & \times \sum_{\nu=0}^{\min[\kappa, l-\kappa]} (-4)^{\nu} \binom{l}{\nu} \binom{2l-2\nu}{l} \binom{l-2\nu}{\kappa-\nu} \\ & - 2 \sum_{\kappa=0}^{l-1} r_1^{-l+2\kappa} r_2^{l-2\kappa-2} \sum_{j=0}^{\min[\kappa, l-\kappa-1]} 4^j \binom{l-2j-1}{\kappa-j} \\ & \left. \times \sum_{\nu=0}^j \frac{(-1)^{\nu} \binom{l}{\nu} \binom{2l-2\nu}{l}}{2j-2\nu+1} \right] P_l(\cos\theta_{12}) \quad (10) \end{aligned}$$

where P_l denotes a Legendre polynomial. The appearance of the logarithmic term in Eq. (10) should alert the reader that the convergence characteristics of any expansion of these more difficult I -integrals will require careful consideration. Effective methods are available to deal with cases such as $\ell = -2$, and m and n not both odd (and the various symmetry related combinations) [56]. The real bottleneck to the calculation of certain expectation values occurs when $\ell = -2$, and m and n are both odd. The techniques currently available [56,57,60,61] lead to a limited precision of 14–16 digits, which becomes restrictive when very large basis sets are employed. The even more difficult I -integral cases having $\ell = -2$ and $m = -2$ [60,61] can be avoided if some restrictions are placed on the basis functions employed in the Hylleraas expansion.

5. Nonrelativistic ground state energy

The nonrelativistic energy discussed in this section is based on the Hamiltonian (in u):

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

where Z is the nuclear charge (equal to 3 for the lithium atom). The specific mass shift (mass polarization correction) is traditionally not included in Eq. (11), even though it is a purely nonrelativistic term. This correction is discussed in Section 6. Eq. (11) represents the infinite nuclear mass approximation for the Li atom. The essential problem to solve is

the Schrödinger equation:

$$H_{\text{NR}} \Psi = E_{\text{NR}} \Psi \quad (12)$$

Several approaches have been invoked to obtain approximate solutions for the nonrelativistic energy E_{NR} , including perturbation theoretical methods, variational methods of different types, local energy methods and other nonvariational procedures. No work appears to have been carried out on the lithium atom using modified variational procedures, where the point-wise behavior of the wave function, or any related quantity, has been used as a constraint to improve the local accuracy of the wave function. However, work along these lines has been pursued for two-electron systems [66,67]. The focus of the discussion below is on variational methods, which have yielded the results of highest precision for the lithium atom.

5.1. Upper bound estimates for E_{NR}

Application of the standard variation method leads to the result

$$\langle \psi | H_{\text{NR}} | \psi \rangle \geq E_{\text{NR}} \quad (13)$$

where ψ is a normalized approximation to the solution of Eq. (12). From a practical point of view, Eq. (13) is a rather powerful result because it provides a prescription for systematically improving the approximate wave function. The two well-known drawbacks are of course that the variational approach gives no explicit information on the expected rate of convergence, and provides no information on how to select a priori the best basis set. The latter is really a ‘‘trial and error’’ (trial and success) approach, with the experience of many past calculations serving as a guide.

The lithium atom has long been of intrinsic interest to many investigators, as well as serving as a benchmark system to test new theoretical methods. The quantity E_{NR} has been a common target property in these investigations [29,32,34–37,39,68–135]. Additional references for values of E_{NR} will be found in later sections in connection with the calculation of other properties.

Table 3 shows a limited selection of efforts to obtain a high precision estimate of E_{NR} . A variety of computational techniques are represented by the entries in Table 3. Improvements in computer

Table 3
Nonrelativistic ground state energy for the lithium atom

Author(s)	Reference	Date	Method of calculation	E_{NR} (u)	
				Explicit calculation	Extrapolated estimate
Wilson	[69]	1933	SD	-7.4192	
James and Coolidge	[70]	1936	HY	-7.476075	
Walsh and Borowitz	[76]	1959	HY	-7.395	
Weiss	[80]	1961	45-CI	-7.47710	
Burke	[86]	1963	13-HY	-7.47795	
Öhrn and Nordling	[90]	1966	5-HY	-7.4741	
Seung and Wilson	[92]	1967	PT	-7.47262	
Larsson	[32]	1968	100-HY	-7.478025	
Sims and Hagstrom	[102]	1975	150-CI-HY	-7.478023	
Perkins	[103]	1976	30-HY	-7.47793	
Muszynska et al.	[109]	1980	139-SCC	-7.478044	
Ho	[110]	1981	92-HY	-7.478031	
Pipin and Woznicki	[111]	1983	170-SCC	-7.478044	
King and Shoup	[112]	1986	352-HY	-7.478058	
Hijikata et al.	[113]	1987	100-HY	-7.478032	
King	[117]	1989	602-HY	-7.478059	
Kleindienst and Beutner	[114]	1989	310-SCC	-7.47805824	
King and Bergsbaken	[118]	1990	296-HY	-7.47805953	
Jitrik and Bunge	[120]	1991	3653-CI	-7.477906662	-7.4780624
Chung	[123]	1991	1017-CI	-7.47792506	-7.4780597
McKenzie and Drake	[124]	1991	1134-HY	-7.478060312	-7.478060326(10)
Pipin and Bishop	[125]	1992	1618-CI-HY	-7.4780601	
Lüchow and Kleindienst	[127]	1992	976-CI-HY	-7.478060252	
Kleindienst and Lüchow	[130]	1993	854-CI-HY	-7.47806021	
Tong et al.	[39]	1993	MCHF	-7.4779686	-7.4780609
Lüchow and Kleindienst	[29]	1994	1420-CI-HY	-7.4780603208	
King	[36]	1995	760-HY	-7.478060	
Yan and Drake	[37]	1995	1589-HY	-7.47806032156	-7.47806032310(31)
King	[135]		HY	-7.47806019	

Recommended value is in bold.

technology have obviously played a pivotal role in the progress indicated by these results.

A significant early result for E_{NR} was obtained in Ref. [70]. It took just over 30 years to obtain a major improvement in E_{NR} [32]. Steady progress on improved calculations of E_{NR} followed in the 1980s and 1990s.

The two approaches that have led to the most precise results for E_{NR} have both employed an explicit dependence on the interelectronic separation distance r_{ij} in the basis set. These are the standard Hylleraas approach and the CI-Hylleraas technique. In the Hylleraas approach, the wave function is taken to be of the form

$$\psi = \mathcal{A} \sum_{\mu=1}^N C_{\mu} \phi_{\mu} \chi_{\mu} \quad (14)$$

where \mathcal{A} is the three-electron antisymmetrizer:

$$\mathcal{A} = 6^{-1/2} \sum_P (-1)^p P \quad (15)$$

The summation in Eq. (15) runs over the six permutations P and p is the parity of the permutation. In Eq. (14), C_{μ} are the variationally determined expansion coefficients. The basis functions ϕ_{μ} are of the form

$$\phi_{\mu}(r_1, r_2, r_3, r_{23}, r_{31}, r_{12}) = r_1^{i_{\mu}} r_2^{j_{\mu}} r_3^{k_{\mu}} r_{23}^{l_{\mu}} r_{31}^{m_{\mu}} r_{12}^{n_{\mu}} e^{-\alpha_{\mu} r_1 - \beta_{\mu} r_2 - \gamma_{\mu} r_3} \quad (16)$$

where the exponents $\{i_{\mu}, j_{\mu}, k_{\mu}, l_{\mu}, m_{\mu}, n_{\mu}\}$ are each ≥ 0 . In Eq. (14), χ denotes the doublet spin

eigenfunctions. There are two such functions:

$$\chi = \alpha(1)\beta(2)\alpha(2) - \beta(1)\alpha(2)\alpha(2) \quad (17)$$

or

$$\chi = 2\alpha(1)\alpha(2)\beta(3) - \beta(1)\alpha(2)\alpha(3) - \alpha(1)\beta(2)\alpha(3) \quad (18)$$

Calculations are usually carried out using the spin eigenfunction given in Eq. (17). The impact of not including basis functions involving the second spin eigenfunction can be offset by modification of the basis set where only the first spin function is employed. Discussion on the impact of the inclusion of both spin eigenfunctions on the convergence of different expectation values can be found in several references [29,32,112,117]. The choice of the indices $\{i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu\}$ can be made in several ways. Terms can be included in the basis set according to the expected contribution to the energy. An alternative procedure is as follows. If the index parameter ω is defined by

$$\omega = i_\mu + j_\mu + k_\mu + l_\mu + m_\mu + n_\mu \quad (19)$$

then all possible values of $i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu$ (subject to any symmetry constraints) are selected so that the basis functions are added according to $\omega = 0, 1, 2, \dots$. This approach does not guarantee the fastest possible convergence, but does avoid any misdirected bias in selecting the basis functions, and generally leads to a convergence pattern that is relatively smooth. For the nonlinear orbital exponent parameters, essentially three distinct approaches have been employed. The first is to work with a fixed set of orbital exponents, such that

$$\left. \begin{array}{l} \alpha_\mu = \alpha \\ \beta_\mu = \alpha \\ \gamma_\mu = \gamma \end{array} \right\} \text{all } \mu \quad (20)$$

The fixed choice of exponents greatly simplifies the calculations in two ways. The computer resources needed are relatively minor, compared with what is required in any calculation requiring exponent optimization. The second feature is that it is feasible to store all the integrals involved in the calculations. For the *S*-states of the lithium atom, it is possible to work with the coordinate variable set $\{r_1, r_2, r_3, r_{12}, r_{23}, r_{31}\}$ and hence re-express Eq. (11)

in the form [32,76,136]

$$H_{\text{NR}} = - \sum_{i=1}^3 \left(\frac{1}{2} \frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i} \frac{\partial}{\partial r_i} + \frac{3}{r_i} + \frac{\partial^2}{\partial u_i^2} + \frac{2}{u_i} \frac{\partial}{\partial u_i} - \frac{1}{u_i} \right) - \frac{1}{2} \sum_{P_{ijk}} \left(\frac{r_i^2 + u_k^2 - r_j^2}{u_k r_i} \frac{\partial^2}{\partial r_i \partial u_k} + \frac{u_i^2 + u_k^2 - u_j^2}{2u_i u_k} \frac{\partial^2}{\partial u_i \partial u_k} \right) \quad (21)$$

where P_{ijk} signifies summation over the six permutations

$$\begin{pmatrix} 1 & 2 & 3 \\ i & j & k \end{pmatrix}, \text{ and } u_1 = r_{23}, u_2 = r_{31} \text{ and } u_3 = r_{12}.$$

Using Eqs. (14), (16) and (21) it is possible to show that all the matrix elements required for the calculation of E_{NR} reduce to integrals of the form given in Eq. (7). When fixed exponents are employed, it is straightforward to show that only two combinations of the set (a, b, c) (see Eq. (7)) arise, namely $(2\alpha, 2\alpha, 2\gamma)$ and $(2\alpha, \alpha + \gamma, \alpha + \gamma)$. It is therefore feasible to store an array of integrals for a wide range of values of (i, j, k, ℓ, m, n) . If the following symmetry is exploited

$$\begin{aligned} I(i, j, k, \ell, m, n, a, b, c) &= I(i, k, j, \ell, n, m, a, c, b) \\ &= I(j, i, k, m, \ell, n, b, a, c) \\ &= I(j, k, i, m, n, \ell, b, c, a) \\ &= I(k, j, i, n, m, \ell, c, b, a) \\ &= I(k, i, j, n, \ell, m, c, a, b) \end{aligned} \quad (22)$$

then a significant reduction in required computer memory can be made.

The fixed exponents that have been employed for calculations of the ground state have typically been in the region of $\alpha = \beta = 2.76$, $\gamma = 0.65$ [32]. The highest precision Hylleraas calculations have employed optimization of the orbital exponents [36,37,118,124]. For a basis with N terms, where N is a large number (say several hundred to two thousand terms), it is not feasible with current computer technology to optimize all the exponents. One approach that yields a rather precise value of E_{NR} is to optimize the exponents of each basis function as it is added, and then to recycle through the basis set and reoptimize the exponents one basis function at a time [118]. The optimization recycling procedure can in principle be continued until no further improvement is obtained at some

preselected precision level. An alternative procedure is to optimize blocks of terms as they are added [37,124]. This particular approach has been very successful, and accounts for the most precise value of E_{NR} given in Table 3.

The second computational approach that has been particularly successful in obtaining high precision estimates of E_{NR} is the CI-HY approach [28,29,102,114,127,130]. The three-electron wave function is taken to be of the form

$$\psi = \sum_K C_K \Phi_K \quad (23)$$

where

$$\Phi_K = O_{L^2} \mathcal{A} \chi r_{ij}^{Y_K} \prod_{\mu=1}^3 \varphi_{K\mu}(r_\mu) \quad (24)$$

and $\varphi_{K\mu}$ denotes the μ th basis orbital in the K th configuration and O_{L^2} is an orbital angular momentum projection operator. The basis functions are taken to be Slater-type orbitals. \mathcal{A} and χ are defined in Eqs. (15) and (17). Early applications have imposed the restriction of one factor of r_{ij} per term. The most recent applications of this technique have used basis functions that employ factors of the form $r_{23}^{\ell} r_{31} m r_{12}^{\prime}$ [29]. The results from this approach [29] (see Table 3) are very encouraging and close to the results from the most precise Hylleraas calculations. From the theoretical work published to date on Li, it appears essential to incorporate factors of r_{ij} in the wave function, if the highest possible precision is to be obtained. This is not a surprising conclusion, since the same result has already been established for calculations on two-electron systems.

5.2. Lower boundaries for E_{NR}

In comparison with efforts to establish the lowest possible upper bound for E_{NR} , there has been relatively little effort devoted to the determination of a lower bound for E_{NR} for the lithium atom. Two basically distinct avenues of research have been employed. In the first approach, methods based on the use of intermediate Hamiltonians have been used [137–143]. Although the method shows some promise, considerable problems remain to be resolved. No high precision estimates for the lower bound to E_{NR} for Li have been obtained using the method of intermediate Hamiltonians, although some success

has been achieved for two-electron systems [144–159]. The second approach involves application of the three classical lower bound formulas, which all involve the variance, σ , defined by

$$\sigma = \langle \psi | H^2 | \psi \rangle - \langle \psi | H | \psi \rangle^2 \quad (25)$$

For the application of interest here, H in Eq. (25) is given in Eq. (11). The three lower bound formulas are the Weinstein (E_W) [160], the Temple (E_T) [161] and the Stevenson (E_S) [162,163], which are respectively

$$E_0 \geq E_W = \langle \psi | H | \psi \rangle - \sigma^{1/2} \quad (26)$$

$$E_0 \geq E_T = \langle \psi | H | \psi \rangle - \frac{\sigma}{E_1 - \langle \psi | H | \psi \rangle} \quad (27)$$

$$E_0 \geq E_S = \alpha - \left(\alpha^2 - 2\alpha \langle \psi | H | \psi \rangle + \langle \psi | H^2 | \psi \rangle \right)^{1/2} \\ = \alpha - \left[\sigma + (\alpha - \langle \psi | H | \psi \rangle)^2 \right]^{1/2} \quad (28)$$

where E_0 denotes the exact nonrelativistic ground state energy. In Eq. (27), E_1 is the energy of the first excited state having the same symmetry as the ground state. The Weinstein bound requires

$$\langle \psi | H | \psi \rangle \leq \frac{1}{2}(E_0 + E_1) \quad (29)$$

and the Temple boundary requires

$$\langle \psi | H | \psi \rangle < E_1 \quad (30)$$

Since E_1 is not known exactly, for practical applications, 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

$$\alpha \leq \frac{1}{2}(E_0 + E_1) \quad (31)$$

Eqs. (26) and (27) can be shown to be special cases of Eq. (28) with appropriate choice of the parameter α . Extensive discussion of these bounds has been given in the literature [160–169]. Most of the applications of these formulas have been restricted to one- and two-electron atomic and molecular systems [10,170–186]. The principal reason for this is the considerable mathematical difficulty associated with the evaluation of $\langle \psi | H^2 | \psi \rangle$. Table 4 lists the results available in the literature [29,36,173] for the lithium atom based on eqns (26)–(28). The first entry reported is questionable, since the upper bound result for E_0 reported in this work [173] has converged to only

Table 4

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

Author(s)	Reference	Method	Lower boundary	Upper boundary
Conroy	[173]	17-term	- 7.614 13	- 7.470 19
Lüchow and Kleindienst	[29]	920-CI-HY	- 7.478 176	- 7.478 060 277
King	[36]	600-HY	- 7.478 30	- 7.478 059 86

three digits of precision, and the convergence of $\langle H^2 \rangle$ is somewhat slower than for $\langle H \rangle$. This first entry is just slightly better than a rough lower bound estimate of -7.6295 u [187] based on the Bopp approximation.

