HIGH-PRECISION CALCULATIONS FOR THE GROUND AND EXCITED STATES OF THE LITHIUM ATOM

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I. Introduction

Over the past decade there has been considerable progress on high-precision cal-culations for the lithium atom. In this chapter, a summary is presented of some of the progress, for selected properties of the ground and excited states of *Li*. The

lithium atom has long served as a test case for newly developed computational methods. This system has also been intensively investigated for its own intrinsic interest. It is a few-body system, so we might expect that calculations of very high precision are possible for the lithium atom. The helium atom and members of its isoelectronic series have been extremely popular targets for computationalists. Very high levels of precision are available for a number of calculated properties of two-electron systems. For example, the nonrelativistic ground state energy of the helium atom is known to around eighteen digits of precision (Goldman, 1998). The lithium atom, with one additional electron, turns out to be a much more complicated system to study. A number of new mathematical difficulties arise, and some of these have hampered progress on the calculation of several properties.

The lithium atom in its ground state represents the simplest atomic system for which it is possible to study valence, core, and valence-core electronic effects. It is an ideal target system for investigating the nature of the Coulomb and Fermi hole structure of highly correlated wave functions.

There has been recent renewed interest in the experimental determination of high-precision values of a number of properties of atomic lithium. These advances have provided additional stimulus for theoretical progress.

Two conventions will be employed in this chapter. Error estimates will be shown in parentheses, so that 23.4 ± 3.2 will be written as $23.4(32)$. Expectation values will employ an implied summation convention, so that $< r_{ij} >$ is equivalent to $\langle \sum_{i=1}^{3} \sum_{j>i}^{3} r_{ij} \rangle$. Absolute atomic units will be used for energies, with the conversion to cm^{-1} being 1 a.u. (absolute) = $219474.6313688(62)$ cm^{-1}.

II. Computational Approaches

A variety of computational techniques have been applied to calculate various properties of the lithium atom. These include the Hylleraas approach (HY), the configuration interaction method (CI), the hybrid CI-Hylleraas technique (CI-HY), many-body perturbation theory (MBPT), multiconfiguration Hartree-Fock methods (MCHF), and others. The CI, MBPT, and MCHF approaches have the advantage that they can be applied to systems beyond the few-electron level. The HY and CI-HY techniques are presently constrained to few-electron systems, but these techniques lead to the highest levels of precision when applied to the lithium atom. The CI-HY method has shown considerable recent promise in yielding results of very high precision. It may be feasible to extend this approach (with some restrictions on the basis functions) to atomic systems with more than four electrons.

The highest precision results for several properties have been obtained using the Hylleraas technique, and a large part of the focus of this chapter will be on this technique. The Hylleraas expansion for the $^2S_{1/2}$ ground state of *Li* takes the form

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

where $\mathscr{A}$ is the three-electron antisymmetrizer, C_{μ} are the variationally determined expansion coefficients, and N designates the number of basis functions employed. The basis functions ϕ_{μ} are expanded in terms of the electron-nuclear (r_i) and electron-electron (r_{ij}) coordinates, and are defined in the following way:

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

The indices $\{i_{\mu}, j_{\mu}, k_{\mu}, l_{\mu}, m_{\mu}, n_{\mu}\}$ take integer values and are ≥ 0, and the orbital exponents α_{μ}, β_{μ} and γ_{μ} are > 0. In Eq. (1), χ_{μ} represents the possible spin eigenfunctions, which take one of the following two forms for the doublet states:

$$\chi = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \tag{3}$$

or

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

The wave function in Eq. (1) is an eigenfunction of the spin operators S^2 and S_Z.

The importance of including both spin eigenfunctions in the wave function has been discussed in a number of papers, particularly in regard to determining precise values of properties such as the energy, and especially, precise hyperfine coupling constants (Larsson, 1968; King and Shoup, 1986; King, 1988, 1989). The majority of Hylleraas calculations on three-electron systems are carried out using just the spin eigenfunction given in Eq. (3). Omission of the second spin eigenfunction (Eq. (4)) can be compensated for by using larger basis sets with only the first spin function (Eq. (3)) included. Spin-dependent expectation values (for example, the Fermi contact term) appear to be more sensitive to the omission of the second spin eigenfunction.

The general topic of the spatial-spin form of the ground state wave function for the Li atom has been discussed by a number of authors. The interested reader might start with the articles by Slater (1970), White and Stillinger (1970) and Smolenskii and Zefirov (1993). Studies on this topic have been fruitful. The well-known determinantal wave function structure so widely employed in atomic and molecular calculations emerged from a consideration of the form of the wave function for the lithium atom (Slater, 1970).

For excited bound states, Eq. (2) is supplemented by the inclusion of appropriate spherical harmonics to account for any angular dependence of the basis terms. If excited quartet states are of interest, the spin function is taken to be

$$\chi = \alpha(1)\alpha(2)\alpha(3) \tag{5}$$

There are several strategies that can be followed for the selection of the indices $\{i_{\mu}, j_{\mu}, k_{\mu}, l_{\mu}, m_{\mu}, n_{\mu}\}$. The earliest approach employed a selection of terms that

in effect minimized the mathematical problems (James and Coolidge, 1936). Given the computer technology available at the time, this was undoubtedly the method of choice. A second procedure was to pick indices based on the expected impact in producing a good energy (Larsson 1968; King and Shoup, 1986). This procedure has been particularly successful at producing some rather precise results for the ground state energy of *Li*. There are two drawbacks to this approach. The first is that it depends on the experience of the theorist in choosing important terms. It is possible, because of a predisposed bias, to omit basis functions that might singly, or collectively with other terms, lead to important contributions to the energy. A second issue is that the convergence behavior of the calculation can be very difficult (if not impossible) to determine. This eliminates the possibility of trying to determine an extrapolated estimate for the energy (or other expectation values) for a basis set of infinite size. A third approach is to define an index, ω:

$$\omega = i_\mu + j_\mu + k_\mu + l_\mu + m_\mu + n_\mu \tag{6}$$

and then add basis functions in order of increasing values of ω; $\omega = 0, 1, 2, \ldots$ (King and Shoup, 1986; McKenzie and Drake, 1991; Lüchow and Kleindienst, 1993; Yan and Drake, 1995a; Barrois *et al.*, 1997a, 1997b, 1997c; King, 1998b). This approach avoids any bias in the selection of the basis terms. It does not provide the fastest possible convergence for the energy, but does in general lead to a reasonable monotonic convergence pattern for the energy. This has the advantage that attempts at determining extrapolated estimates of the energy are more likely to be reliable. The total number of basis functions grows significantly as ω increases. A table of the maximum number of basis functions for values of ω up to 11 is given by King and Shoup (1986).

All the Hylleraas-type calculations on three-electron systems that have been published have restricted the basis functions to integer values for the indices $\{i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu\}$. There are reasons to expect that improved wave functions can be constructed using noninteger values for the set $\{i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu\}$. These indices can be selected as arbitrary floating point values to optimize the energy. This idea has been tried by the author and Feldmann for some preliminary calculations on two-electron systems, with fairly encouraging results. For two-electron systems, there is essentially no increase in the level of difficulty for the integrals required to evaluate the energy and a variety of expectation values. The main change that occurs is that gamma functions of noninteger argument arise, but these can be readily evaluated. For three-electron systems, the switch from integer to noninteger exponent indices leads to a significantly more involved integration problem, when the required matrix elements are evaluated.

The orbital exponent parameters α_μ, β_μ and γ_μ are usually selected in one of the following ways. The simplest choice has been to use fixed values of the orbital exponents, that is,

$$\left.\begin{array}{l} \alpha_\mu = \alpha \\ \beta_\mu = \alpha \\ \gamma_\mu = \gamma \end{array}\right\} \text{ all } \mu \tag{7}$$

The values of α and γ can be determined in one of several ways, such as using the appropriate screened nuclear charge to fix these values, or by optimizing these values by using small to modest size wave functions, and then employing the optimized exponents for larger basis sets. A significant advantage of using Eq. (7) is that it is feasible to store all the calculated integrals. Using modern desktop workstations, with relatively inexpensive memory, it is possible to store almost all the required integrals (about one to two hundred megabytes) needed for the construction of a wave function of considerable size (one to two thousand terms). The same integral file can be employed in the evaluation of a large range of expectation values.

An alternative approach is to optimize the orbital exponents to obtain the minimum energy. This can be done either on a term-by-term basis or by optimizing blocks of terms. The lowest energies have been obtained using approaches involving orbital exponent optimization. In the term-by-term optimization approach, the fraction of matrix elements being reevaluated at each step scales as $2(N + 1)^{-1}$ of the total number of matrix elements. With present computer technology, it is not feasible to optimize simultaneously all the nonlinear parameters of a large number of basis functions.

There are two drawbacks to schemes involving optimization procedures. There is effectively very little gained by attempting to carry out any type of integral store and retrieve strategy. The cpu requirements also increase very significantly in this approach. An additional factor that the reader needs to be aware of is that the energy surface in the multidimensional parameter space $\{\alpha_\mu, \beta_\mu, \gamma_\mu\}$ typically has a number of local minima at any stage of the construction of the wave function. Getting the best energy can then be dependent on making skillful choices for the starting values for $\{\alpha_\mu, \beta_\mu, \gamma_\mu\}$, with the hope that these lead to an energy close to the global minimum. An alternative approach that the author has employed is to use a stochastic global optimization algorithm. The advantage of this approach is that there is minimal bias in locating the best starting set of exponents to determine the energy minimum. The drawback is the significant cpu resources required by this method.

It is possible to supplement the basis functions shown in Eq. (2) with a factor of the form $\exp(-\alpha_{12} r_{12} - \alpha_{23} r_{23} - \alpha_{13} r_{13})$, where α_{12}, α_{23}, and α_{13} are constants that may be separately optimized for each term. This leads to extra flexibility in the basis functions, but at the cost of introducing additional complexity into the integrals that must be evaluated. Methods have been developed to evaluate the integrals that emerge (Fromm and Hill, 1987), but no results appear to have been published for any three-electron species based on these more elaborate basis

functions. For two-electron atomic systems, incorporation of logarithmic functions of the electronic coordinates allows relatively compact wave functions of rather high quality (in the energetic sense) to be constructed. Basis functions of this type have not been employed for calculations on three-electron systems. The integration problems that emerge when logarithmic functions are employed to treat three-electron systems are rather severe, and there are no published procedures to solve the integrals that are required.

A. CONVERGENCE CONSIDERATIONS

All the theoretical methods that have been applied to carry our high-precision calculations on the lithium atom, converge rather slowly as the size of the basis set is increased. A central issue is how well the basis sets employed describe the electron cusps in the wave function. Because the exact analytic structure of the N-electron ($N \geq 2$) nonrelativistic wave function is unknown, the theorist must resort to educated guesswork to select basis functions that will mimic both the shape characteristics of the exact wave function, as well as the form of the wave function at the coalescence points, which occur where the electron-nuclear separation or the interelectronic distances are zero.

There have been a number of studies on the general convergence characteristics of variational calculations (Schwartz, 1962, 1963; Lakin, 1965; Klahn and Bingel, 1977; Klahn and Morgan, 1984; Hill, 1985, 1995; Kutzelnigg, 1985; Klahn, 1985; Kutzelnigg and Klopper, 1991; Kutzelnigg and Morgan, 1992). From these works it is possible to gain insight into the expected rates of convergence of some of the computational techniques currently employed, and to anticipate why the r_{ij}-dependent basis sets lead to particularly good convergence when the nonrelativistic energy is calculated. There has also been some effort expended on investigating the behavior of the electronic wave function in the neighborhood of the coalescence points (Kato, 1957; Hoffmann-Ostenhof and Seiler, 1981; Johnson, 1981; Hoffmann-Ostenhof *et al.*, 1992). With the notable exception of the work of White and Stillinger (1970, 1971), very little attention has been directed toward finding the analytic structure of three-electron wave functions near the singular points of the potential. White and Stillinger (1971) find a logarithmic dependence on the three electronic coordinates, reminiscent of what had been discovered earlier by Fock (1954) for two-electron atoms.