Determination of a high precision estimate for $\langle H^2 \rangle$ requires a wave function that gives an excellent description of the near-nuclear region of configuration space. With this objective in mind, the optimal approach is the technique of variance minimization, which involves the optimization of the appropriate parameters upon which ψ depends so that a minimum is obtained for σ in Eq. (25). In the limit of an exact wave function $\sigma \rightarrow 0$. This approach was employed in Ref. [29], yielding the most precise entry in Table 4. The method employed in Ref. [36] determined $\langle H^2 \rangle$ from the standard variational approach. The precision level is very similar to that obtained in the variance minimization technique. The other point of interest to note from Tables 3 and 4 is the significant difference between the precision levels for the upper and lower bound estimates for E_0 . This is similar to the situation found for two-electron systems. From the best results reported in Tables 3 and 4, the following result is the current state of knowledge for the nonrelativistic ground state energy of atomic lithium [29,37]:

$$-7.478\,176\text{ u} < E_{\text{NR}} < -7.478\,060\,321\,56\text{ u} \quad (32)$$

The nonrelativistic energy cannot be measured by experiment. An indirect experimental estimate for E_{NR} can be obtained as follows. The total energy of the ground state of Li, $E_{\text{T}}(\text{Li})$, and of Li^+ , $E_{\text{T}}(\text{Li}^+)$, can be written as

$$E_{\text{T}}(\text{Li}) = E_{\text{NR}}(\text{Li}) + E_{\text{REL}}(\text{Li}) + E_{\text{MASS}}(\text{Li}) + E_{\text{QED}}(\text{Li}) \quad (33)$$

$$E_{\text{T}}(\text{Li}^+) = E_{\text{NR}}(\text{Li}^+) + E_{\text{REL}}(\text{Li}^+) + E_{\text{MASS}}(\text{Li}^+) + E_{\text{QED}}(\text{Li}^+) \quad (34)$$

where the labels REL, MASS and QED denote, respectively, the relativistic corrections, the finite nuclear mass correction (Bohr plus specific mass shift), and quantum electrodynamical corrections to the energy. On defining

$$\Delta E_{\text{REL}} = E_{\text{REL}}(\text{Li}^+) - E_{\text{REL}}(\text{Li}) \quad (35)$$

$$\Delta E_{\text{MASS}} = E_{\text{MASS}}(\text{Li}^+) - E_{\text{MASS}}(\text{Li}) \quad (36)$$

$$\Delta E_{\text{QED}} = E_{\text{QED}}(\text{Li}^+) - E_{\text{QED}}(\text{Li}) \quad (37)$$

$$I_1 = E_{\text{T}}(\text{Li}^+) - E_{\text{T}}(\text{Li}) \quad (38)$$

where I_1 denotes the first ionization potential of the ground state of Li; then

$$E_{\text{NR}}(\text{Li}) = E_{\text{NR}}(\text{Li}^+) + \Delta E_{\text{REL}} + \Delta E_{\text{MASS}} + \Delta E_{\text{QED}} - I_1 \quad (39)$$

Using the value of $E_{\text{NR}}(\text{Li}^+)$ [15]

$$E_{\text{NR}}(\text{Li}^+) = -7.279\,913\,412\,669\,302\,0\text{ u} \quad (40)$$

and values of ΔE_{MASS} , ΔE_{REL} and ΔE_{QED} discussed in detail later in Sections 6–8

$$\Delta E_{\text{MASS}} = -0.000\,016\,500\,3(4)\text{ u} \quad (41)$$

$$\Delta E_{\text{REL}} = 0.000\,012\,67(6)\text{ u} \quad (42)$$

$$\Delta E_{\text{QED}} = -0.000\,0011(1)\text{ u} \quad (43)$$

and the experimental first ionization potential of ${}^7\text{Li}$ [188]

$$I_1 = 0.198\,142\,04(2)\text{ u} \quad (44)$$

leads to the estimate

$$E_{\text{NR}}(\text{Li}) = -7.478\,060\,38(12)\text{ u} \quad (45)$$

The result in Eq. (45) is close to a recent estimate of $E_{\text{NR}}(\text{Li}) = -7.478\,060\,342\,0(20)\text{ u}$ [124]. The slight difference in estimates is due to the use of a more recent estimate of ΔE_{QED} [37] and a slightly better estimate of ΔE_{REL} given in Section 7. The changes

in these two quantities partially offset each other, so that the value reported in Eq. (45) remains close to the previous estimate. The best upper bound estimate given in Eq. (32) [37] is found to be in excellent agreement with the ‘experimental’ estimate of E_{NR} .

5.3. Correlation energy

A widely employed definition of the correlation energy, E_{corr} , is [189]

$$E_{corr} = E_{HF} - E_{NR} \quad (46)$$

where E_{HF} is the nonrelativistic energy calculated in the restricted Hartree–Fock approximation and E_{NR} is the ‘exact’ nonrelativistic energy for the same state. There are a large number of calculations of E_{HF} for the ground state of the lithium atom (see, for example, Refs. [77], [78], [89], [101], [129] and [133]). The most precise value for the restricted Hartree–Fock energy appears to be [133]

$$E_{HF} = -7.432\,726\,931 \text{ u} \quad (47)$$

and an extrapolated estimate of $-7.432\,726\,932 \text{ u}$ has been proposed [108]. Combining the results from eqns (32), and (47) gives the value

$$E_{corr} = 0.045\,333\,391(2) \text{ u} \quad (48)$$

and the uncertainty is a rough estimate based on the predicted extrapolated values for E_{HF} and E_{NR} .

5.4. The radial lithium atom

In the radial model of the Li atom, the electronic distribution of the electrons does not depend on the angular variables; therefore, this model can be employed to study separately the radial contribution and, indirectly, the angular contribution to the correlation energy. A number of calculations of the radial energy E_{rad} of the lithium ground state have been made [39,80,94,97,105,190–193], and the most precise value currently available is [39]

$$E_{rad} = -7.448\,667\,06 \text{ u} \quad (49)$$

with an extrapolated estimate for the radial limit being $-7.448\,667\,26 \text{ u}$ [39]. In analogy to Eq. (46), the radial correlation energy can be defined as

$$E_{rad,corr} = E_{HF} - E_{rad} \quad (50)$$

Using the values in Eqns (47), and (49) gives a value for the radial correlation energy of the lithium ground state of

$$E_{rad,corr} = 0.015\,940\,1(2) \text{ u} \quad (51)$$

and the uncertainty has been estimated based on the extrapolated value for E_{rad} given above. Eqns. (48) and (51) allow the angular correlation energy, $E_{ang,corr}$, to be determined as

$$E_{ang,corr} = 0.029\,393\,3(2) \text{ u} \quad (52)$$

6. Specific mass shift

There are two stable isotopes of Li, ${}^6\text{Li}$ and ${}^7\text{Li}$, and their corresponding energy levels are slightly different because of several factors. In this section, the two principal mass dependent contributions to the energy are discussed.

The total kinetic energy component of the Hamiltonian for the electrons (mass m_e) and the nucleus of mass M can be written as

$$H_{KE} = \sum_{i=1}^3 \frac{p_i^2}{2m_e} + \frac{P^2}{2M} \quad (53)$$

In the rest frame of an atom, the momentum of the nucleus satisfies

$$P = - \sum_{i=1}^3 p_i \quad (54)$$

and so

$$H_{KE} = \sum_{i=1}^3 \frac{p_i^2}{2\mu} + \frac{1}{M} \sum_{i=1}^3 \sum_{j>i}^3 p_i p_j \quad (55)$$

where μ is the reduced mass

$$\mu = \frac{m_e M}{M + m_e} \quad (56)$$

The kinetic energy contribution given earlier in Eq. (11) corresponds to the infinite nuclear mass approximation of Eq. (55). The first correction for finite nuclear mass arises from the additional term $\sum_{i=1}^3 \frac{p_i^2}{2M}$. The effect of this term can be accommodated by adjustment of the Rydberg constant for the finite nuclear mass:

$$R_M = \frac{M}{M + m_e} R_\infty \quad (57)$$

where R_∞ is the Rydberg constant for infinite nuclear mass; $R_\infty = 109\,737.315\,6844(31)\text{ cm}^{-1}$ [194–197]. For ${}^6\text{Li}$ the nuclear mass is $M_{{}^6\text{Li}} = 6.013\,4766(5)\text{ amu}$, and for ${}^7\text{Li}$ it is $M_{{}^7\text{Li}} = 7.014\,3584(5)\text{ amu}$ [198]. The nuclear masses in atomic units are respectively $10961.897(1)\text{ u}$ and $12786.393(1)\text{ u}$. The appropriate Rydberg constants for Li are (using a rearranged form of Eq. (57))

$$R_{{}^6\text{Li}} = 109\,727.305\,8018(32)\text{ cm}^{-1} \quad (58)$$

$$R_{{}^7\text{Li}} = 109\,728.734\,0045(32)\text{ cm}^{-1} \quad (59)$$

All the energy levels for one isotope are shifted by the same multiplicative factor. This shift is referred to as the normal mass shift or the Bohr shift. An alternative approach is to evaluate the normal mass shift correction ΔE_{nms} as

$$\Delta E_{\text{nms}} = -\frac{1}{2M} \langle \psi_M | \nabla_i^2 | \psi_M \rangle \quad (60)$$

where ψ_M is the nuclear mass dependent approximate wave function based on the Hamiltonian

$$H_M = \sum_{i=1}^3 \left[-\frac{1}{2\mu} \nabla_i^2 - \frac{3}{r_i} \right] - \frac{1}{M} \sum_{i=1}^3 \sum_{j>i}^3 \nabla_i \cdot \nabla_j + \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}} \quad (61)$$

The second correction to the energy due to the finite nuclear mass arises from the second term in Eq. (55)

[199], giving the specific mass shift correction, or the alternative terminology mass polarization correction is also employed. Two distinct approaches have been used in the literature to determine the specific mass shift correction (ΔE_{sms}). In the first, the correction is calculated by first-order perturbation theory, using the formula

$$\Delta E_{\text{sms}} = -\frac{\mu}{M} \langle \psi | \sum_{i=1}^3 \sum_{j>i}^3 \nabla_i \cdot \nabla_j | \psi \rangle \quad (62)$$

where ψ is the wave function obtained from the approximate solution of the infinite nuclear mass Schrödinger equation. This formula is obtained by the scale change of variables:

$$r_i \rightarrow (m_e/\mu)r_i' \text{ and } p_i \rightarrow (\mu/m_e)p_i' \quad (63)$$

A common practice has been to evaluate ΔE_{sms} with (μ/M) replaced by $1/M$ ($m_e = 1\text{ u}$). The errors introduced by this approximation (about $9.1 \times 10^{-3}\%$ for ${}^6\text{Li}$ and $7.8 \times 10^{-3}\%$ for ${}^7\text{Li}$) were previously considered as too small to be of consequence. An alternative approach is to evaluate the specific mass shift using first-order perturbation theory based on wave functions that incorporate the Bohr correction to the Hamiltonian (i.e. the first term in Eq. (55) is part of H_{NR} (see, for example, Ref. [200]).

A number of values of ΔE_{sms} [29,37,39,117,118,

Table 5
Specific mass shift for the ground state of the lithium atom

Author(s)	Reference	Method	$\langle \sum_{i=1}^3 \sum_{j>i}^3 \nabla_i \cdot \nabla_j \rangle$	ΔE_{sms}^a (u)	
				${}^6\text{Li}$	${}^7\text{Li}$
Prasad and Stewart	[202]	CI	-0.3014	2.749×10^{-5}	2.357×10^{-5}
Martensson and Salomonson	[203]	MBPT	-0.3002	2.738×10^{-5}	2.348×10^{-5}
Chambaud et al.	[204]	CI	-0.3055	2.787×10^{-5}	2.389×10^{-5}
Veseth	[205]	MBPT	-0.3047	2.779×10^{-5}	2.383×10^{-5}
King	[206]	352-HY	-0.30185	2.7531×10^{-5}	2.3603×10^{-5}
King	[117]	602-HY	-0.3018467	2.753097×10^{-5}	2.360318×10^{-5}
King and Bergsbaken	[118]	296-HY	-0.3018436	2.753068×10^{-5}	2.360293×10^{-5}
Chung	[123]	CI	-0.30180	2.7528×10^{-5}	2.3600×10^{-5}
Tong et al.	[39]	MCHF	-0.30245	2.7586×10^{-5}	2.3650×10^{-5}
Lüchow and Kleindienst	[127]	976-CI-HY	-0.3018430	2.753063×10^{-5}	2.360289×10^{-5}
Lüchow and Kleindienst	[29]	1420-CI-HY	-0.301842799	2.7530611×10^{-5}	2.3602871×10^{-5}
Yan and Drake	[37]	1589-HY	-0.301842809(15)	2.7530612×10^{-5}	2.3602872×10^{-5}

^a Absolute u are employed in this table.

^b Computed using the values $\mu/M = 7.8202021(6) \times 10^{-5}$ for ${}^7\text{Li}$ and $\mu/M = 9.1216762(8) \times 10^{-5}$ for ${}^6\text{Li}$.

127,201–206] based on the use of the first-order perturbation theory approach are summarized in Table 5. Using Eq. (62) gives the answer in atom-based atomic units, i.e. the conversion to cm^{-1} (the unit useful for comparison with experimental data) is $1 \text{ u (Li)} = 2R_M (\text{cm}^{-1})$, and the required Rydberg constants are given in eqns (58) and (59). The entries given in Table 5 have been converted to absolute atomic units ($1 \text{ u} = 2R_\infty \text{ cm}^{-1}$).

Parenthetically, it is noted that in the Hylleraas coordinate system $\{r_1, r_2, r_3, r_{12}, r_{23}, r_{31}\}$, the specific mass shift operator $\nabla_i \cdot \nabla_j$ can be expressed [206] in terms of the derivatives $\partial/\partial r_i$ and $\partial/\partial u_i$ in much the same way that H_{NR} was written in Eq. (21). This leads to a considerable reduction in algebra for the evaluation of the necessary matrix elements to determine ΔE_{sms} when using a Hylleraas expansion.

An alternative expression for the expectation value in Eq. (62) has been explored, taking the form [207,208]

$$\Delta E_{\text{sms}} = \left(\frac{\mu}{M}\right) \left\{ \frac{1}{2} \left\langle \psi \left| \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}} \right| \psi \right\rangle + Z \left\langle \psi \left| \sum_{i=1}^3 \sum_{j>i}^3 \mathbf{r}_i \cdot \mathbf{r}_j \left(\frac{1}{r_i^3} + \frac{1}{r_j^3} \right) \right| \psi \right\rangle \right\} \quad (64)$$

and is based on the relationship

$$\langle \psi | \nabla_i \cdot \nabla_j | \psi \rangle = - \langle \psi | \mathbf{r}_i \cdot \nabla_j V | \psi \rangle \quad (65)$$

where V is the sum of the electron–nuclear and electron–electron potential terms. The convergence behavior obtained using Eq. (64) is less smooth than that obtained with Eq. (62) [39].

The second general (less commonly employed) approach is to evaluate ΔE_{sms} from the formula

$$\Delta E_{\text{sms}} = - \frac{1}{M} \left\langle \psi_M \left| \sum_{i=1}^3 \sum_{j>i}^3 \nabla_i \cdot \nabla_j \right| \psi_M \right\rangle \quad (66)$$

The results based on Eqs. (62)–(66) will be fairly close, but the current precision level of the calculations is such that Eq. (66) is the recommended approach. The most recent high precision values of ΔE_{sms} obtained using this approach [29,37,206] are summarized in Table 6. The heading entry u refers to absolute atomic units in this table.

The following result for the nonrelativistic ground state of lithium has been given [37] in units of $2R_M$:

$$E_M = -7.47806032310(31) + 0.301842809(15) \frac{\mu}{M} - 1.500(72) \left(\frac{\mu}{M}\right)^2 \quad (67)$$

This result incorporates both the ΔE_{nms} and ΔE_{sms} shift corrections. From Eq. (67), the nonrelativistic ground state energies including nuclear mass effects are (in absolute u)

$$E_{\text{NR}}(^6\text{Li}) = -7.477\,350\,683(2) \text{ u} \quad (68)$$

$$E_{\text{NR}}(^7\text{Li}) = -7.477\,451\,933(2) \text{ u} \quad (69)$$

These values are fairly close to the results $E_{\text{NR}}(^6\text{Li}) = -7.477\,350\,678 \text{ u}$ and $E_{\text{NR}}(^7\text{Li}) = -7.477\,451\,928 \text{ u}$ also obtained using the full mass dependent Hamiltonian, Eq. (61) [29].

The theoretical results presented in Tables 5 and 6 cannot be compared directly with experiment. However, the quality of these results can be assessed indirectly in two ways. The specific mass shift is one component in the determination of the ionization potential. Thus, at least the accuracy of the first few digits of ΔE_{sms} can be indirectly assessed. This comparison is, however, complicated by uncertainties in other contributions such as the relativistic and quantum electrodynamic corrections. This is discussed later in Section 9. A more direct comparison is to

Table 6
Specific mass shift for the ground state of the lithium atom using Eq. (66)

Author(s)	Reference	ΔE_{sms}			
		^6Li		^7Li	
		u	cm^{-1}	u	cm^{-1}
King	[206]	2.75160×10^{-5}	6.039 06	2.35923×10^{-5}	5.177 91
Lüchow and Kleindienst	[29]	2.7505657×10^{-5}	6.036 793 9	2.3584530×10^{-5}	5.176 206 2
Yan and Drake	[37]	2.75181×10^{-5}	6.039 53	2.35937×10^{-5}	5.178 21

derive from ΔE_{sms} the transition isotope shifts, which can be measured experimentally. This is discussed in the next subsection.

Two other small nuclear dependent factors arise in the determination of high precision estimates of state energies. The first of these additional corrections are the relativistic terms depending on the nuclear mass [209–211]. None of them has been accurately evaluated for the ground state of lithium. The reader interested in exploring this avenue might start with Refs. [212] and [213]; in addition, a clear exposition for two-electron systems has recently been published [214].

The second type of correction is the field shift contribution (also referred to as the volume shift) [215]. This shift arises from the interactions of the electrons with the electric field generated by the nuclear charge distribution. For light atoms, this shift is rather small. Very little work has been done on this field shift for Li. An estimate of 0.02168 cm^{-1} has been given for the ground state of ${}^7\text{Li}$ [205]. Similar values of 0.02143 cm^{-1} for the lowest ${}^2\text{P}$ state of ${}^7\text{Li}$ and 0.02147 cm^{-1} for the ground state of ${}^7\text{Li}^+$ have been obtained [205]. The net result is that for a transition energy or ionization potential, the field shift correction is outside the range of detectability based on the best experimental results currently available.

6.1. Transition isotope shift

Transition isotope shifts have been measured for electronic excitations arising from the ground state to a host of excited states [216–220]. In this section,

only the isotope shift associated with the transition to the ionization limit (i.e. the formation of Li^+) is considered.

Like the specific mass shift correction ΔE_{sms} (to which the isotope shift is closely related), the isotope shift is a sensitive measure of the extent to which electron correlation effects have been incorporated in the wave function.