The conventional CI approach does rather poorly at describing the electron-electron cusps in the wave function. The convergence of the CI calculations for the nonrelativistic ground state energy (E_{NR}) of Li is very slow (Chung, 1991), and it is necessary to resort to a careful evaluation of the errors arising from basis set truncation. Armed with these estimates, an extrapolated value for E_{NR} can be obtained. A serious drawback in this extrapolation approach is that the final result is no longer guaranteed to be a strict upper bound estimate for E_{NR}. There are

several recently published results for the ground and several excited states of Li, where the reported energies are *below* the expected "exact" results for E_{NR}. The conventional CI approach is clearly not the method of choice to obtain the highest precision results for the Li atom. When fairly high precision is not required for the calculation of a property, the CI approach is a very viable computational technique. The principal advantage of the CI approach, in contrast to some of the other methods discussed in this section, is that it can be readily extended to treat larger electronic systems. For a recent review of MCHF and CI calculations of atomic properties, see Godefroid *et al.* (1996).

The hybrid CI-Hylleraas technique (Sims and Hagstrom, 1971a) explicitly incorporates r^n_{ij}-dependent terms in the basis set. Early users of this technique restricted the basis functions to a maximum of one r^n_{ij} factor per term. Recent applications of the technique to the Li atom (Lüchow and Kleindienst, 1992b, 1994) have removed this restriction, at a greater cost in terms of the integral complexity of the calculations. A very significant improvement in the rate of convergence for the calculation of E_{NR} is found using the CI-HY technique, relative to what is known from standard CI calculations.

The Hylleraas technique (Hylleraas, 1929), which incorporates factors of r_{ij} into the basis terms, shows the fastest convergence rate for the calculation of E_{NR}. This improved convergence is tied in part to the better description of the electron-electron cusps of the exact wave function. The faster convergence is also due to a superior description of the wave function over a more extended region of configuration space (Gilbert, 1963). These gains are counterbalanced by two other features of the general approach. The first is that the Hylleraas technique has not been extended to systems with more than four electrons. Even for four-electron atomic systems, there are significant unresolved integration problems when Hylleraas basis sets are employed (see, for example, King, 1993). For three-electron systems, there are several expectation values—for example, the relativistic kinetic energy correction and the electron-electron orbital correction—that require integrals that are very difficult to deal with, when a general Hylleraas expansion is employed. Despite these rather severe drawbacks of the Hylleraas approach, the technique has proved to be of considerable value, and has yielded the highest precision and fastest convergence for a number of properties of the lithium atom. Several of these properties are discussed in later sections.

III. Some Mathematical Issues

The essential feature of any high-precision calculation of atomic properties is the interplay between the choice of the mathematical form of the basis functions that are expected to give a good description of the electronic distribution, and the tractable nature of the integrals arising in the evaluation of the required expectation

values. Because we have only very limited knowledge about the functional form
of the atomic wave function for an N-electron ($N > 2$) system in the nonrelativistic
approximation, the construction of quality wave functions is still, to a large de-
gree, a matter of trial and error (trial and success!). Brute force procedures are
prevalent.

The significance of explicitly incorporating factors of the interelectronic coor-
dinates has long been recognized. The importance of the r_{ij} factors for improving
the cusp characteristics of the wave function has been discussed in numerous pa-
pers (see, for example, Morgan, 1989). The inclusion of r_{ij}-dependent terms in
basis sets is becoming increasingly common for atomic and molecular calcula-
tions, which in turn leads to a number of interesting integration problems.

A. INTEGRATION PROBLEMS

For basis functions of the form given in Eq. (2) (which are appropriate for an
S-state of a three-electron atomic system), it is straightforward to show that all the
integrals required for the determination of the energy and a number of other ex-
pectation values reduce to the form

$$I(i, j, k, \ell, m, n, a, b, c) = \int r_1^i r_2^j r_3^k r_{23}^\ell r_{31}^m r_{12}^n e^{-ar_1 - br_2 - cr_3} \, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \quad (8)$$

For an energy determination, only integral cases with $\ell, m, n \geq -1$ arise. Various
cases of Eq. (8) have been discussed extensively in the literature (Huang, 1946;
Szász, 1961; Öhrn and Nordling, 1963; Hinze and Pitzer, 1964; Bonham, 1965;
Burke, 1965; Byron and Joachain, 1966; Roberts, 1966a, 1966b; Larsson, 1968;
Perkins, 1968, 1969; Ho and Page, 1975; Berk *et al.*, 1986; King, 1991c; Remiddi,
1991; King *et al.*, 1992; Lüchow and Kleindienst, 1993; Porras and King, 1994;
Drake and Yan, 1995; Yan and Drake, 1997a; King, 1998a; Pelzl and King, 1998).
The integrals appearing in Eq. (8) can be simplified by using the Sack expansion
(Sack, 1964) for the interelectronic coordinate to obtain the auxiliary function

$$W(I, J, K, \alpha, \beta, \gamma) = \int_0^\infty x^I e^{-\alpha x} \, dx \int_x^\infty y^J e^{-\beta y} \, dy \int_y^\infty z^K e^{-\gamma z} \, dz \quad (9)$$

These auxiliary functions have been well studied in the literature (James and
Coolidge, 1936; Öhrn and Nordling, 1963; McKoy, 1965; Burke, 1965; Larsson,
1968; Berk *et al.*, 1986; Drake and Yan, 1995; Frolov and Smith, 1997).

The most difficult I-integral cases that arise occur when $\ell, m,$ and n are all odd.
This case is typically evaluated by truncation of an infinite summation, which
behaves roughly like $\sum_{k=1}^\infty k^{-6}$ (the convergence of the sum depends explicitly on
the values of $\ell, m,$ and n, but the worst case convergence of any I-integral in an
energy calculation is as indicated). As remarked in Section II, when fixed expo-

nents are employed (Eq. (7)), an integral store and retrieve strategy becomes very effective for dealing with the I-integrals, but this is not practical (or useful) when the exponent parameters are optimized. Ideally, it would be highly desirable if the I-integrals could be expressed in the form

$$I(i, j, k, \ell, m, n, a, b, c) \Rightarrow \sum_u f_u(a, b, c)g_u(i, j, k, \ell, m, n) \qquad (10)$$

The advantage of this simplification is that the function g_u can be calculated and stored as a large array. This is feasible given the relatively inexpensive cost of memory on currently available workstations. The amount of computational activity is thereby significantly reduced when orbital exponent optimization is carried out. The closest form to Eq. (10) that the author has found is

$$I(i, j, k, \ell, m, n, a, b, c) = \sum_u f_u(a, b, c) \sum_v g_{uv}(i, j, k, \ell, m, n) \qquad (11)$$

This expression is obviously less suitable because the g-function has an additional index dependence.

An extended form of the I-integrals given in Eq. (8) has been investigated where the additional factor $\exp(-\alpha_{12}r_{12} - \alpha_{23}r_{23} - \alpha_{13}r_{13})$ is included, and α_{12}, α_{13}, and α_{23} are constants (Fromm and Hill, 1987; Remiddi, 1991; Harris, 1997). Solution of these integrals allows for increased flexibility in the choice of basis functions, by the inclusion of additional exponential factors like $\exp(-\alpha_{12}r_{12})$. Including this type of exponential term in the basis set may offer the advantage of ensuring that the wave function approximately satisfies the electron-electron cusp condition.

We note parenthetically that for four-electron atomic systems, the generalization of Eq. (8) now includes up to six interelectronic coordinates. Although there has been some effort directed at solving these four-electron integrals (Sims and Hagstrom, 1971b; King, 1993; Kleindienst *et al.*, 1995), there are a number of important cases still unresolved. There are clearly formidable mathematical problems to be overcome if Hylleraas-type expansions are to be routinely employed beyond three-electron atomic systems.

For three-electron systems, there are two important problems where more complex I-integrals arise. The first is the evaluation of $\langle\Psi|H_{NR}^2|\Psi\rangle$, where H_{NR} is the nonrelativistic Hamiltonian. This expectation value is required for the determination of lower bounds to the nonrelativistic energies. The second problem is the evaluation of certain relativistic corrections to the energy. For these expectation values, I-integrals arise with at least one of the indices $\ell, m, n = -2$. For both of these problems, it is possible to select the basis functions in such a way that these very difficult integral cases are avoided. However, the resulting wave functions turn out to be of rather poor quality, particular in the near-nuclear region of configuration space. The I-integrals with one (or two) factors of r_{ij}^{-2} are much harder

to evaluate, and these integrals have received considerably less attention in the literature (King, 1991c; King *et al.,* 1992; Lüchow and Kleindienst, 1993; Porras and King, 1994; Yan and Drake, 1997a; King, 1998a). The increased complexity can be appreciated by observing the form for r_{ij}^{-2} (Pauli and Kleindienst, 1984; King, 1991c; Lüchow and Kleindienst, 1992a; Porras and King, 1994), which can be expressed as (King, 1991c)

$$
\frac{1}{r_{12}^2} = \sum_{l=0}^{\infty} \left[\frac{2l+1}{2} \right] 4^{-l} \left[\ell n \left| \frac{r_1 + r_2}{r_1 - r_2} \right| \sum_{\kappa=0}^{l} r_1^{2\kappa - l - 1} r_2^{l - 2\kappa - 1} \right.
$$

$$
\sum_{\nu=0}^{\min[\kappa, l-\kappa]} (-4)^{\nu} \binom{l}{\nu} \binom{2l - 2\nu}{l} \binom{l - 2\nu}{\kappa - \nu} - 2 \sum_{\kappa=0}^{l-1} r_1^{-l+2\kappa} r_2^{l-2\kappa-2} \tag{12}
$$

$$
\sum_{j=0}^{\min[\kappa, l-\kappa-1]} 4^j \binom{l - 2j - 1}{\kappa - j} \sum_{\nu=0}^{j} \frac{(-1)^{\nu} \binom{l}{\nu} \binom{2l - 2\nu}{l}}{2j - 2\nu + 1} \right] P_l(\cos \theta_{12})
$$

where P_l denotes a Legendre polynomial and $\binom{a}{b}$ is a binomial coefficient. This expansion can be contrasted with the familiar expansion of r_{12}^{-1} in terms of Legendre polynomials. The expansion terms for r_{12}^{-2} involve a logarithmic function of the coordinates r_1 and r_2, which adds significantly to the complexities of the integral evaluations. The author (King, 1991c) has succeeded in reducing a large number of integrals of the form $I(i, j, k, -2, m, n, a, b, c)$ to two-electron integrals, which can be computed relatively quickly.

A particularly difficult case to evaluate is $\ell = -2$, and m and n both odd. The methods that are currently available for this case lead to limited precision (about 12–16 digits) for the integral evaluations, which in turn becomes a factor controlling the precision of the required expectation values, when very large basis set expansions are employed. If a general Hylleraas expansion is employed, then the considerably more complicated case $\ell = -2, m = -2$ arises. Although methods are available to deal with these integrals (Lüchow and Kleindienst, 1993; Porras and King, 1994), the precision available is limited. For practical calculations, it appears possible to delete basis functions that lead to these $\ell = -2, m = -2$ cases, without any appreciable loss of quality for the overall wave function.

When excited states of *Li* are under investigation, the additional angular factors in the basis functions lead to more tedious integration problems. A number of the required integrals involving additional angular factors have been evaluated. For a detailed account see, for example, Barrois *et al.* (1997b, 1997c) and Yan and Drake (1997a).

There are three additional mathematical issues that emerge, particularly when large basis sets are employed. As the size of the basis set grows, significant prob-

lems associated with linear dependence in the basis set arise. These are numerical problems that are difficult to circumvent, because increasing the precision level of the calculation can be a very expensive proposition. Using double-precision arithmetic with a 64-bit word or quadruple precision with a 32-bit word will generally allow well over a thousand terms to be incorporated in a Hylleraas-type expansion, though the actual maximum size will obviously depend on the particular basis functions employed. To proceed to several thousand terms would most likely require that extended precision arithmetic be employed. Although Fortran source codes have been developed to deal with this, the high cpu costs would make the routine use of such codes prohibitive.