The isotope shift for a pair of isotopes ${}^{A_1}\text{X}$ and ${}^{A_2}\text{X}$ (with mass numbers $A_1 > A_2$) is determined from

$$\begin{aligned} \Delta E_{\text{TIS}} = & [\Delta E_{\text{sms}}({}^{A_1}\text{X}^+) - \Delta E_{\text{sms}}({}^{A_1}\text{X})] \\ & - [\Delta E_{\text{sms}}({}^{A_2}\text{X}^+) - \Delta E_{\text{sms}}({}^{A_2}\text{X})] \\ = & [\Delta E_{\text{sms}}({}^{A_2}\text{X}) - \Delta E_{\text{sms}}({}^{A_1}\text{X})] \\ & - [\Delta E_{\text{sms}}({}^{A_2}\text{X}^+) - \Delta E_{\text{sms}}({}^{A_1}\text{X}^+)] \end{aligned} \quad (70)$$

where + signifies the ionization limit of the species. In the second line of Eq. (70), the terms in square brackets represent, respectively, the isotope shifts for the three-electron and two-electron atomic systems. These individual shifts, together with the transition isotope shift, are tabulated in Table 7. The standard approach employed in this area is to express the shifts in GHz. The appropriate conversion factor from atomic units to GHz to obtain the isotope shift is

$$1 \text{ u} \equiv 85.61837(7) \text{ GHz} \quad (71)$$

which corresponds to the conversion factor

$$29.9792458 \left\{ \frac{6\mu}{M_{6\text{Li}}} 2R_{6\text{Li}} - \frac{7\mu}{M_{7\text{Li}}} 2R_{7\text{Li}} \right\}$$

Table 7
Transition isotope shift for the ground state of the lithium atom

Author(s)	Reference	Method	Shift for ${}^6\text{Li} - {}^7\text{Li}$ (GHz)	Shift for ${}^6\text{Li}^+ - {}^7\text{Li}^+$ (GHz)	Transition isotope shift (GHz)
Prasad and Stewart	[202]	CI	25.80	24.81	0.99
Martensson and Salomonson	[203]	MBPT			0.962
Chambaud et al.	[204]	CI	25.165	25.077	1.088
Veseth	[205]	MBPT	26.090	25.007	1.083
King	[206]	HY	25.844		1.102
King	[117]	HY	25.843 6		1.102
King and Bergsbaken	[118]	HY	25.843 36		1.102
Lüchow and Kleindienst	[29]	CI-HY	25.843 29(3)	24.741 64(3)	1.101 65(4)
Yan and Drake	[37]	HY	25.843 30(3)	24.741 64(3)	1.101 66(4)
Experiment					
Lorenzen and Niemax	[216]				1.111(6)
Vadla et al.	[217]				1.108(8)

where the reduced mass/atomic mass ratios are given at the bottom of Table 5, and the Rydberg factors are given in Eqs. (58) and (59). The conversion factor above assumes that the expectation value $\langle \sum_{i=1}^3 \sum_{j>i}^3 \nabla_i \cdot \nabla_j \rangle$ is determined in the infinite nuclear mass approximation. The entry in Table 7 based on Ref. [206] employed the value $\langle \nabla_1 \cdot \nabla_2 \rangle = -0.2889758$ u for Li^+ derived from Ref. [221], which leads to an isotopic shift for Li^+ of 24.7416 GHz. The final two entries in Table 7 give more precise expectation values for Li^+ . Also, for these two entries, the precision of the reported shifts for ${}^6\text{Li}-{}^7\text{Li}$ and ${}^6\text{Li}^+-{}^7\text{Li}^+$, and the transition isotope shift are limited by the experimental precision available for the nuclear masses of the two isotopes of Li.

The absolute isotope shifts for ${}^6\text{Li}-{}^7\text{Li}$ and ${}^6\text{Li}^+-{}^7\text{Li}^+$, while of interest to theorists, cannot be directly compared with experimental results. The transition isotope shift reported in Table 7 is in close agreement with the most recent experimental value but, unfortunately, the uncertainty of the experimental result is too high to test the quality of the most precise calculations available.

Two additional refinements need to be kept in mind. Fairly small corrections are necessary to the results reported in Table 7 owing to the field shift correction. For Li, as discussed in Section 6, this correction is expected to make a negligible contribution to the transition isotope shift at the level of precision being presented in Table 7. The second correction takes into account calculations based on the complete nuclear mass dependent Hamiltonian [29,37,206], rather than the perturbation analysis employed to determine the results tabulated in Table 7. A recent high precision calculation [29] reports that the calculated transition isotope shift decreases by about 0.0066 GHz when the full Hamiltonian (i.e. non-perturbative) approach is employed.

7. Relativistic corrections to the ground state energy

Essentially, two distinct approaches have been employed to incorporate relativistic effects. In the first approach, the Breit-Hamiltonian [212] is employed in a first-order perturbation-theoretical

procedure. The standard form is

$$H_B = H_1 + H_2 + H_3 + H_4 + H_5 \quad (72)$$

where (in u)

$$H_1 = -\frac{\alpha^2}{8} \sum_{i=1}^3 \nabla_i^4 \quad (73)$$

$$H_2 = \frac{1}{2} \alpha^2 Z \pi \sum_{i=1}^3 \delta(\mathbf{r}_i) \quad (74)$$

$$H_3 = -\pi \alpha^2 \sum_{i=1}^3 \sum_{j>i}^3 \delta(\mathbf{r}_{ij}) \quad (75)$$

$$H_4 = \frac{8\pi\alpha^2}{3} \sum_{i=1}^3 \sum_{j>i}^3 s_i \cdot s_j \delta(\mathbf{r}_{ij}) \quad (76)$$

$$H_5 = \frac{1}{2} \alpha^2 \sum_{i=1}^3 \sum_{j>i}^3 \left(\frac{\nabla_i \cdot \nabla_j}{r_{ij}} + \frac{\mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_i) \nabla_j}{r_{ij}^3} \right) \quad (77)$$

In these equations, α is the fine structure constant, s_i is the electron spin operator, and $\delta(\mathbf{r})$ is a Dirac delta function. H_1 represents the kinetic energy correction, H_2 is the electron–nuclear Darwin term, H_3 denotes the electron–electron contact Darwin term, H_4 is the spin–spin contact interaction, and H_5 designates the electron–electron orbit interaction (retardation correction). A standard discussion of these terms is given in Ref. [212], with Refs. [222] and [223] providing readable accounts. There has been considerable discussion on the appropriate form of some of the relativistic operators and the appropriate ways to evaluate them. The interested reader is directed to a selection of articles [224–241] which will provide a pathway to additional sources.

For the ground state of the lithium atom, relatively little work is available on high precision estimates of the terms given in Eqs. (72)–(77) [36,37,112,117,118,123,242]. The current status of the higher precision work available is summarized in Table 8.

Of the five corrections, the most precise values are available for $\langle H_2 \rangle$ [37,118], and $\langle H_3 \rangle$ is known with good precision [37]. The most difficult expectation values to evaluate are $\langle H_1 \rangle$ and $\langle H_5 \rangle$. For Li^+ , the CI calculations [123] give results different from the precise values of the relativistic corrections reported previously [1,221], so an adjustment of the CI results was made for the Li calculations to correct for this $1s^2$ core

Table 8
Relativistic (Breit) corrections (u) for the ground state of the lithium atom

Author(s)	Reference	Method	$\langle H_1 \rangle$	$\langle H_2 \rangle$	$\langle H_3 \rangle$	$\langle H_4 \rangle$	$\langle H_5 \rangle$
King and Shoup	[112]	352-HY		3.4734×10^{-3}			
King	[117]	602-HY		3.47348×10^{-3}			
King and Bergsbaken	[118]	296-HY		3.47370×10^{-3}			
Chung ^a	[123]	CI	$\langle H_1 + H_2 \rangle =$ -7.0748×10^{-4} (-7.0942×10^{-4})			$\langle H_3 + H_4 \rangle =$ 9.5340×10^{-5} (-2.3201×10^{-5}) (9.1154×10^{-5})	-2.3331×10^{-5} (-2.3201×10^{-5})
Esquivel et al.	[242]	CI	-4.18769×10^{-3}				
King	[36]	760-HY	$-4.18317(2) \times 10^{-3}$				
Yan and Drake	[37]	1589-HY		3.473663×10^{-3}	-9.10630×10^{-5}		

^a Chung reports the combinations $\langle H_1 + H_2 \rangle$ and $\langle H_3 + H_4 \rangle$. The values in parentheses have been corrected for the discrepancy between Chung's results for Li^+ and those of Pekeris [1,221].

discrepancy. Such corrections improve the results, but add an empirical element to the calculations.

Accurate evaluation of $\langle H_1 \rangle$ is a difficult problem, as this expectation value is sensitive to the near-nuclear region of configuration space, a domain that is less well described in the standard variational treatment. Working out the matrix elements of $\langle \psi | \nabla_i^4 | \psi \rangle$ usually leads to difficult integrals, so it is useful to employ the result

$$\langle \psi | \nabla_i^4 | \psi \rangle = \langle \nabla_i^2 \psi | \nabla_i^2 \psi \rangle \quad (78)$$

which generally simplifies the integration problems. The high precision estimates of $\langle H_1 \rangle$ for Li^+ that have served as a benchmark employed the relationship [1]

$$(\nabla_1^2 \psi)^2 + (\nabla_2^2 \psi)^2 = -2\nabla_1^2 \psi \nabla_2^2 \psi + (E_{\text{NR}} - V)^2 \psi^2 \quad (79)$$

where V is the sum of the electron–electron and electron–nuclear potential terms. The right-hand side of Eq. (79) was used to simplify the calculations. The problem is that Eq. (79) assumes the exact eigenfunction for the nonrelativistic problem to be available, which is of course not the case. No assessment of the error in $\langle H_1 \rangle$ for Li^+ has been given when the replacement in Eq. (79) is employed. The simplification expressed in Eq. (78) is true for a general (approximate) wave function, and is not subject to the aforementioned drawback.

The total relativistic correction for the ground state of Li using the values of $\langle H_1 \rangle$ [36], $\langle H_2 \rangle$ [37], $\langle H_3 + H_4 \rangle$ and $\langle H_5 \rangle$ [123] is

$$E_{\text{REL}} = -0.00064155(4) \text{ u} \quad (80)$$

The error estimate in Eq. (80) has been evaluated using those for $\langle H_1 \rangle$ [36] and $\langle H_2 \rangle$ [37] based on convergence patterns. For $\langle H_3 + H_4 \rangle$ and $\langle H_5 \rangle$ no error estimates have been published [123]. A rough estimate of 2 in the fourth significant digit has been assumed for these expectation values. The $1s^2$ core-corrected CI result for $\langle H_1 + H_2 \rangle$ [123] agrees with the sum of $\langle H_1 \rangle$ [36] and $\langle H_2 \rangle$ [37] to within 1 in the fourth significant digit. If the uncorrected results of Ref. [123] were used as a basis for error analysis, then the error estimate would be around 100 times larger than the estimate given in Eq. (80), and would be dominated by the uncertainty in $\langle H_3 + H_4 \rangle$ and $\langle H_5 \rangle$. The value in Eq. (80) can be contrasted with the uncorrected value [123] $E_{\text{REL}} = -0.00066352 \text{ u}$ and the corrected (for $1s^2$ core discrepancy) value of $E_{\text{REL}} = -0.00064147 \text{ u}$ obtained from CI calculations [123].

There is no way to *directly* assess the quality of E_{REL} given in Eq. (80), but this value is employed later to determine a theoretical ionization potential for Li (see Section 9), which is in very good agreement with the experimental value. While this comparison is complicated by the fact that there might be some cancellations of errors with other small contributions, it does provide indirect support that the value given for E_{REL} is precise to at least the first few digits.

An alternative pathway to relativistic corrections, such as the multiconfigurational Dirac–Fock approach (MCDF), expands the relativistic atomic state function Ψ as a sum of symmetry adapted

configuration state functions Φ_K

$$\Psi = \sum_K C_K \Phi_K \quad (81)$$

where Φ_K are expanded as a linear combination of Slater determinants which can be formed from a basis of Dirac orbitals. The expansion coefficients C_K in Eq. (81) are determined by employing the Dirac–Coulomb Hamiltonian:

$$H_{\text{DC}} = \sum_{i=1}^N \{c\alpha_i p_i + (\beta_i - 1)c^2 - Zr_i^{-1}\} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (82)$$

where c is the speed of light, and α and β are defined in terms of the Pauli spin matrices.

While this approach has been employed in the evaluation of some properties [243–246], no high precision estimates of the ground state energy have been reported. The results from the perturbation analysis discussed above are the best available for the relativistic correction to the ground state energy of Li.

8. Lamb shift

To account for the current level of precision available for the ionization potentials of atomic systems, it is necessary to incorporate some rather small quantum electrodynamic (QED) corrections. These contributions are most often expressed in the form of a correction (to a given order in the fine structure constant α) to the ionization potential.

For the Li^+ ion, the Lamb correction has been frequently evaluated from the formulas (in u)

[212,247–253]

$$E_{L,1}(1s^2) = \frac{4Z\alpha^3}{3} \langle \delta(\mathbf{r}_i) \rangle [-2\ell n\alpha - \ell n(k_0) + \frac{19}{30} + 2.2962\pi\alpha Z] \quad (83)$$

and

$$E_{L,2}(1s^2) = \alpha^3 \left\{ \langle \delta(\mathbf{r}_{12}) \rangle \left[\frac{14}{3} \ell n\alpha + \frac{164}{15} \right] - \frac{7}{6\pi} \lim_{a \rightarrow 0} [\langle r_{12}^{-3}(a) + 4\pi(\gamma + \ell na)\delta(\mathbf{r}_{12}) \rangle] \right\} \quad (84)$$

where

$$r_{12}^{-3}(a) = \begin{cases} 0 & r_{12} \leq a \\ r_{12}^{-3} & r_{12} > a \end{cases} \quad (85)$$

$$\ell n(k_0) = \frac{\sum_m |\langle 0|\nabla_i|m\rangle|^2 (E_m - E_0) \ell n\left(\frac{E_m - E_0}{R_\infty}\right)}{\sum_m |\langle 0|\nabla_i|m\rangle|^2 (E_m - E_0)} \quad (86)$$

and γ is Euler's constant. In Eq. (83), k_0 denotes the Bethe mean excitation energy for a two-electron state. The corresponding Lamb correction for the one-electron ground state is $E_{L,1}(1s)$ and is given in Eq. (83) with $\langle \delta(\mathbf{r}_i) \rangle = Z^3/\pi$. Additional corrections to $E_{L,1}(1s)$ are discussed in Ref. [251]. The level shift for Li^{2+} has been evaluated to be 15.956 cm^{-1} [251]. For Li^+ , the most common practice is to quote the energy shift:

$$\Delta E_L = E_{L,1}(1s) - E_{L,1}(1s^2) - E_{L,2}(1s^2) \quad (87)$$

Table 9
Lamb shifts for the ground states of Li^+ and Li

Author(s)	Reference	$\Delta E_{\text{QED}}(\text{Li}^+) \text{ (cm}^{-1}\text{)}$	$\Delta E_{\text{QED}}(\text{Li}) \text{ (cm}^{-1}\text{)}$
Pekeris	[1]	– 7.83	
Aashamar	[252]	– 8.325	
Aashamar and Austvik	[253]	– 8.54(5)	
Hata	[250]	– 8.95	
Drake	[254]	– 8.938	
McKenzie and Drake	[124]		– 0.22(2)
Chung	[123]		– 0.08
Feldman and Fulton	[260]		– 0.24

which represents the quantity of interest in evaluating the ionization potential of Li^+ . For the transition $\text{Li}^+ \rightarrow \text{Li}^{2+} + e^-$, several values of ΔE_L can be found in the literature [1,250,252–254]. A summary of some of the available results for Li^+ is presented in Table 9. The last two entries for Li^+ account for additional terms not incorporated in the earlier investigations.

For three-electron systems, far less attention has been directed to the Lamb corrections [123,124, 255–260]. Two approaches have been employed. The first, and more approximate approach, assumes that for the ionization process $\text{Li} \rightarrow \text{Li}^+ + e^-$, the QED correction for the core electrons will approximately cancel, and so the correction to the ionization potentials of Li, ΔE_{QED} , can be represented as [123]

$$\Delta E_{\text{QED}} = \frac{4Z_{\text{eff}}^4 \alpha^3}{3\pi n^3} \left[\frac{19}{30} - 2\ell n(\alpha Z_{\text{eff}}) - \ell n(K(n)) \right] \quad (88)$$

where $n = 2$, and Z_{eff} is the effective nuclear charge experienced by the 2s valence electron. This is the analogy of the one-electron term $E_{L,1}(1s)$ modified for $n = 2$ and with Z replaced by a screened nuclear charge. The one drawback with this approach is the semiempirical nature of the one-electron model assumed. In essence, the significance of the two-electron contributions to the Lamb correction for the ionization potential is lost in the adjustment of Z_{eff} .

The second approach that has been explored is to

generalize Eqs. (83) and (84) to cover the many-electron system, i.e. for Li [124,258,260]

$$E_{L,1}(1s^2 2s) = Z\alpha^3 \left\{ F(1s^2 2s) \left\langle \sum_{i=1}^3 \delta(\mathbf{r}_i) \right\rangle - \frac{4}{3} \ell n[(Z - \sigma)/Z]^2 \left\langle \sum_{i=1}^3 \delta(\mathbf{r}_i) \right\rangle \right\} \quad (89)$$

where $F(1s^2 2s)$ denotes a combination of one-electron functions $F(1s)$ and $F(2s)$ (each dependent on Z) [258], which in turn can be written as a sum of one-electron quantum electrodynamic corrections [251]. The second factor in Eq. (89) takes into consideration the correction for screening of the Bethe logarithm term (see Eq. (86)). The two-electron term takes the form

$$E_{L,2}(1s^2 2s) = \alpha^3 \left\{ \left(\frac{14}{3} \ell n \alpha + \frac{164}{15} \right) \left\langle \sum_{i=1}^3 \sum_{j>i}^3 \delta(\mathbf{r}_{ij}) \right\rangle - \frac{7}{6\pi} \lim_{a \rightarrow 0} \left\langle \sum_{i=1}^3 \sum_{j>i}^3 [\mathbf{r}_{ij}^{-3}(a) + 4\pi(\gamma + \ell na)\delta(\mathbf{r}_{ij})] \right\rangle \right\} \quad (90)$$

which has an analogy with the two-electron formula given above in Eq. (84). The second factor in Eq. (90) has been evaluated in a form involving $\langle \delta(\mathbf{r}_{ij}) \rangle$ and a power series in Z [124]. The radiative corrections for a many-electron system (and Li in particular) have recently been investigated in detail [260]. In this work, the factor 164/15 in Eq. (90) is not obtained, but instead these authors find the somewhat smaller

Table 10
Ionization potential for the ground state of the lithium atom

Author(s)	Reference	Method	Ionization potential (u) ^a
Lindgren	[266]	MBPT	0.198 139(3)
Johnson et al.	[268]	MBPT	0.197 97
Johnson et al.	[269]	MBPT	0.198 076(3)
Blundell et al.	[270]	MBPT	0.198 142 9(5)
Chung	[123]	CI	0.198 142 0(4)
Weiss	[128]	CI	0.198 14
Pipin and Bishop	[125]	CI-HY	0.198 131
Tong et al.	[39]	MCHF	0.198 146 1
Yan and Drake	[37]	HY	0.198 141 89(30)
Yan and Drake ^b	[37]	HY	0.198 142 114(20)
Experiment: Johansson	[188]		0.198 142 04(2)

^a Absolute atomic units are employed in this table.

^b Determined from the calculated ionization energy of $1s^2 3d \ ^2D$ and the experimental 2^2S-2^2P and 2^2P-3^2D transition energies.

term $(129/15) - (3\pi/2)$. Some available values for

$$\Delta E_{\text{QED}} = E_L(1s^2) - E_L(1s^2 2s) \quad (91)$$

are given in Table 9. An estimated uncertainty of around 20% has been given for $\Delta E_{\text{QED}}(\text{Li})$ [258] based on a consideration of all the components leading to the calculation of the ionization potential.

9. Ionization potential

The ionization potential for the process $\text{Li} \rightarrow \text{Li}^+ + e^-$ has received considerable attention in the literature for over 60 years [37,39,123,125,128,261–276]. This quantity is an attractive target property for testing computational schemes as a high precision experimental estimate of the first ionization potential is available for comparison.

A summary of some of the higher precision calculations is presented in Table 10. The units employed in reporting the ionization potential are often given in atom-based u, with the conversion to cm^{-1} being obtained by multiplication by $2R_{\gamma_{\text{Li}}}$ (see Eq. (59)). In Table 10 all the values are reported in absolute u (conversion to cm^{-1} is made by multiplication using $2R_{\infty}$). A number of factors enter into the theoretical determination of the ionization potential, I_1 :

$$I_1 = E_{\text{NR}}(\text{Li}^+) - E_{\text{NR}}(\text{Li}) + \Delta E_{\text{REL}} + \Delta E_{\text{MASS}} + \Delta E_{\text{QED}} \quad (92)$$

where the various terms have been defined previously in Eqs. (35)–(37). Table 11 summarizes the separate

Table 11
Contributions to the ground state energy (in absolute u) for Li^+ and Li

	$\text{Li}^+ (1s^2)$	$\text{Li} (1s^2 2s)$
E_{NR}	$-7.279\,913\,412\,669\,302^a$	$-7.478\,060\,323\,1(3)^b$
E_{Bohr}	$0.000\,569\,303\,94(4)$	$0.000\,584\,799\,43(4)$
E_{vns}	$0.000\,022\,588\,912(2)^b$	$0.000\,023\,593\,7(4)^b$
E_{REL}	$-0.000\,628\,88(4)^c$	$-0.000\,641\,55(4)^{b,d,e}$
E_{QED}	$0.000\,113\,43(2)^{f,g}$	$0.000\,114\,5(1)^{g,h}$
E_{TOTAL}	$-7.279\,836\,97(4)$	$-7.477\,978\,98(11)$
IP		$0.198\,142\,0(1)$
Experimental ⁱ		$0.198\,142\,04(2)$

^aThakkar and Koga [15]. ^bYan and Drake [37]. ^cPekeris [1,221]. ^dKing [36]. ^eChung [123]. ^fJohnson and Soff [251]. ^gDrake [254,258]. ^hFeldman and Fulton [260]. ⁱJohansson [188].

contributions leading to the calculation of I_1 . The major part of the error in I_1 is due to uncertainty in the relativistic correction (see Section 7 for a discussion on this) and from the error in ΔE_{QED} [37,258] (see Eq. (43)).

Several literature values of I_1 are available. The value in Ref. [277] is taken from Ref. [188], and the later collection of atomic data [278] is a reprint volume based on earlier experimental work. Two other commonly employed tabulations [279,280] employ the latest experimental value available, which gives $43\,487.150(5) \text{ cm}^{-1}$ [188] (this is $0.198\,142\,04(2) \text{ u}$ or as sometimes reported $0.198\,157\,53(2) \text{ atom-based u}$ for ^7Li). A semiempirical fitting procedure also reproduces this value [281]. There is a hint, based on more recent experimental measurements [220,282], that the error estimate for this value of I_1 may be too small.

An alternative method has recently been suggested which yields a joint theoretical–experimental approach to the determination of I_1 [37]. Combining the experimental $2^2\text{S} - 2^2\text{P}$ and $2^2\text{P} - 3^2\text{D}$ transition energies with the theoretically determined absolute ionization energy of the 3^2D state leads to the value [37]

$$I_1 = 43\,487.167(4) \text{ cm}^{-1} \quad (93)$$

This value is in close agreement with the purely experimental estimate given above. The values for the $3d^2\text{D}_{3/2}$ and $3d^3\text{D}_{5/2}$ levels have recently been determined to high precision, and are $31\,283.0505(10) \text{ cm}^{-1}$ and $31\,283.0866(10) \text{ cm}^{-1}$ (for ^7Li) [220]. From these values, the center of gravity estimate is

$$E(^2\text{D}) = \frac{2}{5}E(^2\text{D}_{3/2}) + \frac{3}{5}E(^2\text{D}_{5/2}) \\ = 31\,283.077\,2(14) \text{ cm}^{-1} \quad (94)$$

If this value is combined with the theoretical estimate of the ionization potential of the $1s^2 3d^2\text{D}$ state, $0.055\,605\,932(20) \text{ u}$ [37], then the value of I_1 obtained is

$$I_1 = 43\,487.163(5) \text{ cm}^{-1} \quad (95)$$

This is in slightly closer agreement with the experimental estimate given above. Further experimental work should prove decisive in resolving the small variation that remains between these slightly different estimates of I_1 .

10. Electron affinity

The electron affinity, EA, of the ground state of Li has received considerable theoretical attention over many years [283–306]. There have also been several experimental measurements of the electron affinity of Li [307–315]. Progress in theoretical and experimental work on electron affinities including work on Li has been reviewed [316]. The electron affinity is the negative of the energy associated with the process $\text{Li}_{(g)} + e^- \rightarrow \text{Li}_{(g)}^-$, i.e.

$$\text{EA}(\text{Li}) = E_{\text{Total}}(\text{Li}) - E_{\text{Total}}(\text{Li}^-) \quad (96)$$

A positive EA implies the anion is more stable than the neutral atom. The total energies for each species in Eq. (96) can be expressed as a sum of contributions as indicated in Eq. (33).

High precision calculations of the EA present a more serious theoretical challenge than calculation

of the ionization potential of the neutral atom. There are two key reasons for this. The first is the obvious problem of having to deal with a system with one additional electron. The second issue is that atomic anions have a more diffuse electronic charge distribution, which requires additional care in building basis sets to describe the regions of configuration space that are more distant from the nucleus. For a quantity like the ionization potential of a neutral species, the Hartree–Fock model is good enough to obtain at least semiquantitative agreement with experiment. However, for the electron affinity, the Hartree–Fock approach is unsatisfactory. E_{NR} for Li^- has been calculated in the HF approximation [302,317,318] and the best available value is [302,317]

$$E_{\text{HF}}(\text{Li}^-) = -7.428\,232\,0\,u \quad (97)$$

The preceding value is above the ground state energy of Li, so the HF model does not predict a stable bound

Table 12
Electron affinity for the ground state of the lithium atom

Author(s)	Reference	Method	Electron affinity (u)
Weiss	[286]	SOC	0.022 6
Schwartz	[287]	CI	0.022 8
Fung and Matese	[290]	MCHF	0.022 5
Grün	[291]	CI	0.021 7
Victor and Laughlin	[288]	CI-MP	0.022 6
Norcross	[293]	ST	0.022 6
Stewart et al.	[294]	MP	0.021 9
Sims et al.	[295]	CI	0.022 4(3)
Cooper and Gerratt	[296]	CI	0.022 5
Lin	[264]	Hyperspherical	0.021 8
Kaldor	[297]	CCSD	0.022 4
Christensen–Dalsgaard	[300]	Hyperspherical	0.021 9(18)
Heully and Salomonson	[298]	CCSD	0.021 53
Canuto et al.	[299]	CCPPA	0.022 3
Ågren et al.	[302]	MCLR	0.022 6
Graham et al.	[301]	MCEP	0.022 7
Moccia and Spizzo	[303]	<i>K</i> -matrix	0.022 69 (0.022 74)
Chung and Fullbright	[304]	CI	0.022 689 6(80)
Fischer	[305]	MCHF	0.022 695 (0.022 698) ^a
Experiment			
Patterson et al.	[310]		0.022 8(3)
Feldmann	[312]		0.022 72(2) ^b
Bae and Peterson	[313]		0.022 69(3)
Dellwo et al.	[314]		0.022 695(7)
Haeffler et al.	[315]		0.022 712 9(8)

^a Extrapolated estimate.

^b A nonsymmetric error estimate is given by Feldmann.

state for Li^- . This signifies that correlation effects will play a critical role in the determination of a high precision estimate of EA for Li.

A summary of a number of theoretical calculations of EA is given in Table 12 along with some of the better experimental estimates for this quantity. The two best estimates of $E_{\text{NR}}(\text{Li}^-)$ are $-7.500\,751\,2(81)$ u [304] and $-7.500\,758$ u [305], which involve extrapolations of ≈ 221 $\mu\text{hartree}$ and ≈ 181 $\mu\text{hartree}$, respectively. A recent explicitly correlated coupled cluster calculation yields $-7.500\,671$ u for E_{NR} [319]. An estimate based on experimental data gives $E_{\text{NR}}(\text{Li}^-) = -7.500\,78(3)$ [317]. No high precision Hylleraas-type calculation is available for $E_{\text{NR}}(\text{Li}^-)$, partly because of the integration problems that must be handled. Although a major part of the four-electron integral problem involving multiple correlation factors r_{ij} has been solved [320–322], there are still several unresolved issues remaining.

For a number of entries in Table 12, the relativistic corrections have been either ignored or treated in a fairly approximate manner. The basic hope in such an approach is that the relativistic corrections for Li and Li^- are very similar, and so cancel when the energy difference is taken. The most detailed consideration of relativistic corrections [304] leads to $E_{\text{REL}}(\text{Li}^-) = -0.000\,640$ u, which can be compared to the value $E_{\text{REL}}(\text{Li}) = -0.000\,641\,55$ u given in Section 7. Assuming both these relativistic corrections to be valid, it appears that the relativistic contribution to the energy difference is small, but still significant at the current level of the best experiment result [315].

The energy estimated for $E_{\text{Total}}(\text{Li}^-)$ is $-7.501\,367(8)$ u [304]. In order to match up with the current experimental estimate, it is necessary to compute $E_{\text{NR}}(\text{Li}^-)$ to an accuracy of a few $\mu\text{hartrees}$. Recent work on the ground state of Be [30,31,323,324] has shown how difficult it is to achieve this level of accuracy for E_{NR} , and it should be expected to be an even more problematic assignment for Li^- . Since the two lowest values reported above for E_{NR} involve extrapolation of about 200 $\mu\text{hartree}$ and require estimates of basis set truncation errors, it is probably safe to assume that $E_{\text{Total}}(\text{Li}^-)$ is not known to better than six digits of precision. The most recent experimental estimate for the EA is $0.022\,712\,9(8)$ u ($4984.90(17)$ cm^{-1} or $0.618\,049(21)$ eV) [315]. The two best computational entries in

Table 12 [304,305], which were in close agreement with the previous best experimental measurement [314], now appear to be in less satisfactory agreement with the latest experimental work. Should the experimental precision for the EA improve by an order of magnitude, then a significant challenge will be presented to theorists. Explicit r_{ij} dependent basis sets (HY-CI, HY) will be required to determine E_{NR} for the anion, and a careful evaluation of relativistic and quantum electrodynamic corrections will also be needed.

11. The hyperfine coupling constant

The Fermi contact operator discussed in this section is

$$H_{\text{F}} = \frac{2}{3}\mu_0 g_J g_I \mu_{\text{B}} \mu_{\text{N}} \mathbf{I} \cdot \sum_{i=1}^3 \delta(\mathbf{r}_i) \mathbf{S}_i \quad (98)$$

which can be written as an effective operator

$$H_{\text{F}} = hA_J \mathbf{I} \cdot \mathbf{J} \quad (99)$$

where μ_0 is the vacuum permeability, g_J is the electronic g -factor (incorporating bound state corrections), g_I is the nuclear g -factor, μ_{B} and μ_{N} are the Bohr and nuclear magneton respectively, \mathbf{I} is the nuclear spin operator, \mathbf{S}_i is the electron spin operator for electron i , $\delta(\mathbf{r}_i)$ is the Dirac δ function, h is Planck's constant, \mathbf{J} is the total electronic angular momentum operator, and A_J is the hyperfine coupling constant. The energy splitting for the ^2S state of Li occurs between the $I+(1/2)$ and $I-(1/2)$ levels for $J=1/2$. That is, in terms of the total angular momentum F

$$hA_J F = E(F) - E(F-1) = h\Delta\nu \quad (100)$$

where $\Delta\nu$ is the experimentally determined frequency. The hyperfine coupling constant can be written as

$$A_{1/2} = \frac{2}{2I+1} \Delta\nu \quad (101)$$

where for ^7Li , $I = 3/2$ and for ^6Li , $I = 1$. It is most common in theoretical calculations to calculate the Fermi contact interaction parameter, f , defined as

$$f = \langle \psi | 4\pi \sum_{i=1}^3 \delta(\mathbf{r}_i) \sigma_{z_i} | \psi \rangle \quad (102)$$

and σ_{z_i} satisfies $\sigma_{z_i} \alpha(i) = \alpha(i)$ and $\sigma_{z_i} \beta(i) = -\beta(i)$.

From Eq. (98) and Eqs. (99), (101) and (102), the connection between the hyperfine coupling constant and f can be written as (using a conventional grouping of terms)

$$A_{1/2} = \left(\frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} \right) \frac{g_J \mu_I}{3I} f \quad (103)$$

Employing the most recent values of μ_B , μ_N , h and a_0 [197], the factor in parentheses in Eq. (103) simplifies to

$$C = \left(\frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} \right) = 95.410672(75) \text{ MHz} \quad (104)$$

An alternative grouping of terms is

$$C = \alpha^2 c R_x (m_e/m_p) = 95.410673(9) \quad (105)$$

where c is the speed of light and m_p is the proton mass. This leads to an eight-fold reduction in the uncertainty. Some authors use a value of $C = 95.521316$ MHz, which incorporates a correction for the anomalous magnetic moment (μ_e/μ_B) of the electron. Since there is a small bound state correction to the electronic g -value, it is preferable to isolate this factor from the collection of fundamental constants and account for this effect using the appropriate g_J factor. Thus, $A_{1/2}$ is given by

$$A_{1/2} = 95.410673(9) \left(\frac{g_J \mu_I}{3I} \right) f \quad (106)$$

There has been considerable discussion in the literature over an extended period of time on the nature and derivation of the correct operator form for H_F . The interested reader could start an exploration of these issues with the following sources: [325–330].

For the ground state of the lithium atom, the calculation of f has received considerable attention [32,34,39,112,117,118,262,266,270,330–384]. Two approaches have been commonly employed. The first has been to evaluate the expectation value in Eq. (102) using nonrelativistic wave functions and then apply some additional corrections that are discussed below. The second approach is to evaluate f using relativistic wave functions [39,270,376].

There are a number of additional corrections that must be made when f is calculated from Eq. (102) using nonrelativistic wave functions, in which case the calculated f is designated f_{NR} . Until relatively recent times, these corrections were usually ignored,

because the precision of the nonrelativistic phase of the calculation was not sufficiently high to justify efforts in calculating these additional small terms. While these small corrections have received considerable attention for atomic hydrogen [385–387], the same is not true for Li, and as a consequence there is still a considerable uncertainty associated with a couple of the corrections. The first and easiest correction to consider is the adjustment for finite nuclear mass. This is handled by multiplication of f_{NR} (from Eq. (102)) by $(1 - \frac{\mu}{M})^3$, where it is assumed that ψ is computed in the infinite nuclear mass approximation. Alternatively, the following correction factor is added to f_{NR} :

$$\Delta f_{MASS} = -\frac{3\mu}{M} \left[1 - \frac{\mu}{M} + \frac{1}{3} \left(\frac{\mu}{M} \right)^2 \right] f_{NR} \approx -\frac{3\mu}{M} f_{NR} \quad (107)$$

For ${}^7\text{Li}$ this correction is -0.000682 u. There is a very small mass dependent correction due to the mass polarization term in the Hamiltonian. This is an order of magnitude smaller than the error in the relativistic correction. The other two corrections are for relativistic effects Δf_{REL} , and for quantum electrodynamic effects, Δf_{QED} . The final expression is therefore

$$f = f_{NR} + \Delta f_{MASS} + \Delta f_{REL} + \Delta f_{QED} \quad (108)$$

The correction for finite nuclear size is often incorporated in Δf_{REL} .