For large basis sets, particularly when ω (Eq.(6)) reaches double-digit values, the precision level of calculated expectation values can significantly decline. This can be easily monitored by separately evaluating the positive and negative contributions to the expectation value of interest. For large values of ω, individual matrix elements can be very large, and consequently a sum of several hundred thousand contributions can lead to a value of considerable size. When the positive and negative components of an expectation value are very large, and the value of the particular expectation value is not, then very significant loss of precision occurs. If the positive and negative components are not tracked separately, then this precision loss can be easily overlooked, particularly if the convergence of the expectation value is nonmonotonic.

Large Hylleraas expansions often lead to many local energy minima in the $\{\alpha_\mu, \beta_\mu, \gamma_\mu\}$ parameter space. There can be significant differences between these minima, so an effective optimization scheme needs to be able to handle a global strategy in a cost-effective manner. Global strategies that perform some type of stochastic sampling require the evaluation of a significant number of matrix elements, so the bottleneck in the calculation of the wave function becomes the evaluation of the three-electron I-integrals (Eq.(8)). Because the all-odd $\{\ell, m, n\}$ I-integral case is significantly slower than the other cases, developing new mathematical approaches for the evaluation of these integrals would have an important impact on progress in the area of high-precision calculations on three-electron atomic systems.

IV. Nonrelativistic Energies

The nonrelativistic Hamiltonian conventionally employed is (in atomic units)

$$H_{\mathrm{NR}} = \sum_{i=1}^{3} \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i=1}^{3} \sum_{j>1}^{3} \frac{1}{r_{ij}} \tag{13}$$

where Z is the nuclear charge ($= 3$ for Li). The specific mass shift (mass polarization correction) is not included in Eq. (13). Several high-precision calculations

have been carried out with this factor incorporated in H_{NR} (King, 1986; Lüchow and Kleindienst, 1994; Yan and Drake, 1995a), but it is more common to evaluate the specific mass shift using first-order perturbation theory.

For the S states of a three-electron atom, it is possible to work with the Hamiltonian in the form

$$
\begin{aligned}
H_{NR} = -\sum_{i=1}^{3} & \left(\frac{1}{2} \frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i} \frac{\partial}{\partial r_i} + \frac{3}{r_i} + \frac{\partial^2}{\partial u_i^2} + \frac{2}{u_i} \frac{\partial}{\partial u_i} - \frac{1}{u_i} \right) \\
& -\frac{1}{2} \sum_{\mathcal{P}_{ijk}} \left(\frac{r_i^2 + u_k^2 - r_j^2}{u_k r_i} \frac{\partial^2}{\partial r_i \partial u_k} + \frac{u_i^2 + u_k^2 - u_j^2}{2 u_i u_k} \frac{\partial^2}{\partial u_i \partial u_k} \right)
\end{aligned}
\tag{14}
$$

In Eq. (14), $\mathcal{P}_{ijk}$ signifies that the summation is over the six permutations ($\begin{smallmatrix} 1 & 2 & 3 \\ i & j & k \end{smallmatrix}$), and the notational simplifications $u_1 = r_{23}$, $u_2 = r_{31}$, and $u_3 = r_{12}$ are employed. The form of H_{NR} in Eq. (14) is very convenient to use, because of the structure of the basis functions employed in the Hylleraas expansion (see Eq. (2)). It is also straightforward to show, using this simplified form of H_{NR}, that the matrix elements required for the determination of the energy reduce to integrals of the form given in Eq. (8).

A. THE GROUND STATE

A considerable amount of attention has been directed at the problem of determining high precision estimates for the nonrelativistic energies of the lithium atom, and much of this activity has focused on the ground state (King and Shoup, 1986; King, 1989, 1995; Kleindienst and Beutner, 1989; King and Bergsbaken, 1990; Jitrik and Bunge, 1991; Chung, 1991; McKenzie and Drake, 1991; Pipin and Bishop, 1992; Lüchow and Kleindienst, 1992b, 1994; Tong *et al.*, 1993; Yan and Drake, 1995a; Jitrik and Bunge, 1997). Recent work with the Monte Carlo technique is discussed by Alexander and Coldwell (1997). A summary of some of the highest precision values is presented in Table 1. An extensive tabulation of earlier calculations of the ground state E_{NR} for Li is given by King (1997). Not surprisingly, progress in obtaining higher precision values of E_{NR} has largely mirrored advances in computer technology.

In Table 1, the last digits for each energy that have been determined by either extrapolation procedures or by estimation of basis set truncation errors are shown in italics. The reader needs to note that neither of these procedures necessarily leads to a strict upper bound for E_{NR}. Except for the CI calculations of Chung (1991), all the E_{NR} values for the ground state presented in Table 1 are based on wave functions involving explicit dependence on the interelectronic coordinates. Chung's result includes a sizeable basis set truncation correction of 134.6 μhartree. Calculations based on the CI-HY technique (Pipin and Bishop, 1992; Lüchow and Kleindienst, 1992b, 1994) lead to rather precise values for

TABLE 1
HIGH-PRECISION ESTIMATES OF THE NONRELATIVISTIC ENERGIES OF THE
LOW-LYING DOUBLET STATES OF *Li*.

State	E_{NR} (a.u.)	Reference
$2\,^2S$	-7.478058	King and Shoup (1986)
$(1s^22s)$	-7.478059	King (1989)
	-7.4780595	King and Bergsbaken (1990)
	-7.4780597	Chung (1991)
	-7.478060326	McKenzie and Drake (1991)
	-7.4780601	Pipin and Bishop (1992)
	-7.478060252	Lüchow and Kleindienst (1992b)
	-7.4780603208	Lüchow and Kleindienst (1994)
	-7.478060	King (1995)
	-7.47806032310	Yan and Drake (1995a)
	$[-7.47806035(12)]$	This chapter
$3\,^2S$	-7.354030	Pipin and Woznicki (1983)
$(1s^23s)$	-7.354076	King (1991)
	-7.3540978	Lüchow and Kleindienst (1992b)
	-7.3540980	Wang, Zhu, and Chung (1992a)
	-7.354098369	Lüchow and Kleindienst (1994)
	-7.354098	King (1998c)
	$[-7.3540981(2)]$	This chapter
$4\,^2S$	-7.318491	King (1992)
$(1s^24s)$	-7.318525	Lüchow and Kleindienst (1992b)
	-7.3185303	Wang, Zhu, and Chung (1992a)
	-7.318530665	Lüchow and Kleindienst (1994)
	-7.318529	King (1998c)
	$[-7.3185306(2)]$	This chapter
$5\,^2S$	-7.303439	King (1991)
$(1s^25s)$	-7.303547	Lüchow and Kleindienst (1992b)
	-7.3035508	Wang, Zhu, and Chung (1992a)
	-7.303546	King (1998c)
	$[-7.3035515(2)]$	This chapter
$6\,^2S$	-7.29583	Lüchow and Kleindienst (1992b)
$(1s^26s)$	-7.295846	King (1998c)
	$[-7.295859(1)]$	This chapter
$2\,^2P$	-7.410106	Pipin and Woznicki (1983)
$(1s^22p)$	-7.4101554	Pipin and Bishop (1992)
	-7.4101541	Wang, Zhu, and Chung (1993)
	-7.4101565218	Yan and Drake (1995a)
	-7.41015652	Barrois, Kleindienst, and Lüchow (1997b)
	-7.410156531763	Yan and Drake (1997b)
	$[-7.41015645(11)]$	This chapter
$3\,^2P$	-7.337059	Pipin and Woźnicki (1983)
$(1s^23p)$	-7.3371503	Wang, Zhu, and Chung (1993)
	-7.33715170	Barrois, Kleindienst, and Lüchow (1997b)
	$[-7.3371516(2)]$	This chapter

TABLE 1 (*Continued*)

State	E_{NR} (a.u.)	Reference
4 ^2P	−7.311736	Sims and Hagstrom (1975)
($1s^24p$)	−7.311*8881*	Wang, Zhu, and Chung (1993)
	−7.3118888	Barrois, Kleindienst, and Lüchow (1997b)
	[−7.3118887(2)]	This chapter
5 ^2P	−7.300142	Sims and Hagstrom (1975)
($1s^25p$)	−7.300*2875*	Wang, Zhu, and Chung (1993)
	[−7.3002883(2)]	This chapter
3 ^2D	−7.3355231	Pipin and Bishop (1992)
($1s^23d$)	−7.335*5239*	Wang, Zhu, and Chung (1992b)
	−7.33552354*110*	Yan and Drake (1995a)
	[−7.3355234(2)]	This chapter
4 ^2D	−7.311187	Pipin and Bishop (1992)
($1s^24d$)	−7.311*190*	Wang, Zhu, and Chung (1992b)
	[−7.3111896(2)]	This chapter
5 ^2D	−7.299928	Wang, Zhu, and Chung (1992b)
($1s^25d$)	[−7.2999277(2)]	This chapter
4 ^2F	−7.311*1687*	Wang, Zhu, and Chung (1992b)
($1s^24f$)	[−7.3111668(2)]	This chapter
5 ^2F	−7.2999*171*	Wang, Zhu, and Chung (1992b)
($1s^25f$)	[−7.2999159(2)]	This chapter

Digits based on extrapolation or estimates of the basis set truncation errors are indicated in italics. Estimates of the nonrelativistic energies are shown in [ ].

E_{NR}. All the other ground state values of E_{NR} shown in Table 1 were determined using Hylleraas-type expansions.

1. Lower Bound Estimates for E_{NR}

When the convergence of the variational calculation of E_{NR} is slow, it is particularly advantageous to have access to precise lower bounds for the nonrelativistic energies. The lower bounds supplement the upper bound estimates obtained via the standard variational approach. Relatively little work has been published on finding lower bounds for the energies of the lithium atom. The principal reason for this is the extremely difficult nature of the integration problems that arise. In fact, almost all of the progress that has been made on finding lower bounds for E_{NR} has been restricted to one- and two-electron atomic and molecular systems. The problem of determining a lower bound for the ground state E_{NR} has been approached using two rather different methods. The first, based on intermediate Hamiltonian techniques (Bazley, 1959, 1960; Bazley and Fox, 1961) has been applied to the lithium atom (Reid, 1972, 1974; Fox and Sigillito, 1972a, b, c; Fox, 1972; Russell and Greenlee, 1985). This approach has not led to precise estimates

for any lower bounds to the nonrelativistic energies of the lithium atom. The second method is based on the more familiar classical lower bound formulas derived by Temple (1928),

$$E_0 \geq E_T = \langle \Psi | H | \Psi \rangle - \frac{\sigma}{E_1 - \langle \Psi | H | \Psi \rangle} \tag{15}$$

by Weinstein (1934),

$$E_0 \geq E_W = \langle \Psi | H | \Psi \rangle - \sigma^{1/2} \tag{16}$$

and by Stevenson (1938) and Stevenson and Crawford (1938),

$$E_0 \geq E_S = \alpha - (\alpha^2 - 2\alpha \langle \Psi | H | \Psi \rangle + \langle \Psi | H^2 | \Psi \rangle)^{1/2} \tag{17}$$

$$= \alpha - [\sigma + (\alpha - \langle \Psi | H | \Psi \rangle)^2]^{1/2}$$

In Eqs. (15–17), E_0 denotes the exact nonrelativistic ground state energy, and E_T, E_W, and E_S designate, respectively, the Temple, Weinstein, and Stevenson lower bound estimates to E_0. The variance, σ, is defined by

$$\sigma = \langle \Psi | H^2 | \Psi \rangle - \langle \Psi | H | \Psi \rangle^2 \tag{18}$$

As Ψ approaches the exact solution of the Schrödinger equation, $\sigma \to 0$. These lower bound formulas have been discussed extensively in the literature (Kato, 1949; Caldow and Coulson, 1961; Fröman and Hall, 1961; Wilson, 1965; Switkes, 1967; Schmid and Schwagner, 1968; Delves, 1972; Coulson and Haskins, 1973; Cohen and Feldmann, 1979; Scrinzi, 1992). Further references on application of these formulas to one- and two-electron systems can be found in King (1995).

There are two high-precision estimates of a lower bound for E_{NR} (Lüchow and Kleindienst, 1994; King, 1995) and an earlier more approximate estimate (Conroy, 1964). The high-precision estimates are

$$-7.478176 \text{ a.u.} < E_0 \tag{19}$$

obtained using a 920-term CI-HY wave function (Lüchow and Kleindienst, 1994) and

$$-7.47830 \text{ a.u.} < E_0 \tag{20}$$

using a 600-term Hylleraas wave function (King, 1995). These estimates are approximately .12 and .24 millihartrees too low, based on the extrapolated value given for E_0 in Table 1.