11.1. Determination of the experimental f

For the lithium atom, several different experimentally derived values of f can be found in the literature. For this reason, a detailed explanation is provided for the value recommended below. The experimental f is determined from Eq. (106) and the case of ${}^7\text{Li}$ is discussed. The nuclear moment needed in Eq. (106) is the unshielded moment, μ_I^0 , which is determined from the experimentally measured shielded moment using the result

$$\mu_I = (1 - \sigma_{Li}) \mu_I^0 \quad (109)$$

where σ_{Li} is the diamagnetic shielding factor for Li. The most recently published table of nuclear moments [388] employs the screening factor $(1 - \sigma_{Li})^{-1}$ which was used in a previous tabulation of nuclear moments

[389]; this in turn attributes the value of σ_{Li} employed, $\sigma_{\text{Li}} = 1.048 \times 10^{-4}$, to a private communication. This value does not match accurate nonrelativistic calculations of this quantity, which give $\sigma_{\text{Li}} = 1.01499062 \times 10^{-4}$ [36] and $\sigma_{\text{Li}} = 1.01499064 \times 10^{-4}$ [37]. Finite nuclear mass corrections and relativistic effects modify these values, but not at a level that has any significant impact on the calculated screening factor $(1 - \sigma_{\text{Li}})^{-1}$. The value employed in Ref. [389] may arise from the accidental omission of the digit 1 in the second decimal place. The nuclear moment μ_I^0 has been re-evaluated using the accurate value for σ_{Li} [36,37] to give

$$(1 - \sigma_{\text{Li}})^{-1} = 1.000101509 \quad (110)$$

$$\mu_I^0 = 3.2564159(17) \text{ nm for } {}^7\text{Li} \quad (111)$$

and

$$\mu_I^0 = 0.82204454(55) \text{ nm for } {}^6\text{Li} \quad (112)$$

The nuclear moments are given in units of nuclear magnetons (nm). The corresponding tabulated values

based on the incorrect σ_{Li} value are 3.2564268(17) and 0.82204728(55) [388]. The nuclear moments based on NMR measurements [390,391] must be corrected for shielding due to the surrounding H_2O molecules;

$$\mu_{\text{atom}} = (1 - \sigma^*)^{-1} \mu_{\text{NMR}} \quad (113)$$

where $\sigma^* = -0.114(8) \times 10^{-4}$ for ${}^6\text{Li}$ and $\sigma^* = -0.110(7) \times 10^{-4}$ for ${}^7\text{Li}$ [392].

The experimental value of $A_{1/2}$ has been measured by several investigators [392–396]. For ${}^7\text{Li}$ the value $A_{1/2} = 401.7520433(5)$ MHz, and for ${}^6\text{Li}$ $A_{1/2} = 152.1368393(20)$ MHz [392] are employed. The value of g_J has been determined experimentally and relies on the measurement of three ratios of g -factors [397,398]. The value $g_J = 2.0023010(7)$ [397] is employed, which was obtained using the result

$$g_J(\text{Li}) = \left(\frac{g_J(\text{Li})}{g_J(\text{K})} \right) \left(\frac{g_J(\text{K})}{g_J(\text{Rb})} \right) \left(\frac{g_J(\text{Rb})}{g_e} \right) g_e$$

and the factors are grouped according to which ratios

Table 13
Fermi contact term f and hyperfine coupling constant A for the ground state of ${}^7\text{Li}$

Author(s)	Reference	Method	$4\pi\langle\delta(r_i)\sigma_z\rangle^a$	$f_{\text{Li}}(\text{u})^b$	$A_{\text{Li}}(\text{MHz})^c$
Sachs	[331]	HF	2.094	2.095	289.6
Bagus et al.	[354]	UHF	2.823	2.824	390.4
Larsson	[32]	100-HY	2.906	2.907	401.9
Lindgren	[266]	MBPT	2.9172	2.9180	403.40
King and Shoup	[112]	352-HY	2.9041	2.905	401.6
King	[117]	602-HY	2.9064	2.9072	401.91
Panigrahy et al.	[376]	REL-MBPT		2.9114	402.49
Blundell et al.	[270]	REL-MBPT		2.9111	402.47
King and Bergsbaken	[118]	296-HY	2.9071	2.9079	402.01
Mårtensson-Pendrill and Ynnerman	[378]	REL-CCSD		2.8999	400.90
Sundholm and Olsen	[381]	MCHF	2.9039	2.9047	401.56
Esquivel et al.	[34]	CI	2.9095	2.9103	402.34
Carlsson et al.	[379]	MCHF	2.9047	2.9055	401.67
Tong et al.	[39]	MCHF	2.9051	2.9059	401.73
Shabaev et al.	[383]	CI		2.904	401.5
Bieron et al.	[384](a)	MCDF		2.90578	401.714
Yan et al.	[384](b)	HY	2.905922(50)	2.90575(22) ^d	401.71(3)
Experimental: Schlecht and McColm	[394]				401.75202(24)
Beckmann et al.	[392]				401.7520433(5)

^a Nonrelativistic expectation value computed in the infinite nuclear mass approximation.

^b Evaluated using Eq. (108).

^c Evaluated using Eq. (106).

^d This value uses the correction factors given in Ref. [384](b).

have been experimentally measured. Within experimental error both ${}^6\text{Li}$ and ${}^7\text{Li}$ give the same value for g_J [398]. In several previous estimates of f_{exp} , the free electron g -value, $g_e = 2.002\,319\,304\,386(20)$, has been employed. Part of the confusion probably arises from the fact that it is very common notation (particularly among ESR spectroscopists) to write g_J as g (or sometimes g_e). It is intended that in this notation, g should incorporate bound state effects, so the use of the free-electron g value is an approximation.

Employing Eq. (106) and the values of μ_I , g_J and $A_{1/2}$ indicated above, gives for ${}^7\text{Li}$

$$f_{\text{exp}}({}^7\text{Li}) = 2.906\,058\,9(18) \text{ u} \quad (114)$$

and for ${}^6\text{Li}$

$$f_{\text{exp}}({}^6\text{Li}) = 2.906\,256\,7(22) \text{ u} \quad (115)$$

A summary of mostly high precision values of f is presented in Table 13. The HF result is shown for comparison. The HF level of theory performs rather poorly in predicting the hyperfine coupling constant. The reasons for this have been discussed widely in the literature [95,325,331–333,342]. The values given for $4\pi\langle\delta(\mathbf{r}_i)\sigma_{Z_i}\rangle$ are all nonrelativistic and computed in the infinite nuclear mass approximation. The listed values of f_{Li} are calculated from Eq. (108) unless the authors carried out a relativistic calculation. The work of Refs [39] and [384] comes closest to the estimate given in Eq. (114).

There are a few different estimates of Δf_{REL} in the literature. Values for Δf_{REL} given in Ref. [39] range from 0.00153 to 0.00176 u, obtained by comparison of MCHF and MCDF calculations for different basis sets. The relativistic correction is then computed from

$$\Delta f_{\text{REL}} = f_{\text{NR,ext}} \left\{ \frac{f_{\text{MCDF}}}{f_{\text{MCHF}}} - 1 \right\} \quad (116)$$

where $f_{\text{NR,ext}}$ denotes the extrapolated nonrelativistic value, and f_{MCDF} and f_{MCHF} designate respectively the values computed in the MCDF and MCHF approximations for the smaller basis sets. An earlier calculation [326] reports a value of $\Delta f_{\text{REL}} = 0.0017$ u, which was evaluated in a similar procedure to that described above.

A recent calculation [383] gives an estimate of the

finite nuclear size correction, Δf_{FIN} :

$$\Delta f_{\text{FIN}} = -0.000\,764 \text{ u} \quad (117)$$

This correction is relative to the calculated f based on a point-nucleus model. These authors determined a combined relativistic and finite nuclear mass correction of 0.00177 u. Based on the procedures employed, it is unlikely that three digits of precision can be assigned to any of the above values. From the available results, the value

$$\Delta f_{\text{REL}} = 0.001\,7(3) \text{ u} \quad (118)$$

seems a reasonable estimate. The error estimate is based on the range of values available, and is probably conservative.

For the Li atom, relatively little work has been done on the radiative correction Δf_{QED} . The approach that has been employed to evaluate Δf_{QED} is based on a Z -dependent one-electron hydrogen-like formula [376]. The value reported is

$$\Delta f_{\text{QED}} = -0.0002 \text{ u} \quad (119)$$

Alternative estimates of 0.00336 u [384](a) and $-0.000\,918(47)$ u [384](b) have been given for Δf_{QED} . The value given in Eq. (119) can be regarded as a first rough approximation only, since no electron–electron interaction effects are included in this estimate and there is an uncertainty associated with the choice of the best effective nuclear charge to employ in the one-electron formula.

The entries appearing for f_{Li} in Table 13 based on published values of $4\pi\langle\delta(\mathbf{r}_i)\sigma_{Z_i}\rangle$ have all been corrected using eqns (108), (107), (118) and (119), and Eq. (106) has been employed to calculate the hyperfine coupling constant. The f values can be compared with the experimental estimate given in Eq. (114). The experimentally derived estimate for f_{NR} (in the infinite nuclear mass approximation) is

$$f_{\text{NR}} = 2.905\,2(8) \text{ u} \quad (120)$$

which is based on the hyperfine coupling constant reported in Ref. [392], and the corrections Δf_{MASS} , Δf_{REL} and Δf_{QED} discussed above. The error estimate in Eq. (120) reflects the range of values given for Δf_{QED} and Δf_{REL} . Several entries in Table 13 are near the estimate given in Eq. (120) [32,112, 117,381,379,39,384], with Ref. [384] providing the closest agreement. Some caution might be appropriate

with this property, because the uncertainty in Δf_{QED} and Δf_{REL} may be somewhat larger than the estimate used to arrive at Eq. (120).

11.2. The Hiller–Sucher–Feinberg (HSF) approach

The standard formula for the determination of f (Eq. (102)) suffers from the point-like nature of the delta function operator. An alternative formulation is based on the following result [399]:

$$\langle \psi | \delta(\mathbf{r}_i) \sigma_{z_i} | \psi \rangle = \langle \psi | D_i \sigma_{z_i} | \psi \rangle \quad (121)$$

with D_i given as

$$D_i = \frac{1}{2\pi} \frac{\partial V}{\partial r_i} - \frac{\ell_i^2}{2\pi r_i^3} \quad (122)$$

where V is the potential term given in Eq. (11) and ℓ_i^2 is the square of the orbital angular momentum for electron i . Eq. (121) and its analogue for the electron density and electron–electron pair distribution function, and related identities, have been discussed at length in the literature [369,370,399–412]. For an S state, the ℓ_i^2 term vanishes, so Eq. (121) simplifies to

$$\langle \psi | \delta(\mathbf{r}_i) \sigma_{z_i} | \psi \rangle = \frac{1}{2\pi} \langle \psi | \frac{\partial V}{\partial r_i} \sigma_{z_i} | \psi \rangle \quad (123)$$

For the lithium atom, this approach has been exploited in several papers [369,370,380,381]. The hope is that the expectation value involving the global operator D_i will lead to a faster convergence for the calculation of f . This is at some cost, however, because of the increased complexity of the integrals required to evaluate $\langle \psi | D_i \sigma_{z_i} | \psi \rangle$.

For the lithium atom, the results obtained using the HSF identity generally give results in better agreement with experiment, although for some smaller basis sets, the standard delta function approach does somewhat better [380]. The latter situations have been regarded as fortuitous [380]. Faster convergence has been reported when the HSF identity is employed using a few different basis sets.

11.3. The hyperfine anomaly

There are two different definitions for the hyperfine anomaly, and the one discussed in this section is

[397,413]

$$\frac{A_1}{A_2} = \frac{g_1}{g_2} (1 + \Delta_{12}) \quad (124)$$

where A_1 and g_1 are the hyperfine coupling constant and nuclear g_I -factor for isotope 1, and Δ_{12} is referred to as the hyperfine anomaly. This effect arises from the distribution of magnetization within a nucleus of finite size.

For the $^2S_{1/2}$ ground state of Li

$$\Delta_{67} = \frac{A_6 g_7}{A_7 g_6} - 1 \quad (125)$$

which simplifies to

$$\Delta_{67} = \frac{f_6}{f_7} - 1 \quad (126)$$

From Eq. (125), the experimental value for the two isotopes of Li is $\Delta_{67} = 6.806(63) \times 10^{-5}$ [397]. If we write

$$f_6 = \left(1 - \frac{6\mu}{6M} \right)^3 (f_{\text{NR}} + \Delta f_6) \quad (127)$$

where Δf_6 incorporates the relativistic, radiative, and finite nuclear size corrections, for isotope ^6Li , and using a similar expression for isotope ^7Li , then

$$\Delta_{67} \approx \frac{(\Delta f_6 - \Delta f_7)}{f_{\text{NR}}} - 3 \left(\frac{6\mu}{6M} - \frac{7\mu}{7M} \right) \quad (128)$$

The second factor in Eq. (128) contributes -3.9044×10^{-5} . The first factor can be estimated using the value of Δ_{67} given above. It should be apparent from the previous discussion of Δf_{REL} and Δf_{QED} that the current calculations are not sufficiently advanced to determine $\Delta f_6 - \Delta f_7$ with the precision necessary for evaluating Δ_{67} .

11.4. Hyperfine pressure shift

The hyperfine pressure shift, f_p , measures the pressure dependence of the hyperfine splitting as a buffer gas is introduced. The most common buffer gases employed are the inert gases. For ^6Li and ^7Li , experimental values are available for buffer gases He, Ne and Ar. The results for f_p are usually reported as a fractional pressure shift, i.e.

$$f_p = \frac{1}{\Delta\nu} \frac{\partial \Delta\nu}{\partial P} \quad (129)$$

Table 14
Calculated correction factor to g_J for the ground state of Li

Author(s)	Reference	Method	$\delta g \times 10^5$ ($\delta g = g_J - g_e$)
Hegstrom	[415]	HF	-1.78(8)
Veseth	[416]	SEHF	-1.844
Veseth	[417]	MBPT	-1.778
Lindroth and Ynnerman	[419]	REL-CCSD	-1.772(20)
Marketos	[420]	REL-SD	-1.406
Experiment	[397,398,421]		-1.83(7)

For helium as the buffer gas, the result for f_p is $77.7(10) \times 10^{-9} \text{ torr}^{-1}$ at 387°C [396].

There has been relatively little theoretical work carried out for the calculation of the hyperfine pressure shifts for Li [414]. One approach employed has been to determine f_p from $\langle \Delta\nu(R) \rangle$, the latter term representing a weighted average of $\Delta\nu(R)$ (see Eq. (100)) over all possible values of the internuclear separation (R) between Li and the buffer gas atom. This type of calculation is limited by the accuracy of the interatomic potential used in the weighted average. For the buffer gas He, using two different potential forms, the results $44.7 \times 10^{-9} \text{ torr}^{-1}$ and $83.3 \times 10^{-9} \text{ torr}^{-1}$ at 387°C have been obtained [414]. These results fall on either side of the experimental result given above. This is obviously a much more challenging problem than the calculation of a hyperfine coupling constant for a gas phase atomic system.

11.5. Calculation of g_J

The magnetic moment of the lithium atom is given by

$$\boldsymbol{\mu} = g_J \mu_B \mathbf{J} \quad (130)$$

and so for a magnetic field \mathbf{B} applied in the z -direction, the expectation value of the magnetic moment-field interaction is (where H_{mag} denotes the magnetic Hamiltonian)

$$\begin{aligned} \langle \psi | H_{\text{mag}} | \psi \rangle &= \langle \psi | -\boldsymbol{\mu} \cdot \mathbf{B} | \psi \rangle \\ &= -g_J \mu_B B \langle J_Z \rangle \end{aligned} \quad (131)$$

i.e. g_J is determined from

$$g_J = \frac{\langle \psi | -H_{\text{mag}} | \psi \rangle}{\mu_B B \langle J_Z \rangle} \quad (132)$$

If the magnetic Hamiltonian for the ^2S ground state is approximated by

$$H_{\text{mag}} = -g_e \mu_B \mathbf{B} \cdot \mathbf{S} \quad (133)$$

then the approximation $g_J \approx g_e$ follows.

The appropriate form for H_{mag} has been discussed in several articles [415–420]. H_{mag} includes contributions from the Zeeman interaction, spin-orbit coupling contributions, spin-other-orbit contributions and some additional relativistic refinements. These additional corrections have been evaluated using Hartree-Fock theory [415], spin-extended HF theory [416], MBPT [417], and using relativistic wave functions in a coupled cluster single- and double-excitation scheme [419]. Table 14 collects the results of these calculations. The results are reported in terms of

$$\delta g = g_J - g_e \quad (134)$$

where g_e is the free electron g -value. The value of g_e employed in Table 14 is 2.002 319 304 376(8) [421]. The results of the best calculations in Table 14 are in reasonably close agreement with the experimental value. If additional precision for the experimental result becomes possible, this will provide an interesting challenge for theorists. The calculation of g_J also provides a very useful testing ground for the theoretical formulation of magnetic interactions, which has fundamental importance in a number of areas.

12. Nuclear magnetic shielding constant

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

$$\sigma_d = \frac{1}{3} \alpha^2 \left\langle \psi \left| \sum_{i=1}^3 \frac{1}{r_i} \right| \psi \right\rangle \quad (135)$$

Table 15
Nuclear magnetic shielding constant for the ground state of Li

Author(s)	Reference	Method	σ_d (u)
Malli and Froese	[427]	HF	1.0145×10^{-4}
King	[117]	602-HY	$1.01499043(25) \times 10^{-4}$
King	[36]	760-HY	$1.01499062(9) \times 10^{-4}$
Yan and Drake	[37]	1589-HY	$1.01499064(9) \times 10^{-4}$
Yan and Drake ^a	[37]	1589-HY	$1.01498857(9) \times 10^{-4}$

^a Includes finite nuclear mass correction (for ${}^7\text{Li}$).

Since the expectation value $\langle r_i^{-1} \rangle$ is one component used to determine the energy, variational calculations usually yield fairly precise and well converged values for σ_d . Values of this quantity (or information necessary for its calculation) have been determined by a variety of theoretical methods [29,35–37,112, 117,422–428]. A summary of some calculated values of σ_d is given in Table 15. The HF value of σ_d reported in Table 15 is in reasonably good agreement with the high precision nonrelativistic Hylleraas results. Relativistic corrections to σ_d are generally observed to be fairly small for light atoms [429]. The first three results in Table 15 based on the Hylleraas method are for the infinite nuclear mass approximation. The final entry in Table 15 includes the effects of finite nuclear mass.