The lower bound calculations converge at a significantly slower rate than the corresponding variational calculations of the upper bound estimates of E_0. The key expectation value required in the lower bound evaluation, $\langle H^2 \rangle$, samples the region of configuration space close to the nucleus. This region is less well described in the standard variational approach. To significantly improve upon the

results indicated in Eqs. (19, 20), the strategy most likely to be successful is to build a wave function that has been optimized to minimize σ (Eq. (18)) directly, or as an auxiliary constraint in the standard variational approach. This idea has been in the literature for a considerable time (see, for example, Preuss, 1961).

2. Distribution Functions

The radial electronic density function for the ground state of Li has been evaluated in closed form, starting from a Hylleraas-type wave function (King and Dressel, 1989). To obtain the density in a compact analytic form, it is necessary to make some restrictions on the basis functions employed in the Hylleraas expansion. For example, terms with three odd powers of the interelectronic coordinates must be excluded, otherwise a finite expansion for the density does not appear possible. The moments $\langle r_i^n \rangle$, for $n = -2$ to 6, generated from the calculated radial density, are found to be in good agreement with other calculations using much larger basis sets (King, 1995). For the excited states of Li, there has been relatively little work devoted to determining precise densities. King (1991b) has evaluated radial densities for some excited S states using Hylleraas basis sets of modest size.

Whereas the spin density at the nucleus has received a considerable amount of attention, the radial dependence of the spin density has received almost no attention. The most precise results available for the radial dependence of the spin density are due to Esquivel et al. (1991), who used large-scale CI calculations to study this function.

Starting from a Hylleraas-type basis set, Dressel and King (1994) have managed to determine a compact analytic expression for the electron-electron distribution function. Once again, it was necessary to make some simplifications on the possible terms in the basis set, otherwise a compact and finite series expansion could not be obtained. Extension of this work to allow for more general basis set expansions would be desirable, as the electron-electron distribution function plays an important role in discussions of the Coulomb hole.

B. Excited States

The calculation of nonrelativistic energies for the excited states of lithium has received considerable attention. Progress in this area can be summarized most easily in terms of the following four groups: single valence-electron excited doublet states, low-lying quartet states, core-excited doublet states, and doubly core-excited quartet states. The next four subsections discuss each of these states.

1. The Low-Lying Excited Doublet States

The calculation of E_{NR} for the low-lying ^2S states has been carried out with a variety of computational techniques (Larsson, 1972; Perkins, 1972; Sims and

Hagstrom, 1975; Sims et al., 1976a; Pipin and Woźnicki, 1983; Hijikata et al., 1987; King, 1991a, 1998c; Lüchow and Kleindienst, 1992b; Wang et al., 1992a; Yan and Drake, 1995a). The determination of the nonrelativistic energies for the low-lying ^2P states has also attracted considerable attention (Ahlenius and Larsson, 1973, 1978; Sims and Hagstrom, 1975; Sims et al., 1976a; Muszyńska et al., 1980; Pipin and Woźnicki, 1983; Hijikata et al., 1987; Pipin and Bishop, 1992; Chung and Zhu, 1993; Wang et al., 1993; Yan and Drake, 1995a; Yan and Drake, 1997b). The low-lying ^2D and ^2F states have received far less attention, but there has been some very recent progress on the calculation of E_{NR} for some of these states (Wang et al., 1992b; Pipin and Bishop, 1992; Yan and Drake, 1995a). A selection of the highest precision results for the nonrelativistic energies of these states is presented in Table 1. Also included in Table I is an estimate of the nonrelativistic energy, which was derived using

$$E_{NR}(^2X) = E_{NR}(Li^+) + \Delta E_{REL} + \Delta E_{MASS} + \Delta E_{QED} - I_1 + \Delta E(^2X) \ (21)$$

where

$$\Delta E_{REL} = E_{REL}(Li^+) - E_{REL}(^2X) \qquad (22)$$

$$\Delta E_{MASS} = E_{MASS}(Li^+) - E_{MASS}(^2X) \qquad (23)$$

$$\Delta E_{QED} = E_{QED}(Li^+) - E_{QED}(^2X) \qquad (24)$$

and I_1 designates the first ionization potential of the ground state of Li, and $\Delta E(^2X)$ is the transition energy from the ground state to the ^2X state of interest. REL, MASS, and QED refer to the relativistic correction, nuclear mass dependent correction, and quantum electrodynamic shift, respectively. The excitation energies have been taken from Radziemski et al. (1995) or Sansonetti et al. (1995). All the relativistic corrections are taken from the work of Wang et al. (1992a, 1992b, 1993), except the result for the 2 ^2S state, which is taken from King (1997). The latter result is a combination of individual relativistic corrections taken from Chung (1991), King (1995) and Yan and Drake (1995a). The mass correction includes both the Bohr mass shift and the specific mass shift. The specific mass shifts used to evaluate ΔE_{MASS} were taken from Yan and Drake (1995a) and Wang et al. (1992a, 19992b, 1993). For the 2 ^2S state, the value of ΔE_{QED} based on the work of Feldman and Fulton (1995) was employed, and for the 3 ^2S state, ΔE_{QED} was taken from Wang et al. (1992a). For the other doublet states, ΔE_{QED} has been set to zero, which should be a satisfactory approximation, at least for the higher lying states, based on the values calculated from the standard one-electron formula for ΔE_{QED} (which is given later in Section VII). The results for Li^+ that enter Eqs. (21–24) are taken from Yan and Drake (1995a), Pekeris (1958, 1962), Johnson and Soff (1985) and Drake (1988). The semiempirical estimates for E_{NR} are in

particularly good agreement with the results obtained from variational calculations. The error estimates are only rough, as the uncertainties for the $E_{REL}(^2X)$ values are not available, and have been estimated at two in the last quoted digit of the published calculations. Also, the error associated with ΔE_{QED} is rather difficult to gauge.

2. The Low-Lying Quartet States

There has been renewed interest in high precision calculations on the low-lying quartet states of the lithium atom (Fischer, 1990; Hsu *et al.*, 1991, 1994; Lüchow *et al.*, 1993; Barrois *et al.*, 1996, 1997a; King, 1998d). Efforts to improve model-potential calculations for these states have also attracted recent attention (Chen, 1996). A summary of some of the higher precision calculations is presented in Table 2. All the states presented in Table 2 lie below the $1s2s\ ^3S$ state of Li^+. There has been extensive experimental work on these states (see Feldman and Novick, 1967; and for reviews, Berry, 1975; Mannervik, 1989).

A semiempirical estimate of the nonrelativistic energy of a number of the ^4X states can be determined using

$$E_{NR}(^4X) = E_{NR}(Li^+, 1s2s\ ^3S) + \Delta E_{MASS}(^4X)$$
$$+ \Delta E_{REL}(^4X) + \Delta E_{QED}(^4X) - I_4 + \Delta E(^4X) \tag{25}$$

where $\Delta E(^4X)$ is the transition energy from the $1s2s2p\ ^4P$ state, and

$$\Delta E_{MASS}(^4X) = E_{MASS}(1s2s,\ ^3S\ Li^+) - E_{MASS}(^4X) \tag{26}$$

$$\Delta E_{REL}(^4X) = E_{REL}(1s2s,\ ^3S\ Li^+) - E_{REL}(^4X) \tag{27}$$

$$\Delta E_{QED}(^4X) = E_{QED}(1s2s,\ ^3S\ Li^+) - E_{QED}(^4X) \tag{28}$$

Experimental values of $\Delta E(^4X)$ have been taken from the work of Mannervik and Cederquist (1983). In Eq. (25), I_4 designates the ionization potential of the $1s2s2p$ ^4P state (to yield Li^+ $(1s2s)\ ^3S$). This ^4P state is the lowest in energy of the quartet states, and is metastable against both radiative decay and autoionization. The values of E_{NR}, E_{SMS} (a part of E_{MASS}) and E_{REL} for Li^+ $(1s2s^3S)$ are taken from Pekeris (1962). There are several estimates available for the ionization potential of $1s2s2p$ ^4P. These include an experimental determination of 56473(5) cm^{-1} (Mannervik and Cederquist, 1983) and five theoretically derived estimates of 56460.6 cm^{-1} (Bunge, 1981a), 56459.6(5)cm^{-1}, and 56460.1(2)cm^{-1} (Hsu *et al.*, 1991), 56461.7 cm^{-1} (Barrois *et al.*, 1997a) and 56462.2(2) cm^{-1} (King, 1998d). The experimental result appears too high; it leads to estimates of $E_{NR}(^4X)$ that are significantly different from the results of some recent well-converged calculations. The estimates of Hsu *et al.* are based on nonrelativistic energies of the states $1s2s2p$ ^4P and $1s2s3s$ ^4S, which are too high by approximately 2.0 cm^{-1}. The value of E_{NR} for the $1s2s3s$ ^4S state used by Bunge is too high by about 1.6 cm^{-1}.

TABLE 2
NONRELATIVISTIC ENERGIES OF THE LOW-LYING QUARTET STATES OF Li.

State	E_{NR} (a.u.)	Reference
$(1s2s3s)\ ^4S$	-5.212396	Larsson (1972)
	-5.21259	Larsson, Crossley, and Ahlenius (1979)
	-5.212737	Bunge and Bunge (1978a)
	-5.212741	Bunge (1981a)
	-7.212739	Hsu, Chung, and Huang (1991)
	-5.212748246	Barrois, Lüchow, and Kleindienst (1996)
	-5.212748	King (1998d)
	$[-5.212748(1)]$	This chapter
$(1s2s4s)\ ^4S$	-5.15823	Larsson and Crossley (1982)
	-5.15839345	Barrois, Lüchow, and Kleindienst (1996)
	-5.158391	King (1998d)
	$[-5.15844(2)]$	This chapter
$(1s2s5s)\ ^4S$	-5.13816	Larsson and Crossley (1982)
	-5.1384624	Lüchow, Barrois, and Kleindienst (1993)
	-5.138460	King (1998d)
	$[-5.13845(2)]$	This chapter
$(1s2s6s)\ ^4S$	-5.12829	Larsson and Crossley (1982)
	-5.128880	Lüchow, Barrois, and Kleindienst (1993)
	-5.128872	King (1998d)
	$[-5.12893(4)]$	This chapter
$(1s2s2p)\ ^4P^o$	-5.367948	Bunge and Bunge (1978b)
	-5.36783	Larsson and Crossley (1982)
	-5.367917	Fischer (1990)
	-5.368001	Hsu, Chung, and Huang (1991)
	-5.3680059	Hsu, Chung, and Huang (1994)
	-5.36801014	Barrois, Bekavac, and Kleindienst (1997a)
	$[-5.368013(2)]$	This chapter
$(1s2s3p)\ ^4P^o$	-5.186742	Glass (1978)
	-5.18687	Larsson and Crossley (1982)
	-5.187278	Bunge (1981b)
	-5.1872793	Hsu, Chung, and Huang (1994)
	-5.18728815	Barrois, Bekavac, and Kleindienst (1997a)
	$[-5.18731(2)]$	This chapter
$(1s2s4p)\ ^4P^o$	-5.14338	Larsson and Crossley (1982)
	-5.149722	Bunge (1981b)
	-5.1497361	Hsu, Chung, and Huang (1994)
$(1s2s5p)\ ^4P^o$	-5.134454	Bunge (1981b)
	-5.1344767	Hsu, Chung, and Huang (1994)[a]
$(1s2p3s)\ ^4P^o$	-5.1195222	Hsu, Chung, and Huang (1994)
	$[-5.119533(6)]$	This chapter
$(1s2s3d)\ ^4D$	-5.1730806	Hsu, Chung, and Huang (1994)
	$[-5.173086(2)]$	This chapter
$(1s2s4f)\ ^4F$	-5.142818	Galán and Bunge (1981)

[a] Additional higher states in the quartet P series were studied by these authors.

An accurate way to determine the ionization potential of the $1s2s2p$ ^4P state is to use the relationship

$$I_4 = E(1s2s\ ^3S\ Li^+) - E(1s2s3s\ ^4S) + \Delta E(1s2s3s \rightarrow 1s2s2p) \quad (29)$$

where $\Delta E(1s2s3s \rightarrow 1s2s2p)$ is the energy for the transition $1s2s3s$ $^4S \rightarrow 1s2s2p$ ^4P, and $E(1s2s,\ ^3S\ Li^+)$ and $E(1s2s3s\ ^4S)$ are the energies for the lowest ^3S Li^+ state and the lowest ^4S state, respectively. The transition energy $\Delta E(1s2s3s \rightarrow 1s2s2p)$ was reported (as a then unassigned line) by Herzberg and Moore (1959) in their study of the spectrum of Li^+. It was later suggested that several of the unassigned lines in the observed spectrum of Li^+ were actually transitions between quartet levels of Li I (Feldman and Novick, 1963; Garcia and Mack, 1965). The series of lines at approximately 2934 Å observed by Herzberg and Moore were assigned to be the $1s2s3s$ $^4S \rightarrow 1s2s2p$ ^4P transition by Holøien and Geltman (1967) on the basis of calculations, and confirmed by Feldman et al. (1968) and Levitt and Feldman (1969). The latter authors gave for this transition energy the value $\Delta E(1s2s3s \rightarrow 1s2s2p) = 34071.91(5)$ cm^{-1}. If this value for ΔE is employed in Eq. (29) along with $E(1s2s,\ ^3S\ Li^+) = 1121722.13(1)$ cm^{-1} (Accad et al., 1971) and the calculated values for E_{NR} (King, 1998d) and E_{REL} (Hsu et al., 1991) for the $1s2s3s$ ^4S state, then $I_4 = 56462.25\ (22)$ cm^{-1}. The error estimate is determined primarily by the uncertainty in the value of E_{REL}. This is the value of I_4 that has been employed in Eq. (25). Other values of E_{REL} (^4X) were taken from Hsu et al., (1991, 1994).

The semiempirical estimates of E_{NR} reported in Table 2 are in satisfactory agreement with the results from recent high-precision calculations. The error estimates are rather large, particularly in comparison with those given in Table 1. The experimental transition energies between quartet levels are not known with the same high precision as the transition energies between the low-lying doublet states. There are significant uncertainties in the relativistic corrections for some quartet states, and there are difficulties associated with pinning down precise estimates of $\Delta E_{QED}(^4X)$.

There has been considerable interest in the modes of decay of some of the low-lying quartet states. The reader can pursue this avenue of research starting with the following works: Manson (1971), Nicolaides and Aspromallis (1986, 1988), Mannervik and Cederquist (1986), Davis and Chung (1987, 1988), and Sonnek and Mannervik (1990).

3. The Core-Excited Doublet States

Core-excited doublet states of the Li atom have received considerable attention. These states play an important role in electron scattering and various collision experiments, as well as certain photoabsorption processes. The core-excited dou-

blet states have energies above the first ionization energy of the neutral atom. They are not discrete states in the same sense as the bound excited doublet states. These core-excited states are in most cases coupled to the $1s^2 \epsilon \ell$ continua via interelectron Coulomb interactions. The standard variational method cannot be *directly* applied to treat these autoionizing states, the exceptions being states like $1s2p^2$ $^2P^e$ (or more generally, $1s2p \, \epsilon \ell \, ^2L \, (L = \ell)$), which are bound metastable core-excited states.

A variety of theoretical techniques have been employed to treat a number of the core-excited resonances (see for example, Ho, 1983; Chung and Davis, 1985). Most of the standard techniques available have been applied to various core-excited states of the lithium atom (Bhatia, 1978; Bunge, 1979; Wakid *et al.,* 1980; Chung, 1981a, 1981b, 1982; Jáuregui and Bunge, 1981; Woźnicki *et al.,* 1983; Davis and Chung, 1984, 1985, 1990b; Jaskólska and Woźnicki, 1989a, 1989b; Chung and Gou, 1995; Barrois *et al.,* 1997c; Chung, 1997a, 1997b). The majority of these calculations deal only with the nonrelativistic energy contribution. The only workers that have attempted any evaluation of the relativistic contributions to the energy are Chung and coworkers. Much of this work has employed the CI technique. There has been experimental interest in these states for many years (see, for example, Ederer *et al.,* 1970; Berry *et al.,* 1972; Pegg *et al.,* 1975; Ziem *et al.,* 1975; Cantù *et al.,* 1977; Rassi *et al.,* 1977; McIlrath and Lucatorto, 1977; Rødbro *et al.,* 1979; Cederquist and Mannervik, 1985; Mannervik and Cederquist, 1985; Mannervik *et al.,* 1986; Meyer *et al.,* 1987; Kiernan *et al.,* 1996). Most recently, interest has focused on "hollow" atomic states of *Li*. These states of *Li* have an empty K shell. The reader interested in this avenue of work might start with the work of Journel *et al.* (1996).

The $^2P^e$ states have attracted attention from several authors (Bunge, 1979; Chung, 1982; Woźnicki *et al.,* 1983 and Barrois *et al.,* 1997c). For the lowest three $^2P^e$ terms, Barrois *et al.* (1997c) have used large scale CI-HY wave functions to obtain high-precision estimates of E_{NR}. The E_{NR} values reported by these authors have converged to better than 1 μhartree. Barrois *et al.* have also evaluated the expectation value $\langle \nabla_i \cdot \nabla_j \rangle$, which allows the specific mass shift correction to the energy levels to be calculated.

Some of the theoretical energies for the core-excited states are collected in Table 3. For most of the other core excited doublets that have been investigated theoretically, the nonrelativistic energies have not been determined to the same level of precision as the best results for the $^2P^e$ terms. The precision available for the experimental energies for the core-excited states is around 10 cm^{-1} (or better) (Mannervik, 1989), and clearly does not rival the results available, particularly the most recent ones, for the bound low-lying excited doublet states. Generally, the agreement between the theoretically determined energies and experimental results is satisfactory.

TABLE 3

ENERGIES FOR THE LOW-LYING CORE EXCITED DOUBLET STATES OF *Li.*

State	E_{NR} (a.u.)	E_{TOTAL} (a.u.)	Reference
$(1s2s^2)\ ^2S$	-5.405219	-5.405833	Davis and Chung (1984)
$[(1s2s)\ ^3S\ 3s]\ ^2S$	-5.199641	-5.200237	Davis and Chung (1985)
$[1s(2s2p)\ ^3P]\ ^2P^o$	-5.312761	-5.313056	Davis and Chung (1985)
	-5.312936		Jaskólska and Woźnicki (1989a)
	-5.313212	-5.313312	Chen and Chung (1994)
$[1s(2s2p)\ ^1P]\ ^2P^o$	-5.256864	-5.257464	Davis and Chung (1985)
	-5.257499		Jaskólska and Woźnicki (1989a)
	-5.258351	-5.258471	Chen and Chung (1994)
$1s2p^2\ ^2P^e$	-5.21365		Bunge (1979)
	-5.213702	-5.213734	Chen and Chung (1994)
	-5.21373920		Barrois, Lüchow, and Kleindienst (1997c)
$[(1s2s)\ ^3S\ 3p]\ ^2P^o$	-5.183387	-5.183993	Davis and Chung (1985)
	-5.183842		Jaskólska and Woźnicki (1989a)
	-5.184006	-5.184057	Chen and Chung (1994)
$[(1s2s)\ ^3S\ 4p]\ ^2P^o$	-5.149599		Jaskólska and Woźnicki (1989a)
	-5.149695	-5.149725	Chen and Chung (1994)
$[(1s2s)\ ^3S\ 5p]\ ^2P^o$	-5.134334		Chung (1981a)
	-5.134940		Jaskólska and Woźnicki (1989a)
$[(1s2p)\ ^3S\ 6p]\ ^2P^o$	-5.126683		Chung (1981a)
	-5.127315		Jaskólska and Woźnicki (1989a)
$[(1s2p)\ ^3P\ 3p]\ ^2P^e$	-5.10429		Bunge
	-5.104364	-5.104374	Chen and Chung (1994)
	-5.10438176		Barrois, Lüchow, and Kleindienst (1997c)
$[(1s2p)\ ^3P\ 4p]\ ^2P^e$	-5.07012		Bunge (1979)
	-5.070284	-5.070305	Chen and Chung (1994)
	-5.0703159		Barrois, Lüchow, and Kleindienst (1997c)
$[(1s2pS)\ ^1P\ 3p]\ ^2P^e$	-5.06214		Bunge (1979)
	-5.061841		Jaskólska and Woźnicki (1989a)
$(1s2p^2)\ ^2D^e$	-5.233703	-5.234200	Davis and Chung (1985)
	-5.233789		Jaskólska and Woźnicki (1989b)
	-5.234138	-5.234236	Chen and Chung (1994)
$[(1s2s)\ ^3S\ 3d]\ ^2D^e$	-5.166023	-5.166619	Davis and Chung (1985)
	-5.166187		Jaskólska and Woźnicki (1989b)
	-5.166434	-5.166475	Chen and Chung (1994)
$[(1s2s)\ ^3S\ 4d]\ ^2D^e$	-5.141919		Jaskólska and Woźnicki (1989b)
	-5.142194	-5.142220	Chen and Chung (1994)
$[1s2p)\ ^3P\ 3d]\ ^2D^o$	-5.08929		Jáuregui and Bunge (1981)
	-5.089285	-5.089293	Chen and Chung (1994)
$[(1s2p)\ ^3P\ 4d]\ ^2D^o$	-5.06163		Jáuregui and Bunge (1981)
	-5.061584	-5.061594	Chen and Chung (1994)
$[(1s2p)\ ^1P\ 3d]\ ^2D^o$	-5.05367		Jáuregui and Bunge (1981)
	-5.053853	-5.053884	Chen and Chung (1994)

For the CI results shown in Table 3 (Chung and coworkers, Bunge, and others), the estimates of basis set truncation errors are typically ten or more μhartrees. The work of Barrois *et al.* (1997c), using the CI-HY technique, provides a valuable check on the reliability of these estimates of the CI basis set truncation errors.

Not all the term designations in Table 3 are straightforward. For example, $^2P^e(4)$, denoted in Table 3 as $[(1s2p)\ ^1P\ 3p]\ ^2P^e$ has a significant admixture of $[(1s2p)\ ^3P\ 4p]\ ^2P^e$, with CI coefficients of magnitude 0.71 for the latter configuration, and 0.66 for the former configuration (Bunge, 1979). Bunge (1979) reports that the $^2P^e(3)$ state has similar principal CI configurations and coefficients.

4. Highly Excited Quartet States

The higher lying quartet states of *Li* have attracted some theoretical attention (see, for example, Davis and Chung, 1990a, 1990b; Chung and Gou, 1995). For a number of the triply excited states, interelectron correction effects would be expected to be of importance. Theoretical results for the energies for some of the high-lying states are presented in Table 4. These results are all based on large-scale CI calculations. No Hylleraas-type calculations appear to have been carried out on these states.

The $2p^3\ ^4S^o$ state is particularly interesting. This is a bound metastable state; it has an energy lying below the $2p^2\ ^3P$ threshold of Li^+. There has been theoretical interest in this state of *Li* going back many years (Wu and Shen, 1944). The $2p^3\ ^4S$ state does not couple to the $1s2s\epsilon s\ ^4S$ continuum, but can decay via radiative autoionization to the $1s2p\ ^3P^o$ continuum. For the decay process $2p^3\ ^4S^o \rightarrow 1s2p^2$ ^4P, the theoretically determined wave length was found to be 145.009 Å, which is in close agreement with the experimental result of 145.02(5) Å (Agentoft *et al.*, 1984). A more recent experimental result yields 145.016(6) Å (Mannervik *et al.*, 1989), and a subsequent theoretical reevaluation gives 145.019 Å (Davis and Chung, 1990b), which is in very close agreement with the aforementioned experimental measurement.

TABLE 4

ENERGIES FOR SOME DOUBLY AND TRIPLY CORE-EXCITED QUARTET STATES OF *Li*.