12.1. Connection with X-ray scattering

For spherically symmetric states, it can be shown that [430]

$$\sigma_d = \frac{2\alpha^2}{3\pi} \int_0^\infty f(k) dk \quad (136)$$

where $f(k)$ (also very commonly denoted $F(k)$) is the coherent X-ray scattering amplitude. Eq. (136) opens

up an experimental route to σ_d . For lithium, no experimental determination of σ_d via Eq. (136) appears to have been carried out. Since σ_d can be obtained theoretically with high precision, Eq. (136) serves as a useful sum rule check on calculated X-ray scattering factors. An application along these lines using Hylleraas-type wave functions to calculate the scattering factors for Li can be found in Ref. [431].

13. Diamagnetic susceptibility

The diamagnetic susceptibility is defined (in u) by

$$\chi = -\frac{1}{6}\alpha^2 \left\langle \psi \left| \sum_{i=1}^3 r_i^2 \right| \psi \right\rangle \quad (137)$$

The molar diamagnetic susceptibility, χ_m , (in the standard employed units of $\text{cm}^3 \text{mol}^{-1}$) is given by

$$\chi_m = N_A a_0^3 \chi \quad (138)$$

where N_A is Avogadro's constant. Using the available values for N_A , α and a_0 [197] gives

$$\chi_m = -0.7920153(5) \times 10^{-6} \left\langle \psi \left| \sum_{i=1}^3 r_i^2 \right| \psi \right\rangle \quad (139)$$

Table 16
Molar diamagnetic susceptibility for the ground state of Li

Author(s)	Reference	Method	χ_m ($\text{cm}^3 \text{mol}^{-1}$)
Mendelsohn et al. ^a	[432]	HF	1.47568×10^{-5}
Mendelsohn et al. ^a	[432]	REL-HF	1.47544×10^{-5}
King	[117]	602-HY	1.45372×10^{-5}
King	[36]	760-HY	$1.4537145(10) \times 10^{-5}$
Yan and Drake	[37]	1589-HY	$1.4537135(9) \times 10^{-5}$
Yan and Drake ^b	[37]	1589-HY	$1.4537274(9) \times 10^{-5}$

^a The value from this work has been recalculated using the conversion factor in Eq. (139).

^b Includes finite nuclear mass correction (for ${}^7\text{Li}$).

Values for χ (or the expectation value necessary to calculate it) have been determined by a number of methods [34–37,117,432]. Table 16 presents a summary of some values. The Hartree–Fock value is observed to be in reasonable agreement (about 1.6% too high) with the high precision estimates based on Hylleraas-type wave functions.

The forward ($\theta = 0^\circ$) scattering factor for elastic electron scattering in the first Born approximation can be related to the diamagnetic susceptibility, and the forward differential cross section for elastic scattering is [433–435]

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta=0^\circ} = \frac{\gamma^2}{9} \langle v_i^2 \rangle^2 \quad (140)$$

where γ^2 is the factor $[1 - (v^2/c^2)]^{-1}$, v is the electron velocity and c is the speed of light. Given accurate elastic differential cross section data it is possible to extract values of χ . This approach will provide a useful check on the theoretical calculations.

14. Polarizability and hyperpolarizability

The theory of polarizabilities is well described in several sources [436–438]. The various polarizabilities can be determined from the perturbation theory formulas [125,439]:

$$\alpha_{\alpha\beta}(-\omega_\sigma; \omega_1) = \hbar^{-1} \sum_P \sum_{m(\neq g)} \frac{\langle g | \mu_\alpha | m \rangle \langle m | \mu_\beta | g \rangle}{\omega_{mg} - \omega_\sigma} \quad (141)$$

$$C_{\alpha\beta, \gamma\delta}(-\omega_\sigma; \omega_1) = \hbar^{-1} \sum_P \sum_{m(\neq g)} \frac{\langle g | \Theta_{\alpha\beta} | m \rangle \langle m | \Theta_{\gamma\delta} | g \rangle}{(\omega_{mg} - \omega_\sigma)} \quad (142)$$

$$B_{\alpha\beta, \gamma\delta}(-\omega_\sigma; \omega_1, \omega_2) = \hbar^{-2} \sum_P \sum_{m, n(\neq g)} \frac{\langle g | \mu_\alpha | m \rangle \langle m | \mu_\beta | n \rangle \langle n | \Theta_{\gamma\delta} | g \rangle}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_2)} \quad (143)$$

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} \sum_P \times \left[\sum_{m, n, p(\neq g)} \frac{\langle g | \mu_\alpha | m \rangle \langle m | \mu_\beta | n \rangle \langle n | \mu_\gamma | p \rangle \langle p | \mu_\delta | g \rangle}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_1 - \omega_2)(\omega_{pg} - \omega_1)} - \sum_{m, n, p(\neq g)} \frac{\langle g | \mu_\alpha | m \rangle \langle m | \mu_\delta | g \rangle \langle g | \mu_\gamma | n \rangle \langle n | \mu_\beta | g \rangle}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_1)(\omega_{ng} + \omega_2)} \right] \quad (144)$$

where $|g\rangle$ is the ground state wave function, $|m\rangle$, $|n\rangle$ and $|p\rangle$ are excited state wave functions, and μ_α and $\Theta_{\alpha\beta}$ denote the α component of the electric dipole moment operator and the $\alpha\beta$ component of the electric quadrupole moment operator, respectively. ω_{mg} denotes a transition frequency and

$$\omega_\sigma \equiv \sum_i \omega_i \quad (145)$$

and the sum runs over the arguments after the semi-colon in each expression. \sum_P denotes an appropriate permutation for each expression. The connection between the susceptibilities and the polarizabilities can be found in several references (see, for example, Ref. [440]).

The static polarizabilities are obtained by setting ω_i equal to zero in eqns (141)–(144). The calculation of the static polarizabilities for the ground state of Li has received considerable attention in the literature [441–500]. The early literature on measurements has been reviewed in Ref. [501] and a compilation of older results on ground state atomic dipole polarizabilities has been published [502]. Interest has probably focused so heavily on the dipole polarizability because of its connection with several important topics that include van der Waals interactions, refraction, collision processes and others. A few measurements of α have been reported for the ground state of Li [503–505].

Table 17 summarizes the results from a large number of calculations. Literature values of α are often published in units of \AA^3 . The conversion factor $1 \text{\AA}^3 = 6.74833304 \text{ u}$ has been employed for Table 17. For the static dipole polarizability, α , also frequently denoted as $\alpha(0)$ or α_d , the best HF level calculations are often within 5% of the highest precision theoretical estimates. The best theoretical calculations [500](b) lead to a value of $164.111(2) \text{ u}$, which is in close agreement with the experimental value of $164.0(34) \text{ u}$ [505]. Unfortunately, the uncertainty associated with this experimental value is rather large.

Table 17

Static dipole polarizability α , quadrupole polarizability C , dipole–quadrupole polarizability B , and hyperpolarizability γ for the ground state of the lithium atom in u

Authors	Reference	Method	α	C	B	γ
Dalgarno and Kingston	[441]	Oscillator sum rule	165			
Flannery and Stewart	[443]	PV	169.4			
Stacey	[445]	CI	161.8			
Langhoff et al.	[449]	HF-PT				7.547×10^5
Langhoff et al.	[448]	Coupled HF	170.1	1.50×10^3		
Lahiri and Mukherji	[450]	PV	170			
Boyle and Coulson	[451]	SCF				2.4×10^5
Drake and Cohen	[453]	PT	157.9			-6.73×10^5
Stacey and Dalgarno	[454]	CI	163.1			
Chang et al.	[455]	MBPT	167.6			
Sternheimer	[456]	PT	167.0			
Sternheimer	[457]	PT		1.45×10^3		
Heaton and Stewart	[458]	PT	168.4			
Tiwari et al.	[459]	PT	163	1.50×10^3		
Mukherjee et al.	[460]	PV	170.3			
Moitra and Mukherjee	[462]	HF	174.0			
Stevens and Billingsley	[465]	HF	171.2			
Adelman and Szabo	[463]	Coulomb approx.	164	1.41×10^3		
Bhattacharya and Mukherjee	[464]	Coupled HF			-5.821×10^3	
Kouba and Meath	[468]	Pseudospectral		$1.413(26) \times 10^3$		
Roy and Bhattacharya	[471]	Coupled HF				-96.3×10^3
Werner and Meyer	[472]	PNO-CEPA	164.5			
Sims et al.	[473]	CI-HY-PV	163.8			
Tang et al.	[474]	Coulomb approx.	164			
Zeiss and Meath	[479]	Pseudospectral	163.6(16)			
Reinsch and Meyer	[481]	PNO-CEPA		1.428×10^3		
Maeder and Kutzelnigg	[483]	PP	164.3	1.383×10^3		
Voegel et al.	[482]	HF	170.1			-5.98×10^4
Muszynska et al.	[485]	CI-HY-PV	163.8			
Pipin and Woznicki	[111]	CI-HY-PV	163.9			
Pouchan and Bishop	[438]	CI-point charge	164(2)			
Muller et al.	[265]	CI	163.7			
Mahapatra and Rao	[488]	MBPT		1.472×10^3		
Maroulis and Bishop	[489]	SCF			-5.888×10^4	-8.64×10^4
Maroulis and Thakkar	[491]	MBPT	164.5	1.428×10^3	-5.493×10^4	4.3×10^3
Pipin and Bishop	[125]	CI-HY	164.1	1.423×10^3	-5.43×10^4	3×10^3
Nicolaides and Themelis	[494]	CEA	164.9			37×10^3
Fuentealba and Reyes	[495](a)	PP	164	1.45×10^3	-5.55×10^4	65×10^3
Themelis and Nicolaides	[492]	CEA	169.3			
Wheatley and Meath	[493]	CI	162.92			
Wang and Chung	[496]	CI	164.08			
Kassimi and Thakkar	[498]	CCSD(T)	164.2(1)			$2.9(3) \times 10^3$
Laughlin	[499]	One-electron MP	163.91			3.93×10^3
Yan et al.	[500](b)	HY	164.111(2)	1423.266(5)		
Experimental						
Molof et al.	[505]		164.0(3.4)			

The refractive index $n(\omega)$ is related to $\alpha(\omega)$ [454]. For gaseous Li, the refractive index has been evaluated as a function of wavelength [454]. Higher precision values of $n(\omega)$ could be determined from the more recent calculations of $\alpha(\omega)$ [125].

Refinements of the above expression for the dipole polarizability of alkali metal vapors have been treated theoretically. The interested reader can pursue this topic in Ref. [506].

For the quadrupole polarizability, C , sometimes denoted α_q , the best calculations lead to a value of 1423.266(5) u [500](b). No experimental value appears to be available for this quantity. The same authors calculate the octupole polarizability to be 39 650.49 u [500](b).

For the dipole–dipole–quadrupole polarizability, B , there are fewer reported calculations. The best results available [125,491] give B as -5.43×10^4 to -5.49×10^4 u, with the former value probably being the better estimate. Once again, no experimental result appears to be available. The static $B(0)$ can be related to the static hypermagnetizability anisotropy, the experimental quantity of interest in the Cotton–Mouton effect [437]. For values of B , C and α at several different values of ω , the reader is directed to the tabulation of Ref. [125].

For the hyperpolarizability, γ , the scatter of the theoretical results is rather noticeable. Until recently, even the correct sign for γ was not resolved. The approximate methods of calculation indicated in Table 17 either give the wrong sign, or are often in error by two orders of magnitude. The best calculations currently available give values of 3×10^3 u [125] and $2.9(3) \times 10^3$ u [498]. No experimental result is available for comparison.

15. Shielding constants

The dipole shielding constant β_∞ (the notation γ_d is also commonly employed) is usually defined [507] as the induced electric field at the nucleus due to the perturbed electronic charge distribution divided by the electric field at the nucleus due to the external charge alone. This definition gives

$$\beta_\infty = 2 \left\langle \psi_1^{(1)} \left| \sum_{i=1}^N \frac{P_1(\cos \theta_i)}{r_i^2} \right| \psi_0 \right\rangle \quad (146)$$

where ψ_0 is the unperturbed wave function and $\psi_1^{(1)}$ is the perturbed wave function arising from the presence of an external charge. In a similar fashion, the 2^L -pole shielding factor is defined as the ratio of the change in the L th-order electric field gradient at the nucleus due to the electronic charge distribution to the L th-order gradient due to the external charge alone. The quadrupole shielding factor γ_∞ (often denoted γ_q) is

$$\gamma_\infty = 2 \left\langle \psi_1^{(2)} \left| \sum_{i=1}^N \frac{P_2(\cos \theta_i)}{r_i^3} \right| \psi_0 \right\rangle \quad (147)$$

and the general 2^L -pole shielding factor is

$$\gamma_{2^L} \equiv 2 \left\langle \psi_1^{(L)} \left| \sum_{i=1}^N \frac{P_L(\cos \theta_i)}{r_i^{L+1}} \right| \psi_0 \right\rangle \quad (148)$$

A positive value of γ_{2^L} corresponds to shielding and a negative value to antishielding.

The dipole shielding factor has been evaluated in a number of applications for the ground state of Li [450,455,456,459,460]. Since it can be shown that β_∞ satisfies

$$\beta_\infty = \frac{N}{Z} = 1 \quad (149)$$

the principal interest in this quantity is that it provides a check on the accuracy of the wave functions ψ_0 and $\psi_1^{(1)}$.

A number of calculations of γ_∞ (γ_q) have been reported [444,448,459,460,508]. The results are summarized in Table 18. The higher 2^L -pole shielding factors have received less attention. A few values of the octupole shielding factor (γ_o) are also included in Table 18. For γ_∞ there is a significant spread in values. From the results available, it appears that γ_∞ lies in the interval 0.7–0.9, with the lower end of the range being most likely nearer the exact result.

16. Oscillator strength sums

The dipole oscillator strength sum is defined by

$$S(k) = \sum_n' f_{n0} E_{n0}^k \quad (150)$$

where f_{n0} is the dipole oscillator strength for the transition $0 \rightarrow n$ (0 is taken to be the ground state):

$$f_{n0} = 2 \left| \left\langle \psi_0 \left| \sum_{i=1}^3 r_i P_1(\cos \theta_i) \right| \psi_n \right\rangle \right|^2 E_{n0} \quad (151)$$

Table 18
 Quadrupole and octupole shielding factors for the ground state of the lithium atom

Author(s)	Reference	Method	Shielding factors	
			$\gamma_{\times}(\gamma_q)$	γ_o
Langhoff and Hurst	[444]	Uncoupled-HF	1.08	0.536 0.703
Langhoff et al.	[448]	Coupled-HF	0.912	
		Uncoupled-HF	0.743	
Tiwari et al.	[459]		0.9	
Mukherjee et al.	[460]	Coupled-HF	2.81	
Mahapatra and Rao	[508]	MBPT	0.7156	

and E_{n0} is the corresponding transition energy. The prime on the summation signifies $n \neq 0$ (only important for negative k), and the summation is over all states, both discrete and continuous. Oscillator strength sums are of interest because they determine various properties that include the dipole polarizability, scattering properties of atoms and dispersion coefficients, as well as providing an important test for ab initio calculations.

The following relationships can be readily derived [509]:

$$S(0) = N \quad (152)$$

$$S(-1) = 2 \left\langle \psi_0 \left| \sum_{i=1}^3 r_i^2 \right| \psi_0 \right\rangle - \frac{2}{3} \left\langle \psi_0 \left| \sum_{i=1}^3 \sum_{j>i}^3 r_{ij}^2 \right| \psi_0 \right\rangle \quad (153)$$

$$S(1) = -\frac{2}{3} \left\langle \psi_0 \left| \sum_{i=1}^3 \nabla_i^2 \right| \psi_0 \right\rangle - \frac{4}{3} \left\langle \psi_0 \left| \sum_{i=1}^3 \sum_{j>i}^3 \nabla_i \cdot \nabla_j \right| \psi_0 \right\rangle \quad (154)$$

$$S(2) = \frac{4\pi Z}{3} \left\langle \psi_0 \left| \sum_{i=1}^3 \delta(\mathbf{r}_i) \right| \psi_0 \right\rangle \quad (155)$$

$$S(-2) = \alpha(0) \quad (156)$$

In Eq. (152), N is the number of electrons in the system. This expression represents a useful check on the quality of the wave functions when the sum is explicitly evaluated. This relationship might also be taken as a useful condition to impose on the calculations. $S(1)$ is related to the kinetic energy plus a term that appears in the evaluation of the mass polarization correction to the energy (see Section 6). $S(2)$ is directly related to the electron density

at the nucleus, and $S(-2)$ determines the static dipole polarizability. In addition, the dipole–dipole dispersion coefficient, C_6 , can be related to various values of $S(k)$ [510], as can several other properties [511].

For the ground state of atomic lithium, results for $S(k)$ are available for integer k values from -14 to 2 , and some fractional values of k [125,510,512–519]. A selection of these values are presented in Table 19. Since the ground state expectation values appearing in eqns (153)–(155) are known with high precision [29,35,37,117], the most precise values of $S(-1)$, $S(1)$ and $S(2)$ appearing in Table 19 are based on these relationships, rather than a direct evaluation of $S(k)$ using Eq. (150). These values should provide useful benchmark tests for calculations carrying out the direct summation. The most precise values of $S(-3)$, $S(-4)$ and $S(-5)$ are those of Ref. [125].

Under appropriate circumstances, the refractive index $n(\omega)$ can be developed in terms of an infinite power series of terms involving $S(k)$, for $k = -2, -4, \dots$. From this expansion, the Verdet constant (which is proportional to $\partial n(\omega)/\partial \omega$) can be readily extracted. This line of research has been explored for several systems, but does not appear to have attracted much attention for atomic lithium.