State	E_{NR}	E_{TOTAL}	Reference
$(1s3s3p)\ ^4P^o$	-4.878651	-4.879214	Davis and Chung (1990a)
$(1s3p3p)\ ^4P^e$	-4.846711	-4.847261	Davis and Chung (1990a)
$2s2p2p\ ^4P$	-2.239379	-2.239559	Chung and Gou (1995)
$2s2p3p\ ^4P$	-1.961782	-1.961972	Chung and Gou (1995)
$2p^3\ ^4S^o$	-2.103588	-2.103684	Davis and Chung (1990b)
$2p^23p\ ^4S^o$	-1.873415	-1.873516	Davis and Chung (1990b)
$2p^24p\ ^4S^o$	-1.835481	-1.835583	Davis and Chung (1990b)

The $2p^3$ $^4S^o$ state is of special interest for the isoelectronic species He^-. It is one of the few bound (metastable) states of this anion, and as a result has been subject to a fair amount of attention (Beck and Nicolaides, 1978; Chung, 1979; Nicolaides *et al.*, 1981; Nicolaides and Komninos, 1981).

V. Relativistic Corrections to the Energies

The standard approach by which the relativistic corrections to the energy are incorporated is to use a first-order perturbation theoretic procedure using the relativistic Breit-Pauli Hamiltonian

$$H_{\text{rel}} = H_{\text{mass}} + H_{\text{enD}} + H_{\text{eeD}} + H_{\text{ssc}} + H_{\text{oo}}, \tag{30}$$

where the various terms in Eq. (30) are (in atomic units)

$$H_{\text{mass}} = -\frac{\alpha^2}{8} \sum_{i=1}^{3} \nabla_i^4 \tag{31}$$

$$H_{\text{enD}} = \frac{1}{2} \alpha^2 Z \pi \sum_{i=1}^{3} \delta(\mathbf{r}_i) \tag{32}$$

$$H_{\text{eeD}} = -\pi \alpha^2 \sum_{i=1}^{3} \sum_{j>i}^{3} \delta(\mathbf{r}_{ij}) \tag{33}$$

$$H_{\text{ssc}} = -\frac{8\pi\alpha^2}{3} \sum_{i=1}^{3} \sum_{j>i}^{3} \mathbf{s}_i \cdot \mathbf{s}_j \delta(\mathbf{r}_{ij}) \tag{34}$$

$$H_{\text{oo}} = \frac{1}{2} \alpha^2 \sum_{i=1}^{3} \sum_{j>i}^{3} \left(\frac{\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j}{r_{ij}} + \frac{\mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \boldsymbol{\nabla}_i) \boldsymbol{\nabla}_j}{r_{ij}^3} \right) \tag{35}$$

The fine structure constant is denoted by α, $\delta(\mathbf{r})$ is a Dirac delta function, and $\mathbf{s}_i$ is an electron spin operator. H_{mass} represents the kinetic energy mass correction, H_{enD} is the electron-nuclear Darwin term, H_{eeD} denotes the electron-electron Darwin term, H_{ssc} is the spin-spin contact interaction, and H_{oo} designates the electron-electron orbit interaction. Only the nonfine-structure contributions have been shown in Eq. (30). In addition to these terms, there are fine-structure contributions that include spin-orbit, spin-other-orbit, and spin-spin interactions.

Almost all the estimates of the relativistic corrections for the energies of the ground and excited states of the lithium atom have been calculated by Chung and coworkers using the CI approach (see Tables 2, 3, 4, and 5 for specific references). Some Hylleraas calculations have been carried out for parts of H_{rel} for the ground state of *Li* and a few excited states. A summary of some of the relativistic results is presented in Table 5. For the ground state of *Li*, Hylleraas-type calculations of the Breit-Pauli terms given in Eqs. (31–35) have just been completed by King

TABLE 5

RELATIVISTIC CORRECTIONS FOR SOME LOW-LYING DOUBLET STATES OF Li in Atomic Units.

State	$\langle H_{\text{mass}}\rangle$	$\langle H_{\text{enD}}\rangle$	$\langle H_{\text{mass}} + H_{\text{enD}}\rangle$	$\langle H_{\text{eeD}}\rangle$	$\langle H_{\text{eeD}} + H_{\text{ssc}}\rangle$	$\langle H_{\text{oo}}\rangle$	Reference
$2\,^2S$	-4.18317×10^{-3}						King (1995)
	-4.18769×10^{-3}						Esquivel *et al.* (1992)
		3.4734×10^{-3}					King and Shoup (1986)
		3.47348×10^{-3}					King (1989)
		3.47370×10^{-3}					King and Bergsbaken (1990)
		3.473663×10^{-3}		-9.10630×10^{-5}			Yan and Drake (1995a)
			-7.0748×10^{-4}		9.5340×10^{-5}	-2.3331×10^{-5}	Chung (1991)[a]
			-7.0942×10^{-4}		9.1154×10^{-5}	-2.3201×10^{-5}	Chung (1991)[a]
$3\,^2S$		3.4457×10^{-3}					King (1991a)
			-6.968×10^{-4}		9.43×10^{-5}	-2.30×10^{-5}	Wang *et al.* (1992a)[a]
$4\,^2S$		3.4397×10^{-3}					King (1991a)
			-6.947×10^{-4}		9.40×10^{-5}	-2.30×10^{-5}	Wang *et al.* (1992a)
$5\,^2S$		3.4378×10^{-3}					King (1991a)
			-6.940×10^{-4}		9.40×10^{-5}	-2.30×10^{-5}	Wang *et al.* (1992a)
$2\,^2P$		3.431887×10^{-3}		-8.90484×10^{-5}			Yan and Drake (1995a)
			-6.933×10^{-4}		9.36×10^{-5}	-2.13×10^{-5}	Wang *et al.* (1993)
$3\,^2P$			-6.935×10^{-4}		9.38×10^{-5}	-2.24×10^{-3}	Wang *et al.* (1993)
$4\,^2P$			-6.939×10^{-4}		9.39×10^{-5}	-2.27×10^{-5}	Wang *et al.* (1993)
$5\,^2P$			-6.934×10^{-4}		9.39×10^{-5}	-2.28×10^{-5}	Wang *et al.* (1993)
$3\,^2D$		3.438817×10^{-3}		-8.92896×10^{-5}			Yan and Drake (1995a)
			-6.956×10^{-4}		8.93×10^{-5}	-2.28×10^{-5}	Wang *et al.* (1992b)
$4\,^2D$			-6.954×10^{-4}		8.93×10^{-5}	-2.28×10^{-5}	Wang *et al.* (1992b)
$5\,^2D$			-6.954×10^{-4}		8.93×10^{-5}	-2.28×10^{-5}	Wang *et al.* (1992b)

[a] Chung and Wang *et al.* report only $\langle H_{\text{mass}} + H_{\text{enD}}\rangle$ and $\langle H_{\text{eeD}} + H_{\text{ssc}}\rangle$.

et al. (1998e). The limited number of Hylleraas results available provides a useful check on some of the CI calculations.

There has been limited application of the Hylleraas technique to calculating relativistic corrections for the three-electron systems, primarily because of the difficult nature of the integrals that arise. Along with cases $\ell = -2$ (or the more difficult case, $\ell = -2, m = -2$) in Eq. (8), integrals such as

$I_1(i, j, k, \ell, m, n, a, b, c)$

$$= \int r_1^i r_2^j r_3^k (r_1^2 - r_2^2) r_{23}^\ell r_{31}^m r_{12}^{-3} e^{-ar_1 - br_2 - cr_3} \, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \tag{36}$$

and

$I_2(i, j, k, \ell, m, n, a, b, c)$

$$= \int r_1^i r_2^j r_3^k (r_{23}^2 - r_{31}^2) r_{23}^\ell r_{31}^m r_{12}^{-3} e^{-ar_1 - br_2 - cr_3} \, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \tag{37}$$

also arise. The I_1 and I_2 integrals cannot be separated into the obvious two parts, because the separate contributions are divergent. These integrals have recently been studied by Feldmann *et al.* (1998).

For the ground state of *Li*, a comparison of theoretical methods is possible for the principal part of the relativistic correction to the energy, that is, the contribution $\langle H_{mass} + H_{enD} \rangle$. Chung (1991) calculates $\langle H_{mass} + H_{enD} \rangle = -7.0748 \times 10^{-4}$ a.u., and he also evaluates this quantity for the $1s^2 \, {}^1S$ state of Li^+. He finds a difference with the results of Pekeris (1958, 1962) for Li^+, and accordingly adopts a core correction procedure. When this core correction is included for the *Li* ground state, Chung finds $\langle H_{mass} + H_{enD} \rangle = -7.0942 \times 10^{-4}$ a.u. If the Hylleraas results for $\langle H_{mass} \rangle$ (King, 1995) and $\langle H_{enD} \rangle$ (Yan and Drake, 1995a) are combined, the value found for $\langle H_{mass} + H_{enD} \rangle$ is -7.0951×10^{-4} a.u., which is in fairly close agreement with Chung's result. This close comparison does validate Chung's core correction approach, at least for $\langle H_{mass} + H_{enD} \rangle$. The most complicated contribution to evaluate is H_{oo}, and there are no published Hylleraas results available to check the CI results of Chung and coworkers.

The level of precision of the relativistic corrections calculated using the CI technique is generally adequate to aid in the assignment of spectral lines arising from a wide variety of states. However, when a high-precision theoretical calculation of the ionization potential is the target, for example for the *Li* ground state, six-digit accuracy is required for the relativistic corrections in order to match up with the currently available experimental result, for which eight digits of precision are available. As higher precision spectroscopic work continues for *Li*, there will be increased interest in knowledge of higher precision values for the relativistic corrections.

VI. Specific Mass Shift Correction to the Energy Levels

The extension of Eq. (13) to incorporate the effect of finite nuclear mass is

$$H_M = \sum_{i=1}^{3} \left[-\frac{1}{2\mu} \nabla_i^2 - \frac{3}{r_i} \right] - \frac{1}{M} \sum_{i=1}^{3} \sum_{j>i}^{3} \nabla_i \cdot \nabla_j + \sum_{i=1}^{3} \sum_{j>i}^{3} \frac{1}{r_{ij}} \tag{38}$$

where μ is the reduced mass,

$$\mu = \frac{m_e M}{M + m_e} \tag{39}$$

and M and m_e denote the nuclear mass and the electron mass, respectively. The effect of finite nuclear mass involves two principal contributions. The normal mass shift (also referred to as the Bohr mass shift) can be determined using

$$\Delta E_{\text{Bohr}} = \frac{-\mu \,^{\infty}E}{M} \tag{40}$$

where $^{\infty}E$ is the state energy computed in the infinite nuclear mass approximation. The second contribution is specific mass shift, ΔE_{sms} (also referred to as the mass polarization correction). Two methods have been used to evaluate ΔE_{sms}. The most commonly employed approach is to evaluate ΔE_{sms} using the first-order perturbation theory formula

$$\Delta E_{\text{sms}} = -\frac{\mu}{M} \left\langle \Psi \left| \sum_{i=1}^{3} \sum_{j>i}^{3} \nabla_i \cdot \nabla_j \right| \Psi \right\rangle \tag{41}$$

where Ψ is the approximate solution of the infinite nuclear mass Schrödinger equation. An alternative operator form is available (Vinti, 1932, 1940), which gives

$$\Delta E_{\text{sms}} = \left(\frac{\mu}{M} \right) \left\{ \frac{1}{2} \left\langle \Psi \left| \sum_{i=1}^{3} \sum_{j>i}^{3} \frac{1}{r_{ij}} \right| \Psi \right\rangle \right.$$
$$\left. + Z \left\langle \Psi \left| \sum_{i=1}^{3} \sum_{j>i}^{3} \mathbf{r}_i \cdot \mathbf{r}_j \left(\frac{1}{r_i^3} + \frac{1}{r_j^3} \right) \right| \Psi \right\rangle \right\} \tag{42}$$

The result given in Eq. (42) has been less frequently employed, but for an application to Li, see Tong et $al.$ (1993).

A different approach that has been investigated for Li is to evaluate ΔE_{sms} using the result

$$\Delta E_{\text{sms}} = -\frac{1}{M} \left\langle \Psi_M \left| \sum_{i=1}^{3} \sum_{j>i}^{3} \nabla_i \cdot \nabla_j \right| \Psi_M \right\rangle \tag{43}$$

where Ψ_M is the nuclear mass-dependent approximate solution of the Schrödinger equation using H_M (Eq. (38)). High-precision calculations using this procedure

have been carried out by King (1986), Lüchow and Kleindienst (1994), and Yan and Drake (1995a).