16.1. 2^ℓ -pole oscillator strength sums

The generalization of Eq. (151) beyond the dipole approximation is

$$S_\ell(k) = \sum_n f_{n0}^{(\ell)} E_{n0}^k \quad (157)$$

Table 19
Dipole oscillator strength sums for the ground state of the lithium atom

Author(s)	Reference	$S(k)$ (u) ^a					
		$S(2)$	$S(1)$	$S(-1)$	$S(-3)$	$S(-4)$	$S(-5)$
Stacy and Dalgarno	[454]			12.17	2354	3.4191×10^4	
Kramer ^b	[510]			11.91	2357	3.425×10^4	
Zeiss and Meath	[479]					3.5038×10^4	
Kouba and Meath	[514]			12.32(23)	2450(3)	$3.5999(22) \times 10^4$	
Zeiss et al. ^c	[477]	180.0	10.44	12.14	2385	3.504×10^4	
Tang et al. ^d	[474]					3.53×10^4	
Kouba and Meath	[480]			12.09(14)	2383(2)	$3.5011(21) \times 10^4$	
Cummings	[515]	173.855	9.91035	12.422	1072.7		
Pipin and Bishop	[125]			12.13	2394	3.517×10^4	5.176×10^5
King	[117]	173.941 ^e	10.373 21 ^f	12.144 1 ^g			
King and Bergsbaken	[118]	173.9524 ^e	10.373 204 ^f				
Lüchow and Kleindienst	[29]		10.373 204 16^f				
Yan and Drake	[37]	173.9505^e	10.373 204 18^f	12.144 003 65^g			

^a See Table 17 and Eq. (156) for $S(-2)$.

^b This author also gives $S(k)$ for $k = -1/2, -3/2, -5/2$ and $-7/2$.

^c These authors also give $S(k)$ for $k = -6, -8, -10, -12$ and -14 , as well as the fractional values $-1/2, -3/2$ and $-5/2$.

^d These authors also give values for $S(-6)$ and $S(-8)$.

^e Computed using Eq. (155).

^f Computed using Eq. (154).

^g Computed using Eq. (153).

where $f_{n0}^{(\ell)}$ is the 2^ℓ -pole oscillator strength defined by

$$f_{n0}^{(\ell)} = 2 \left| \left\langle \psi_0 \left| \sum_{i=1}^3 r_i^\ell P_\ell(\cos \theta_i) \right| \psi_n \right\rangle \right|^2 E_{n0} \quad (158)$$

Most investigations of Eq. (157) have dealt exclusively with the case $\ell = 1$. Far less work is available for other cases. For the case where $\ell = 2$, there are some quadrupole sum rules of interest [468]:

$$S_2(0) = 6 \left\langle \psi_0 \left| \left(\sum_{i=1}^3 r_i P_1(\cos \theta_i) \right)^2 \right| \psi_0 \right\rangle = 3S_1(-1) \quad (159)$$

$$S_2(-1) = 2 \left\langle \psi_0 \left| \left(\sum_{i=1}^3 r_i^2 P_2(\cos \theta_i) \right)^2 \right| \psi_0 \right\rangle \quad (160)$$

$$S_2(-2) = \alpha_q \quad (161)$$

Values of $S_2(0)$ can be determined from the $S(-1)$ entry given in Table 19. In Eq. (161), α_q denotes the static quadrupole polarizability, and values for this are given in Table 17 under the entry heading C. A summary of some available values of $S_2(k)$ is presented in Table 20. A result is available for $S_\ell(0)$ [517]:

$$S_\ell(0) = \ell \left\langle \psi_0 \left| \sum_{i=1}^3 r_i^{2\ell-2} \right| \psi_0 \right\rangle \quad (162)$$

Table 20
Quadrupole oscillator strength sums for the ground state of the lithium atom

Authors	Ref.	$S_2(k)$ ^a					
		$S_2(1)$	$S_2(-1)$	$S_2(-3)$	$S_2(-4)$	$S_2(-5)$	$S_2(-6)$
Kouba and Meath	[468]	10.54	217(4)	$9.38(23) \times 10^3$	$6.32(22) \times 10^4$	$4.29(19) \times 10^5$	$2.94(15) \times 10^6$
Proctor and Stwalley ^b	[517]	6.019	215.9				

^a For $S_2(-2)$ see Eq. (161) and Table 17, and for $S_2(0)$ see Eq. (159) and Table 19.

^b These authors use a valence electron model. They also report the octupole oscillator sums $S_3(-1)$ and $S_3(1)$.

Table 21
Log-weighted dipole oscillator strength sums for the ground state of the lithium atom

Author(s)	Ref.	$L(k)$ (u)									
		$L(-6)$	$L(-5)$	$L(-4)$	$L(-3)$	$L(-2)$	$L(-1)$	$L(0)$	$L(1)$	$L(2)$	
Stacy and Dalgarno	[454]							2.68			
Dalgarno	[521]							3.14			
Garcia	[512]							2.66(30)			
Dehmer et al.	[516]							2.749	56.10		
McGuire	[520]							2.765			
Zeiss et al.	[477]							0.6107	20.04		814.5
Experimental estimate											
Turner et al.	[522]							3.03			

16.2. Log-weighted oscillator strength sums

By analogy with the definition of $S(k)$ given above, a log-weighted dipole oscillator sum can be defined as

$$L(k) = \sum_n f_{n0} E_{n0}^k \ell n(E_{n0}/u) \quad (163)$$

If $S(k)$ is considered to be a function of a continuous variable k , then $L(k)$ is the derivative $dS(k)/dk$. $L(k)$ is useful for the evaluation of several qualities. The stopping power for fast charged particles depends on $L(0)$, and is discussed in terms of the mean excitation energy I_0 , defined by

$$I_0 = e^{L(0)/S(0)} \quad (164)$$

Calculated values of I_0 for Li [454,477,512, 516,520,521] range from 33 eV [454] to 38.8 eV [522], with the experimental value being 37.4 eV [522]. Some values of $L(k)$ are presented in Table 21.

The mean excitation energy which is required in the theory of the Lamb shift is connected with $L(2)$ as follows:

$$\frac{d\ell n S(k)}{dk} \Big|_{k=2} = \frac{L(2)}{S(2)} = \frac{\sum_n f_{n0} E_{n0}^2 \ell n(E_{n0}/Ry)}{\sum_n f_{n0} E_{n0}^2} \quad (165)$$

Relatively little work has been carried out on the evaluation of estimates of $L(2)$ for the Li atom [477]. None of the values of $L(k)$ reported in Table 21 are of high precision, but they might serve as approximate reference results for future high precision calculations.

17. Electronic density and spin density

Although the electronic density is a key variable in modern quantum theory, relatively little attention has been directed towards finding compact expressions for this quantity. For highly correlated densities, there is only a modest amount of published work, and this is also the situation that prevails for the lithium atom. For the ground state of Li, the following result has been obtained [35]:

$$D_0(r) = \sum_{l=1}^7 \sum_{K=0}^{gl} \mathcal{A}_{lK} r^K e^{-\alpha_l r} \quad (166)$$

where $D_0(r)$ is the radial electronic density function

$$D_0(r) = \int_0^\pi \int_0^{2\pi} r^2 \rho(\mathbf{r}) d\Omega \quad (167)$$

and

$$\rho(\mathbf{r}) = N \int \psi^*(x_1, x_2, x_3, \dots, x_n) \psi(x_1, x_2, x_3, \dots, x_n) \times ds_1 dx_2 dx_3 \dots dx_n \quad (168)$$

In Eq. (167) the standard notation $d\Omega = \sin \theta d\theta d\varphi$ is employed, and in Eq. (168) x_i denotes a combined spatial and spin coordinate. The form given in Eq. (166) is based on analysis of Hylleraas-type wave functions of the form given in Eqs. (14), (16) and (20). The parameters α_l , g_l and \mathcal{A}_{lK} have been tabulated for the ground state of Li and other three-electron systems [35]. Because the Hylleraas wave functions employed to determine the parameters in Eq. (166) included relatively few basis functions describing the large r -region of configuration space, the resulting accuracy of $\rho(\mathbf{r})$ at large r is expected to be poor. This can be confirmed by comparing the moments $\langle r_i^n \rangle$ for large n computed from Eq. (166) and those available from more accurate calculations [36]. Comparison of moments $\langle r_i^n \rangle$ (and other expectation values) is an imperfect test, because of the possibilities of cancellation of errors from different regions of configurational space when the integral involving $\rho(\mathbf{r})$ is evaluated. The work leading to Eq. (166) was motivated by earlier efforts on two-electron systems [523], which was subsequently extended to higher precision in several investigations [524–526].

Assessing the quality of $D_0(r)$ is difficult. The cusp condition [527]

$$\frac{\partial \rho(r)}{\partial r} \Big|_{r=0} = -2Z\rho(0) \quad (169)$$

provides a stringent test. Other than the expected asymptotic behavior [528–530] and the subharmonic character of $\rho(\mathbf{r})$ beyond a certain radial distance [531], there are unfortunately few rigorous checks to test the local accuracy of $\rho(\mathbf{r})$. Although there are many bounds known for $\rho(\mathbf{r})$ [532–546], none are sufficiently sharp to serve as a stringent quality control test for electronic densities determined from highly correlated wave functions. Whether such bounds can be found is still an open question.

The pseudoconvexity behavior of the lithium electronic density has been studied with both HF and highly correlated wave functions [547]. These authors have also investigated the separate spin- α , spin- β contributions, ρ_α and ρ_β , to the curvature of the Li electronic density.

A large scale CI study of $\rho(\mathbf{r})$ has been undertaken [34]. The moments $\langle r_i^n \rangle$ obtained from this study are in generally good agreement with high precision estimates [36]. These authors have also evaluated the spin density for the ground state of Li and this work is the best currently available for the spin density as a function of the radial coordinate.

17.1. The Hiller–Sucher–Feinberg approach

The electronic density can be computed from the relationship

$$\rho(\mathbf{r}) = \langle \psi | \delta(\mathbf{r}_i - \mathbf{r}) | \psi \rangle \quad (170)$$

which can be expressed in the form

$$\rho(\mathbf{r}) = \langle \psi | D_i(\mathbf{r}) | \psi \rangle \quad (171)$$

Eq. (171) is analogous to the result given earlier in Eq. (121). For the case $\mathbf{r} = 0$ (see Eq. (122))

$$\rho(0) = \left\langle \psi \left| \frac{1}{2\pi} \frac{\partial V}{\partial r_i} - \frac{\ell_i^2}{2\pi r_i^3} \right| \psi \right\rangle \quad (172)$$

The result in Eq. (172) was independently derived at almost the same time [533], and had been found earlier for restricted cases [548,549]. For the lithium atom, SCF calculations of $\rho(\mathbf{r})$ converge more quickly using the HSF identity compared to the Dirac δ function approach. A similar situation prevails for CI calculations of $\rho(0)$ [381].

18. Intracule functions

The radial electron–electron distribution function is given by [550]

$$P(r_{ij}) = \int \Gamma^{(2)}(\mathbf{r}_i, \mathbf{r}_j | \mathbf{r}_i, \mathbf{r}_j) \frac{d\mathbf{r}_i d\mathbf{r}_j}{dr_{ij}} \quad (173)$$

where $\Gamma^{(2)}$ is the spin-free 2-matrix defined by

$$\Gamma^{(2)}(\mathbf{r}_i, \mathbf{r}_j | \mathbf{r}_i, \mathbf{r}_j) = \binom{N}{2} \int \Psi(x_1, x_2, \dots, x_i, \dots, x_j, \dots, x_N) \times \Psi(x_1, x_2, \dots, x_i, \dots, x_j, \dots, x_N) ds_i ds_j dx_k \quad (174)$$

where dx_k denotes combined integration over all

coordinates except those with $k = i$ and j , and $\binom{N}{2}$ is

a binomial coefficient. The normalization for $P(r_{ij})$ employed is

$$\int_0^\infty P(r_{ij}) dr_{ij} = \frac{1}{2} N(N-1) \quad (175)$$

The spherical average of the intracule function is given by [551,552]

$$h(r_{ij}) = \frac{1}{4\pi r_{ij}^2} P(r_{ij}) \quad (176)$$

A cusp condition for h can be written as [551,552]

$$\left. \frac{\partial h(r_{ij})}{\partial r_{ij}} \right|_{r_{ij}=0} = h(0) \quad (177)$$

Starting from a restricted Hylleraas-type expansion, the following result has been obtained for the ground state of three-electron systems [553]:

$$P(r_{ij}) = \sum_{l=1}^3 \sum_{K=1}^{g_l} \mathcal{A}_{lK} r_{ij}^K e^{-\alpha_l r_{ij}} \quad (178)$$

Numerical values for the parameters α_l , g_l and \mathcal{A}_{lK} (which are not related to those reported in Eq. (166)) have been tabulated. This work was developed in the same spirit as earlier work on two-electron systems [523].

An important difficulty arises when the jump from two- to three-electron systems is made. Severe restrictions on the choice of basis functions must be made if a simple compact analytical form for $P(r_{ij})$ such as Eq. (178) is to be obtained. The problem arises with basis functions involving odd powers of the interelectronic coordinate. Unfortunately, these are important terms if high precision estimates of all properties are required. The accuracy of moments $\langle r_{ij}^n \rangle$ computed from Eq. (178) is typically around 0.1–0.2%, except for $\langle r_{ij}^{-2} \rangle$, and the expectation value $\langle \delta(r_{ij}) \rangle$. Both of the latter two expectation values are more difficult to evaluate. The cusp condition (Eq. (177)) was not

satisfied for the Hylleraas wave functions employed, and since

$$h(0) = \left[\frac{P(r_{ij})}{4\pi r_{ij}^2} \right]_{r_{ij} \rightarrow 0} = \langle \delta(r_{ij}) \rangle \quad (179)$$

it is probably not too surprising that the expectation value of $\langle \delta(r_{ij}) \rangle$ is obtained with less precision than the other expectation values.

A recent investigation [554] has discussed the evaluation of the intracule density, $I(\mathbf{R})$, using

$$I(\mathbf{R}) = \binom{N}{2} \langle \psi | \delta(\mathbf{r}_{ij} - \mathbf{R}) | \psi \rangle \quad (180)$$

If the δ function operator in Eq. (180) is replaced by an operator less sensitive to a specific region of configuration space, i.e. if the appropriate HSF identity is employed, then the hope is that better precision will result for the intracule density. For $I(0)$, this situation was realized for calculations on the ground state of Li and for several other systems [554].

19. Moments $\langle r_i^n \rangle$

The moments $\langle r_i^n \rangle$ can be calculated from

$$\langle r_i^n \rangle = \int r^n \rho(r) dr \quad (181)$$

The case $n = -1$ leads to the electron–nuclear potential energy and the nuclear magnetic shielding

constant; $n = 2$ is required to evaluate the diamagnetic susceptibility, and some of the moments can be related to various oscillator strength sums. A summary of some of the more precisely known values is presented in Table 22, which are all nonrelativistic values based on the infinite nuclear mass approximation. These results, particularly those for the smaller n values, could serve as benchmark expectation values for other calculations.

20. Moments $\langle r_{ij}^n \rangle$

The moments of the interelectronic separation can be determined from the formula

$$\langle r_{ij}^n \rangle = \int_0^\infty P(r_{ij}) r_{ij}^n dr_{ij} \quad (182)$$

Unfortunately, $P(r_{ij})$ is not currently available with sufficient precision, so the moments $\langle r_{ij}^n \rangle$ are determined directly from the wave function. A small selection of results for $n = -2, -1, 1$ and 2 are given in Table 23. These are all nonrelativistic values computed in the infinite nuclear mass approximation. The most difficult moment to determine is $\langle r_{ij}^{-2} \rangle$. If the wave function is of Hylleraas type, as was employed to determine this entry in Table 23, then difficult cases of the three-electron integrals discussed in Section 4 must be evaluated.

21. Electron correlation studies

The lithium atom is the simplest system which affords the opportunity to study both intra- and inter-shell correlation effects; not surprisingly, this system has proved to be a popular test case for studying such effects [555–577].

Table 22

Moment $\langle r_i^n \rangle$ for the ground state of Li

Moment $\langle r_i^n \rangle$	Result (u)	Reference
$\langle r_i^{-2} \rangle$	30.240965 15(25)	[37]
$\langle r_i^{-1} \rangle$	5.718 110 883 61(13)	[37]
$\langle r_i \rangle$	4.989 523 148 59(75)	[37]
$\langle r_i^2 \rangle$	18.354 614 517(72)	[37]
$\langle r_i^3 \rangle$	92.603 6	[117]
$\langle r_i^4 \rangle$	550.04	[34]
	550.07	[36]
$\langle r_i^5 \rangle$	3 695.8	[34]
$\langle r_i^6 \rangle$	27 649	[34]
	27 729	[36]
$\langle r_i^7 \rangle$	2.2784×10^5	[34]
$\langle r_i^8 \rangle$	2.050×10^6	[34]
	2.073×10^6	[36]
$\langle r_i^9 \rangle$	2.001×10^7	[34]
$\langle r_i^{10} \rangle$	2.103×10^8	[34]
	2.16×10^8	[36]

Table 23

Moments $\langle r_{ij}^n \rangle$ for the ground state of the lithium atom

Moment $\langle r_{ij}^n \rangle^a$	Result (u)	Reference
$\langle r_{ij}^{-2} \rangle$	4.381 2	[36]
$\langle r_{ij}^{-1} \rangle$	2.198 212 002 47(71)	[37]
$\langle r_{ij} \rangle$	8.668 396 813 4(36)	[37]
$\langle r_{ij}^2 \rangle$	36.848 033 170(39)	[37]

^a Lower precision values for $\langle r_{ij}^3 \rangle$ and $\langle r_{ij}^4 \rangle$ can be found in Ref. [553].