A selection of high-precision results for ΔE_{sms} for various low-lying states of *Li* is given in Table 6. These results are all based on the use of Eq. (41), and the values $\mu/M = 7.8202022(6) \times 10^{-5}$ for ^7Li, and $\mu/M = 9.1216762(8) \times 10^{-5}$ for ^6Li have been employed. These values of μ/M are calculated from the nuclear masses of 7.0143584(5) amu for ^7Li, and 6.0134766(5) amu for ^6Li (Audi and Wapstra, 1993, 1995). For the most precise results for the $2\,^2S$ ground state, using the full H_{M} approach, a significant fraction of the uncertainty in ΔE_{sms} comes from the error in determining the nuclear masses of ^6Li and ^7Li.

There are two smaller mass-dependent contributions to the energy. The first are the nuclear mass-dependent relativistic corrections. No high-precision calculations of these contributions have been carried out for the lithium atom. A second correction is the field shift contribution (also called the volume shift) (King, 1984). This correction arises from the electric field generated by the nuclear charge distribution. For light atoms, this contribution is usually regarded as negligible. However, the accuracy of recent isotope shift measurements (Sansonetti *et al.*, 1995) suggests that a high-precision calculation of this field shift correction would be of value. There is relatively little published work on this correction for the lithium atom. Veseth (1985) has determined values of 0.02168 cm^{-1} for the ground state of ^7Li, 0.02143 cm^{-1} for the $2\,^2P$ state of ^7Li and 0.02147 cm^{-1} for $^7Li^+(1s^2)$. There is, not unexpectedly, a significant cancellation of these contributions when transitions such as $^7Li(2s) \rightarrow\, ^7Li(2p)$ and $^7Li(1s^22s) \rightarrow\, ^7Li^+(1s^2) + e^-$ are considered. Improvements in the experimental precision of isotope shift measurements will provide some significant challenges for theorists in this area.

A. TRANSITION ISOTOPE SHIFTS

The transition isotope shift (TIS) for a transition from state X to state Y for isotopes with mass numbers A_1 and A_2 ($A_1 > A_2$) is

$$\Delta E_{\mathrm{TIS}} = [E(^{A_1}Y) - E(^{A_1}X)] - [E(^{A_2}Y) - E(^{A_2}X)]$$
$$= E(^{A_1}Y) - E(^{A_2}Y) - [E(^{A_1}X) - E(^{A_2}X)] \tag{44}$$

where $E(^{A_1}Y)$ is the energy of state Y for the isotope of mass A_1. If this energy is factored into a value that is computed in the infinite nuclear mass approximation and a mass correction shift to the energy,

$$E(^{A_1}Y) = {}^\infty E(Y) + \Delta E_{\mathrm{MASS}}(^{A_1}Y) \tag{45}$$

then the mass-dependent form of ΔE_{TIS} is

$$\Delta E_{\mathrm{TIS,mass}} = \Delta E_{\mathrm{mass}}(^{A_1}Y) - \Delta E_{\mathrm{mass}}(^{A_2}Y) - [\Delta E_{\mathrm{mass}}(^{A_1}X) - \Delta E_{\mathrm{mass}}(^{A_2}X)] \tag{46}$$

TABLE 6

Specific Mass Shifts for the Ground and Selected Excited States of Li.

State	$\left\langle \sum_{i=1}^{3} \sum_{j>i}^{3} \nabla_i \cdot \nabla_j \right\rangle$ (absolute a.u.)	ΔE_{sms} (μhartree)		Reference
		^6Li	^7Li	
2 ^2S	−0.30185	27.531	23.603	King (1986)
	−0.3018467	27.53097	23.60318	King (1989)
	−0.3018436	27.53068	23.60293	King and Bergsbaken (1990)
	−0.30180	27.527	23.600	Chung (1991)
	−0.301842799[a]	27.530611	23.602871	Lüchow and Kleindienst (1994)
	−0.301842809[a]	27.530612	23.602872	Yan and Drake (1995a)
3 ^2S	−0.29212	26.644	22.843	King (1991a)
	−0.292039995[a]	26.636513	22.836332	Lüchow and Kleindienst (1994)
4 ^2S	−0.29033	26.481	22.703	King (1991a)
	−0.2901575[a]	26.46481	22.68913	Lüchow and Kleindienst (1992b)
5 ^2S	−0.28969	26.422	22.653	King (1991a)
	−0.289540	26.4085	22.6408	Lüchow and Kleindienst (1992b)
6 ^2S	−0.28942	26.398	22.631	Lüchow and Kleindienst (1992b)
2 ^2P	−0.24673781[a]	22.50457	19.29389	Yan and Drake (1995a)
	−0.24674181	22.50494	19.29420	Barrois et al. (1997b)
3 ^2P	−0.27589098	25.16357	21.57355	Barrois et al. (1997b)
3 ^2D	−0.288928837[a]	26.352749	22.59305	Yan and Drake (1995a)
$1s2s3s\,^4S$	−0.019098739	1.741966	1.493443	Barrois et al. (1996)
$1s2s4s\,^4S$	−0.018619609	1.698266	1.455977	Barrois et al. (1996)
$1s2s5s\,^4S$	−0.01791668	1.634151	1.401011	Lüchow et al. (1993)
$1s2s6s\,^4S$	−0.0175922	1.60456	1.37564	Lüchow et al. (1993)
$1s2s2p\,^4P$	0.1975568	−18.01885	−15.44813	Barrois et al. (1997a)
$1s2s3p\,^4P$	0.02001852	−1.825858	−1.565366	Barrois et al. (1997a)
$1s2p2p\,^2P^e$	−0.15493607	14.13148	12.11537	Barrois et al. (1997c)
$1s2p3p\,^2P^e$	0.23991361	−21.88215	−18.76026	Barrois et al. (1997c)

[a] A more precise value calculated using the finite mass Hamiltonian is available for this state (see Lüchow and Kleindienst, 1994; and Yan and Drake, 1995a).

There are two principal components to ΔE_{TIS}. The Bohr mass shift (put MASS = Bohr in Eq. (46)) is straightforward to calculate (see Eq (40)). Of greater interest to theorists, is the specific mass shift contribution to the transition isotope shift,

$$\Delta E_{TIS,sms} = \Delta E_{sms}(^{A_1}Y) - \Delta E_{sms}(^{A_2}Y) - [\Delta E_{sms}(^{A_1}X) - 1\Delta E_{sms}(^{A_2}X)] \quad (47)$$

This quantity is a sensitive measure of the adequate description of correlation effects (it is zero in the Hartree-Fock approximation), and can be compared directly with experimental results.

For transitions of the type $Li(^2X) \rightarrow Li^+(1s^2) + e^-$, there has been considerable theoretical interest (Prasad and Stewart, 1966; Mårtensson and Salomonson, 1982; Chambaud et al. 1984; King, 1986, 1989; King and Bergsbaken, 1990; Lüchow and Kleindienst, 1994; Yan and Drake, 1995a; Barrois et al. 1997b). These authors either explicitly calculate ΔE_{TIS} or provide the necessary expectation values to determine it. There has also been a good deal of experimental interest in $\Delta E_{TIS,sms}$ for the same process (Hughes, 1955; Mariella, 1979; Lorenzen and Niemax, 1982; Goy et al., 1986; Vadla et al., 1987; Sansonetti et al., 1995; Radziemski et al., 1995). A summary of some of the higher precision theoretical results is presented in Table 7. In most cases, the theoretical results fall within the error limits of the experimental results. Unfortunately, the error limits are rather large in a number of cases where the theoretical precision is high. The precision of the best theoretical results for $\Delta E_{TIS,sms}$ is limited by the present uncertainties in the nuclear masses of ^6Li and ^7Li.

A small but notable discrepancy between theory and experiment occurs for the 2 ^2P state of Li. Radziemski et al. (1995) report values of $-3.6100(6)$ GHz for 2 $^2P_{1/2}$ and $-3.6103(5)$ GHz for 2 $^2P_{3/2}$. Two high-precision theoretical estimates are -3.61635 GHz and -3.61601 GH$_z$ (Yan and Drake, 1995a; Barrois et al., 1997b); which are both smaller than the aforementioned experimental results. The specific mass shift contribution to the 2 ^2P_J level is given by

$$\Delta E_{TIS,sms}(2p_j) = \Delta E_{TIS,sms}(2s) - \Delta E_{TIS,sms}(2s \rightarrow 2p_j) \quad (48)$$

Using the value of the $2s \rightarrow 2p$ TIS from Sansonetti et al. (1995), the Bohr shift contribution as 5.813 GHz, and the shift for the ground state of 1.109(8) GHz (Vadla et al., 1987), leads to a shift for the 2 ^2P state of $-3.612(8)$ GHz. If the alternative value of 1.111(6) GHz for the specific mass shift of the 2 ^2S state (Lorenzen and Niemax, 1982) is used, then the shift for the 2 ^2P state is $-3.609(6)$ GHz. The error bars are too large to distinguish any difference between the 2 $^2P_{1/2}$ and 2 $^2P_{3/2}$ states. The first estimate, $-3.612(8)$ GHz, is close to the results of high-precision calculations, and the second estimate, $-3.609(6)$ GHz, almost overlaps the theoretical results. The error bars on these two values are too large for these results to provide a tight check on the theoretical calculations.

The specific mass shift contribution for a transition between any pair of levels

TABLE 7

SPECIFIC MASS SHIFT CONTRIBUTION TO THE TRANSITION ISOTOPE SHIFTS (TIS) FOR THE
GROUND AND SELECTED EXCITED STATES OF Li.

State	Shift for ^6Li–^7Li (GHz)	Specific mass shift contribution to the TIS (GHz)[a]	Experimental specific mass shift (GHz)	Reference for theoretical calculation
2 ^2S	25.844	1.102	1.108(8)[b]	King (1986)
	25.8436	1.1020	1.111(6)[c]	King (1989)
	25.84336	1.10172		King and Bergsbaken (1990)
	25.84329(3)	1.10165(4)		Lüchow and Kleindienst (1994)
	25.84329(3)	1.10165(4)		Yan and Drake (1995a)
3 ^2S	25.011	0.269	0.276(26)[b]	King (1991a)
	25.00399	0.26235	0.260(30)[d]	Lüchow and Kleindienst (1994)
4 ^2S		0.088	0.111(12)[c]	Mårtensson and Salomonson (1982)
	24.858	0.116	0.094(30)[d]	King (1991a)
	24.84281	0.10117		Lüchow and Kleindienst (1994)
5 ^2S		0.042	0.053[b,e]	Mårtensson and Salomonson (1982)
	24.803	0.061	0.027(30)[d]	King (1991a)
	24.7899	0.0483		Lüchow and Kleindienst (1992b)
6 ^2S		0.024	0.029[b,e]	Mårtensson and Salomonson (1982)
	24.780	0.038	−0.046(120)[d]	Lüchow and Kleindienst (1992b)
2 ^2P	21.12529	−3.61635	−3.596(26)[b]	Yan and Drake (1995a)
	21.12563	−3.61601	−3.608(8)[f]	Barrois et al. (1997b)
			−3.611(6)[g]	
			−3.6100(6)[h,i]	
			−3.6103(5)[h,j]	
			−3.603(15)[d,i]	
			−3.603(15)[d,j]	
3 ^2P		−1.034	−1.105(8)[b]	Mårtensson and Salomonson (1982)
	23.62134	−1.12030	−1.116(30)[d]	Barrois et al. (1997b)
4 ^2P		−0.442	−0.504(45)[d]	Mårtensson and Salomonson (1982)
5 ^2P		−0.227	−0.308(60)[d]	Mårtensson and Salomonson (1982)
3 ^2D		−0.00205	−0.011(45)[d]	Mårtensson and Salomonson (1982)
	24.73762	−0.00402		Yan and Drake (1995a)
4 ^2D		−0.00058	−0.024(45)[d]	Mårtensson and Salomonson (1982)

[a] The shift for $1s^2$ $^6Li^+$ − $1s^2$ $^7Li^+$ has been taken as 24.74164(3) GHz, which has been computed from the available value of $\langle \nabla_i \cdot \nabla_j \rangle$ (Lüchow and Kleindienst, 1994; Yan and Drake, 1995a) and the conversion factor 1 a.u. = 85.61837(7) GHz.