Table 24

Impact of electron correlation on the calculation of various one- and two-electron properties for the ground state of the lithium atom

Expectation value	HF result	Correlated result	Δ (%) ^a	Reference ^b
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.432 726 876	7.478 060 325 26	0.60	[129,37]
$\langle r_i^{-2} \rangle$	30.217	30.240 965 15	0.79	[573,37]
$\langle r_i^{-1} \rangle$	5.715 48	5.718 110 883 61	0.04	[578,37]
$\langle r_i \rangle$	5.019 75	4.989 523 148 59	-0.61	[574,37]
$\langle r_i^2 \rangle$	18.622	18.354 614 517	-1.52	[563,37]
$\langle r_i^3 \rangle$	94.583	92.603 6	-2.14	[563,36]
$\langle r_i^4 \rangle$	564.32	550.07	-2.59	[563,36]
$\rho(0)$	13.835	13.842 543	0.05	[573,37]
$\langle 4\pi\delta(r_i)\sigma_z \rangle$	2.094	2.90592	27.9	[331,384](b)
$\langle r_{ij}^{-1} \rangle$	2.281 2	2.198 212 002 47	-3.78	[565,37]
$\langle r_{ij} \rangle$	8.687 7	8.668 396 813 4	-0.22	[565,37]
$\langle r_{ij}^2 \rangle$	37.235 7	36.848 033 170	-1.05	[565,37]
$\langle \nabla_i \cdot \nabla_j \rangle$	0	-0.301 842 809	100	[37]
$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle$	0	-0.069 402 068	100	[37]
$\langle 1/r_i r_j \rangle$	8.988 6	8.789 478	-2.265	[565,36]

^a See Eq. (183).^b The first reference is the HF result and the second is the correlated result.

Activity in this area of research can be broken down into seven broad areas. These are: (1) studies of atomic correlation energy contributions [555–560], (2) studies of electron correlation effects for the electronic density [318,561], (3) work on the coulomb and Fermi hole structure, and local structure of various correlated wave functions [562–568], (4) studies on statistical correlation effects via correlation coefficients [568,569], (5) the impact of electron correlation on the calculation of various expectation values [570–573], (6) natural orbital analysis of correlated wave functions [563,574], and (7) Z-dependent perturbation treatments [555,575–577].

For the ground state of Li the correlation energy is now known with high precision (see Section 5.3). This should serve as a benchmark value for more approximate computational schemes. In Table 24 some representative expectation values are reported based on Hartree–Fock calculations [129,331,563, 565,573,578] and from highly correlated wave functions [36,37,117]. From a comparison of the two sets of data, an approximate idea of the importance of electron correlation on the calculation of the various one- and two-electron expectation values can be determined. The comparison is not a perfect illustration of the significance of electron correlation effects,

because some of the HF wave functions employed to evaluate several of the expectation values were tailored to produce precise HF energies, and are less well suited to the calculation of several properties that depend on regions of configuration space not emphasized in the standard variational approach. All the values listed are in u and are based on the infinite nuclear mass approximation. Table 24 also reports the percentage deviation, Δ , defined by

$$\Delta = \frac{100(\langle \hat{O} \rangle_{\text{correlated}} - \langle \hat{O} \rangle_{\text{HF}})}{\langle \hat{O} \rangle_{\text{correlated}}} \quad (183)$$

For the one-electron expectation values reported in Table 24, the deviation (as measured by Δ) between the HF and correlated results is small (though of important significance when spectroscopic accuracy is considered) for those expectation values emphasizing the energy important region of configuration space. For the higher moments $\langle r_i^3 \rangle$ and $\langle r_i^4 \rangle$, the deviations increase, but this may be tied to HF calculations that are not well converged, rather than a true reflection of correlation effects. A key one-electron property not well described with the HF formalism is the Fermi contact entry in Table 24. Electron correlation effects play an important role for this property, which has been discussed in numerous accounts in the

literature. For two-electron expectation values, the biggest differences arise for $\langle \nabla i \cdot \nabla j \rangle$ and $\langle r_i \cdot r_j \rangle$, both of which are zero in the HF formalism. These two expectation values are sensitive measures of the inadequate description of electron correlation. This has been discussed extensively in the literature, particularly for $\langle \nabla i \cdot \nabla j \rangle$, an important quantity which enters into the determination of both the specific mass shift correction to the total ground state energy, and to the transition isotope shift (see Section 6).

22. Momentum space properties

High precision calculations of momentum space properties for the Li atom have received relatively little attention in comparison to work carried out in position space. The highest precision results currently available are based on large scale CI calculations [242]. The same authors have also considered spin-dependent momentum-space properties.

The moments of the electron momentum density are given by

$$\langle p^n \rangle = 4\pi \int_0^\infty p^{n+2} \bar{\pi}(p) dp \quad (184)$$

where $\bar{\pi}$ is the spherically averaged momentum density defined by

$$\bar{\pi}(p) = \int \gamma(\mathbf{p}, \mathbf{p}')_{p=p'} d\Omega \quad (185)$$

and $\gamma(\mathbf{p}, \mathbf{p}')$ is the spin-traced one-particle density matrix. In Table 25 a summary of the moments $\langle p^n \rangle$ for $n = -2$ to 4 is shown based on CI calculations, and the values can be compared with the results from UHF calculations. The accuracy of some of the CI results

Table 25

Some expectation values based on the momentum density for the ground state of Li (in u)

Expectation value	CI result ^a	UHF result ^a
$\langle p^{-2} \rangle$	26.134	26.539
$\langle p^{-1} \rangle$	5.1519	5.18496
$\langle p \rangle$	4.9196	4.90563
$\langle p^2 \rangle$	14.955	14.8655
$\langle p^3 \rangle$	71.643	70.9811
$\langle p^4 \rangle$	629.120	622.626

^a From Esquivel et al. [242].

can be ascertained by comparison with results presented in Table 8 for $\langle p^4 \rangle$ using Eq. (73), and Table 24 for $\langle p^2 \rangle$. Two forms of the relativistic kinetic energy have also been discussed by the same authors [242]; they are (in the notation used by these authors)

$$E_4 = \frac{\langle p^2 \rangle}{2m_e} - \frac{\langle p^4 \rangle}{8m_e c^2} \quad (186)$$

and

$$\langle H_0 \rangle = \left\langle m_e c^2 \left[\left(1 + \frac{p^2}{m_e^2 c^2} \right)^{1/2} - 1 \right] \right\rangle \quad (187)$$

The interested reader can consult this work for further discussion. Information on the isotropic Compton profile is also given by these authors.

The influence of correlation effects in momentum space for the ground state of Li has been studied [566]. This work leads to an understanding of the effects of intra-shell and inter-shell correlation effects on the interparticle momentum distribution. Additional values of several momentum related expectation values for the Li ground state can be found in this work.

23. Form factors

The atomic scattering (form) factor $F(\mathbf{k})$ is determined from the result [579,580]

$$F(\mathbf{k}) = \left\langle \psi \left| \sum_{j=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_j) \right| \psi \right\rangle \quad (188)$$

which can also be expressed as

$$F(\mathbf{k}) = \int \rho(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \quad (189)$$

Integration over the angles in Eq. (189) gives

$$F(k) = \int_0^\infty D(r) \frac{\sin kr}{kr} dr \quad (190)$$

where $D(r)$ is the radial electronic distribution, $4\pi r^2 \rho(r)$, and $k = |\mathbf{k}|$ is the magnitude of the momentum transfer vector. Several tabulations of $F(k)$ are available [431,581–588], including results calculated from a large scale CI wave function [581] and from a highly correlated Hylleraas-type wave function [431].

Table 26
Form factors for the ground state of the lithium atom

$k(a_0^{-1})$	$F(k)$			$k (\text{\AA}^{-1})$	$S(k)^b$
	RHF ^a	UHF ^a	CI ^a		
0	3.00000	3.00000	3.00000	0.20	0.066
0.10	2.96941	2.96943	2.96985	0.40	0.240
0.20	2.88300	2.88304	2.88460	0.60	0.467
0.30	2.75498	2.75505	2.75807	0.80	0.688
0.40	2.60402	2.60412	2.60849	1.00	0.869
1.00	1.90192	1.90202	1.90509	2.00	1.276
2.00	1.51081	1.51076	1.50934	3.00	1.562
3.00	1.14612	1.14609	1.14495	4.00	1.863
4.00	0.82027	0.82024	0.81962	5.00	2.136
5.00	0.57456	0.57453	0.57439	6.00	2.362
6.00	0.40196	0.40193	0.40212	8.00	2.668
8.00	0.20309	0.20312	0.20348	10.00	2.831
10.00	0.10908	0.10913	0.10941	40.00	3.000

^a Results from Schmider et al. [581].

^b Results from Meyer et al. [589].

A concise tabulation of a few representative results is given in Table 26. The HF results are observed to be in rather close agreement with the CI results for a range of k values.

The integral of $F(k)$ over all k provides a route to σ_d (see Eq. (136)). Also, knowledge of $F(k)$ provides a pathway to the radial density $D(r)$ [579], and to the intensity of elastically scattered radiation [579]. For the latter quantity, the tabulated form factor [431,581] allows this quality to be readily calculated.

Working in the first Born approximation the inelastic scattering factor $S(\mathbf{k})$ for an N -electron atom is determined by

$$S(\mathbf{k}) = \sum_{\epsilon} |F_{\epsilon}(\mathbf{k})|^2 \quad (191)$$

where $F_{\epsilon}(\mathbf{k})$ is a generalized form factor given by

$$F_{\epsilon}(\mathbf{k}) = \left\langle \psi_{\epsilon} \left| \sum_{j=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_j) \right| \psi \right\rangle \quad (192)$$

and ψ_{ϵ} designates an excited state. Using the closure property in Eqs. (191) and (192), $S(\mathbf{k})$ can be expressed as [580]

$$S(\mathbf{k}) = \left\langle \psi \left| \sum_{m=1}^N \sum_{n=1}^N \exp[i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_n)] \right| \psi \right\rangle - |F(\mathbf{k})|^2 \quad (193)$$

The spherically averaged inelastic scattering factor is

given by

$$S(k) = \frac{1}{4\pi} \int S(\mathbf{k}) d\Omega \quad (194)$$

For the ground state of Li values of $S(k)$ have recently been determined from CI calculations [589]. A few representative values are tabulated in Table 26.

From the available published data for $F(k)$ and $S(k)$, values of the elastic, inelastic and total X-ray scattering cross sections (within the first Born approximation) can be determined. The interested reader can pursue the cited references for further details.

23.1. Magnetic form factors

The spherically averaged magnetic form factor $M(k)$ is given by [581]

$$M(k) = 4\pi \int \rho_s(r) j_0(kr) r^2 dr \quad (195)$$

where $j_0(x)$ is the spherical Bessel function of the first kind ($j_0(x) = x^{-1} \sin x$) and $\rho_s(r)$ is the spin density. This definition has an obvious analogy with Eq. (190). For the ground state of the lithium atom, $M(k)$ has been evaluated from large scale CI calculations [581]. This work represents the best results available, and no other high precision calculations

appear to be available for this quantity. The same authors have also examined the momentum space analogs of $F(k)$ and $M(k)$. The interested reader is directed to the original work for further details.

24. Some miscellaneous results

Table 27 contains a number of miscellaneous expectation values, most of which have been evaluated from highly correlated wave functions. All values are based on the nonrelativistic Hamiltonian discussed in Eq. (11). The following notation has been employed: V_{ee} denotes the electron–electron potential operator, V_{en} represents the electron–nuclear potential operator, V is the total potential operator and T is the kinetic energy operator. All other high precision expectation values not included in Table 27 (that

could be found) are presented in the preceding tables of this work.

Several of the expectation values in Table 27 are rather sensitive to the near-nuclear region of configurational space. In particular, $\langle V_{ee}^2 \rangle$, $\langle T^2 \rangle$ and $\langle VT \rangle$, which are required to evaluate $\langle H^2 \rangle$, have a sensitive dependence on the quality of the wave function in the near-nuclear region. These values should serve as useful benchmarks for the construction of wave functions to describe Li. Unfortunately, the precision levels for several of these values is significantly below those of a number of other entries in Table 27.

The last pair of entries in Table 27 are available only at the HF level and so the level of precision for these expectation values is limited. The two expectation values of the form $\langle \mathbf{r}_i \cdot \mathbf{r}_j (r_i r_j)^n \rangle$ for $n = -1$ and $n = -2$ have been computed [565] using a fairly compact CI wave function, so the precision for these expectation values is also somewhat limited. A hint of the level of precision can be obtained by comparing the expectation value $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle$ computed in the same work [565] with the value reported in Table 27. This table entry was computed indirectly using the result

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \langle r_i^2 \rangle - \frac{1}{2} \langle r_{ij}^2 \rangle \quad (196)$$

and the high precision results for $\langle r_i^2 \rangle$ and $\langle r_{ij}^2 \rangle$ were taken from Ref. [37].

The photoelectron spectrum of atomic lithium has been measured, and this technique provides valuable information on a number of excitation processes from the ground state. This topic has recently been reviewed in detail [590].

25. Some future directions

It should be clear that the theoretical treatment of some properties of atomic lithium has advanced to the point that the results could serve as a calibration guide for experimental work. The list is subjective, but perhaps it might include the polarizability, the transition isotope shift, the nuclear magnetic shielding constant, and a few other properties. At the other extreme, for some properties the theoretically determined value is

Table 27
Some miscellaneous expectation values for the ground state of Li

Expectation value	Result (u)	Reference
$\langle -\frac{1}{2} \nabla_i^2 \rangle$	7.478 060 320 8	[29]
	7.478 060 325 26	[37]
$\langle V_{ee} \rangle$	2.198 212 002 47(71)	[37]
$\langle V_{en} \rangle$	-17.154 332 650 83(39)	[37]
$\langle V \rangle$	-14.956 120 642	[29]
	-14.956 120 648 36	[37]
$\langle 1/r_i r_j \rangle$	8.789 478	[36]
$\langle \delta(\mathbf{r}_i) \rangle \equiv \rho(0)$	13.842 7	[118]
	13.842 543(53)	[37]
$\langle \delta(\mathbf{r}_{ij}) \rangle \equiv h(0)$	0.544 329 0(37)	[37]
$\langle \nabla_i \cdot \nabla_j \rangle$	-0.301 842 799	[29]
	-0.301 842 809(15)	[37]
$\langle 1/r_{ij} r_{jk} \rangle$	1.101 687	[36]
$\langle V_{ee}^2 \rangle$	6.584 6	[36]
$\langle V_{ee} V_{en} \rangle$	-43.097 23	[36]
$\langle V_{en}^2 \rangle$	430.379 2	[36]
$\langle V^2 \rangle$	350.769 3(4)	[36]
$\langle V_{en} T \rangle$	-259.000 6(8)	[36]
$\langle V_{ee} T \rangle$	20.076(2)	[36]
$\langle VT \rangle$	-238.925	[36]
$\langle \nabla_i^2 \nabla_j^2 \rangle$	628.441(3)	[36]
$\langle \nabla_i^2 \nabla_j^2 \rangle$	51.787 9(2)	[36]
$\langle T^2 \rangle$	183.001(2)	[36]
$\langle \mathbf{r}_i \cdot \mathbf{r}_j (r_i r_j)^{-2} \rangle$	-0.239 5	[565]
$\langle \mathbf{r}_i \cdot \mathbf{r}_j (r_i r_j)^{-1} \rangle$	-0.064 11	[565]
$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle^a$	-0.069 402 068	[37]
$\langle r_i r_j \rangle$	4.752	[565]
$\langle r_i^2 r_j^2 \rangle$	15.949	[565]

^a See Eq. (196).

in only modest agreement with the current experimental result. A classic example of a property in this group is the hyperfine coupling constant, where the experimental result is known with about five additional digits of precision. This situation becomes worse for the next member of the isoelectronic series (Be^+) where the gap between theory and experiment is larger [591,592], in part due to the very high accuracy ion-trap measurements that have been made on this system [592]. For the hyperfine coupling constant, a theoretical match with experiment is only likely when a diverse group of topics including nuclear structure, QED, relativistic effects and of course electronic effects are adequately understood. There are a host of properties for which no experimental results are available, which is more problematic when there is a spread of theoretical values for a particular property.

Future theoretical progress on the lithium atom will probably (according to my crystal ball!) take place on three major fronts. Methods will be developed which allow for the more efficient evaluation of three-electron correlated integrals (including some of the more difficult cases discussed in Section 4). These will take advantage of the very low cost associated with large storage available on desk top work stations. This will be an essential ingredient in improving the performance of codes that do any significant exponent optimization. The next major effort will focus on the excited states of Li. These states are of intrinsic interest, as attested by the considerable attention they have already received in the literature, e.g. [37,99,125, 593–609]; these will provide a pathway to a large number of additional references, which is a subject for a future review. Accurate determination of excited state wave functions is essential if high precision calculations of various ground state polarizabilities and nonlinear susceptibilities are to be undertaken. A third likely avenue for future exploration concerns the possibility of working with improved correlated basis functions that handle the electron–electron and electron–nuclear cusp conditions, as well as incorporating the correct asymptotic behavior at large r . The integration problems associated with this will be severe, but the expected accelerated convergence will be a significant pay off. Hand in hand with this third avenue of research will be the need for mathematical investigations of the appropriate structure of the required basis functions for three-electron systems.

This area of investigation has been dormant far too long [557].

On the experimental front, there is a considerable list of desirable properties to be determined, as well as properties for which a higher precision determination would be of considerable interest. If some recent signs of experimental progress are noted [219,220], one can be optimistic that experimentalists will take up the challenge of working with this rather reactive element. A measurement of the gas phase molar Kerr constant would be welcome, as this would allow an assessment of recent attempts to calculate the atomic hyperpolarizability. Refined measurements of the dipole polarizability with higher precision would provide the next level of challenge for this property, where relativistic and perhaps small quantum electrodynamics corrections must be accounted for. Measurements of the gas phase refractive index as a function of frequency would be welcome. A refined determination of the ionization potential would provide additional theoretical challenges, but this would largely be a task for the relativistic computationalists and QED theorists. An improved measurement of the electron affinity for Li would provide additional impetus to achieve high precision calculations for four-electron atomic systems. Advances in laser cooling and trapping of neutral atoms [610] will open up significant possibilities for high precision work on various atoms, of which lithium would be a most interesting target.

The lithium atom has served quantum theoreticians well for over 60 years as a benchmark system. I expect this situation to be maintained for some years to come.

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