[b] Results from Vadla et al. (1987).

[c] Result from Lorenzen and Niemax (1982).

[d] Results from Radziemski et al. (1995).

[e] These experimental results are derived by extrapolation using scaling formulas.

[f] Result from Mariella (1979).

[g] Result from Fuchs and Rubahn (1986).

[h] Results from Radziemski et al. (1995) based on measurements of Sansonetti et al. (1995).

[i] Result for 2 $^2P^o_{1/2}$.

[j] Result for 2 $^2P^o_{3/2}$.

can be evaluated using the level shift information for the various states given in Table 7, and the result

$$\Delta E_{\text{TIS,sms}}(^2X_J \rightarrow {}^2Y_J') = \Delta E_{\text{TIS,sms}}(^2X_J) - \Delta E_{\text{TIS,sms}}(^2Y_J') \qquad (49)$$

Precise experimental results for a number of transitions for *Li* can be found in Mariella (1979), Fuchs and Rubahn (1986), Vadla *et al.* (1987), Windholz *et al.* (1990), and Sansonetti *et al.* (1995).

VII. Quantum Electrodynamic Corrections

A high-precision calculation of transition energies or ionization potentials requires a determination of the Lamb shift correction, ΔE_{QED}. For the lithium atom there has been limited work in this area. One approach to calculating ΔE_{QED} for a transition from the $1s^2 2s$ ground state of *Li*, is to ignore the $1s^2$ core, effectively reducing the problem to a one-electron correction. ΔE_{QED} can then be calculated using (Bethe and Salpeter, 1977)

$$\Delta E_{\text{QED}}(n, \ell) = \frac{4Z_{\text{eff}}^4 \alpha^3}{3\pi n^3} \left\{ \delta_{\ell,0} \left[\frac{31}{120} - 2\ell n(\alpha Z_{\text{eff}}) \right] \right.$$
$$\left. + \frac{3}{8} \frac{c_{\ell j}}{(2\ell + 1)} - \ell n \left[\frac{k_0(n\ell)}{Z_{\text{eff}}^2 R_\infty} \right] \right\} \qquad (50)$$

and the dependence of $c_{\ell j}$ on the quantum numbers ℓ and j is given by

$$c_{\ell j} = (\ell + 1)^{-1} \delta_{j,\ell+1/2} - \ell^{-1} \delta_{j,\ell-1/2} \qquad (51)$$

In Eq. (51), R_∞ denotes the infinite nuclear mass Rydberg constant, Z_{eff} is the effective nuclear charge, and $\delta_{m,n}$ is a Kronecker delta. Values of the Bethe logarithm $\ell n[k_0(n\ell)/R_\infty]$ have been tabulated as a function of the quantum numbers n and ℓ (Drake and Swainson, 1990).

The principal problem with the use of Eq. (50) for transitions from the *Li* ground state is that Z_{eff} is not known with any precision. Using a value of Z_{eff} that would be characteristic of a $Z = 3$ nucleus screened by a pair of $1s$ electrons leads to the value $\Delta E_{\text{QED}}(2, 0) = -0.08$ cm^{-1}. This value is about one-third the size of estimates based on more refined calculations (McKenzie and Drake, 1991; Feldman and Fulton, 1995). The other drawback of the application of Eq. (50) is that the many-electron nature of the correction is lost.

For transitions from higher excited doublet states, $\Delta E_{\text{QED}}(n, \ell)$ makes a negligible contribution to the transition energy, based on the current levels of precision available experimentally. For such transitions, the QED effects for the $1s^2$ core effectively cancel for the two states in question.

For a precise theoretical determination of the first ionization energy of *Li*, an improved estimate of ΔE_{QED} based on the three-electron nature of the problem is required. This can be determined using

$$\Delta E_{QED} = E_L(1s^2) - E_L(1s^2 2s) \tag{52}$$

where $E_L(1s^2)$ can be calculated from

$$E_{L,1}(1s^2) = \frac{4Z\alpha^3}{3}\langle\delta(\mathbf{r}_i)\rangle \left\{-2\ell n\alpha - \ell n(k_0/R_\infty) + \frac{19}{30} + 2.2962\pi\alpha Z\right\} \tag{53}$$

and

$$E_{L,2}(1s^2) = \alpha^3\left[\langle\delta(\mathbf{r}_{12})\rangle\left\{\frac{14}{3}\ell n\alpha + \frac{164}{15}\right\} - \frac{7}{6\pi}\lim_{a\to 0}\{\langle r_{12}^{-3}(a) \right.$$
$$\left. + 4\pi(\gamma + \ell na)\delta(\mathbf{r}_{12})\rangle\}\right] \tag{54}$$

where

$$r_{12}^{-3}(a) = \begin{cases} 0 & r_{12} \le a \\ r_{12}^{-3} & r_{12} > a \end{cases} \tag{55}$$

and γ is Euler's constant. Similarly, $E_L(1s^2 2s)$ can be determined from

$$E_{L,1}(1s^2 2s) = Z\alpha^3\left\{F(1s^2 2s)\right.$$
$$\left. \cdot \left\langle\sum_{i=1}^{3}\delta(\mathbf{r}_i)\right\rangle - \frac{4}{3}\ell n[(Z - \sigma)/Z]^2\left\langle\sum_{i=1}^{3}\delta(\mathbf{r}_i)\right\rangle\right\} \tag{56}$$

and

$$E_{L,2}(1s^2 2s) = \alpha^3\left[\left(\frac{14}{3}\ell n\alpha + \frac{164}{15}\right)\left\langle\sum_{i=1}^{3}\sum_{j>i}^{3}\delta(\mathbf{r}_{ij})\right\rangle\right.$$
$$\left. - \frac{7}{6\pi}\lim_{a\to 0}\left\{\left\langle\sum_{i=1}^{3}\sum_{j>i}^{3}[r_{ij}^{-3}(a) + 4\pi(\gamma + \ell na)\delta(\mathbf{r}_{ij})]\right\rangle\right\}\right] \tag{57}$$

In Eq. (56), $F(1s^2 2s)$ denotes a combination of one-electron functions $F(1s)$ and $F(2s)$, which can be written as a sum of one-electron quantum electrodynamic corrections (Drake, 1993; Johnson and Soff, 1985), and σ is a screening constant. Feldman and Fulton (1995) find a different result in place of Eq. (57); the factor 164/15 is found as $(129/15) - (3\pi/2)$.

The correction to the ionization energy of *Li* using Eqs. (52–57) is $-0.22(2)$ cm^{-1} (McKenzie and Drake, 1991) or -0.24 cm^{-1} (Feldman and Fulton, 1995). The uncertainty in this correction is a major component in the error associated

with the theoretical determination of the first ionization potential of *Li*. Further progress in this area will be needed as higher precision experimental data becomes available for the *Li* atom.

The previous discussion has focused on transitions involving the low-lying doublet states. Complications arise when more excited states are considered. No detailed calculations appear to have been published. For a state like $[(1s2p)\ {}^3P,3d]$ ${}^2D^o$, an estimate of the QED contribution to the term energy can be made by combining the ΔE_{QED} contributions to the ionization potentials of the $1s^2\ Li^+$, $1s^22s\ Li$ and $1s2p\ {}^3P\ Li^+$ states (Chen and Chung, 1994). Implicit in this type of calculation is the assumption that the contribution from the $3d$ electron is negligible. This can be verified to be a reasonable assumption using the one-electron formula, Eq. (50). A more problematic situation arises for states like $1s2s2p\ {}^4P$. It would probably be an inadequate approximation to estimate the QED contribution to the term energy of this state, using a combination of the ΔE_{QED} contributions to the ionization potentials of the $1s^2\ Li^+$, $1s^22s\ Li$ and $1s2s\ {}^3S\ Li^+$ states. The estimate could be improved by trying to determine the QED contribution of the $2p$ electron using the one-electron formula, but this would be a rather rough approximation in this case. For states such as $1s2s2p\ {}^4P$, where there would be expected to be significant correlation effects in the valence shell, the QED contribution should therefore be evaluated using the many-electron expression for ΔE_{QED}.

VIII. The First Ionization Potential

The calculation of the first ionization potential of *Li* has attracted considerable attention over many years. The ionization potential has been a benchmark property to test different computational techniques, some of which include many-body perturbation theory (Lindgren, 1985; Johnson *et al.*, 1987, 1988; Blundell *et al.*, 1989), CI (Chung, 1991; Weiss, 1992; Morrison *et al.*, 1996), CI-HY (Pipin and Bishop, 1992), MCHF (Tong *et al.*, 1993), and HY (Yan and Drake, 1995a; King *et al.*, 1998e).

The first ionization potential, I_1, can be determined from the formula

$$I_1 = E_{NR}(Li^+) - E_{NR}(Li) + \Delta E_{REL} + \Delta E_{MASS} + \Delta E_{QED} \qquad (58)$$

where the various terms in Eq. (58) have been defined previously in Eq. (22–24). A breakdown of the component contributions has been given recently by King (1997) and King *et al.* (1998e). The theoretical value of I_1 (in absolute a.u.) is $0.1981420(1)$ ($43487.14(2)$ cm^{-1}), which compares closely with the experimental value of $0.19814203(2)$ a.u. ($43487.150(5)$ cm^{-1}) (Johansson, 1959). The major sources of error in the theoretical determination of I_1 lie with ΔE_{REL} and ΔE_{QED}. A combined experimental–theoretical approach has been suggested by Yan and

Drake (1995a) to evaluate I_1. Because the experimental 2 ^2S–2 ^2P and 2 ^2P–3 ^2D transition energies are known to high precision, combining these values with the theoretical ionization energy of the 3 ^2D state leads to the precise value $I_1 = 43487.167(4)$ cm^{-1} (Yan and Drake, 1995a). A recalculation using more recent experimental results (Sansonetti *et al.*, 1995; Radziemski *et al.*, 1995) yields the value $I_1 = 43487.163(5)$ cm^{-1} (King, 1997). An essential advantage of this approach is that ΔE_{QED} for the 3 ^2D state is negligibly small.

A. TRANSITION ENERGIES

In Table 8, precise theoretical estimates are presented for the term energies of the lower-lying doublet states relative to the Li ground state. The term energies (relative to the ground state energy) are obtained theoretically using

$$T(^2X) = E_{\text{NR}}(^2X) - E_{\text{NR}}(1s^22s) + \Delta E_{\text{REL}} + \Delta E_{\text{MASS}} + \Delta E_{\text{QED}} \quad (59)$$

with

$$\Delta E_{\text{REL}} = E_{\text{REL}}(^2X) - E_{\text{REL}}(1s^22s) \quad (60)$$

$$\Delta E_{\text{MASS}} = E_{\text{MASS}}(^2X) - E_{\text{MASS}}(1s^22s) \quad (61)$$

$$\Delta E_{\text{QED}} = E_{\text{QED}}(^2X) - E_{\text{QED}}(1s^22s) \quad (62)$$

An alternative approach is to use a rearranged form of Eq. (21),

$$T(^2X) = I_1 + E_{\text{NR}}(^2X) - E_{\text{NR}}(Li^+) - \Delta E_{\text{MASS}} - \Delta E_{\text{REL}} - \Delta E_{\text{QED}} \quad (63)$$

with ΔE_{MASS}, ΔE_{REL} and ΔE_{QED} defined in Eqs. (22–24). Equation (63) has the advantage that the relativistic and quantum electrodynamic corrections need to be explicitly evaluated for only one three-electron state, rather than the two required for Eq. (59). This is partially offset by the need for a high-precision value of I_1. If the experimental result for I_1 is employed, we have a combined experimental–theoretical determination of $T(^2X)$, with the error resulting principally from the uncertainties in ΔE_{REL} and ΔE_{QED}. For a higher lying doublet state, ΔE_{REL} and ΔE_{QED} can be evaluated from one-electron formulas, with a corresponding reduction in the estimated uncertainty for $T(^2X)$ when Eq. (63) is used.

The E_{NR} values used to construct the theoretical entries in Table 8 are taken from Table 1 (the least-upper-bound result for each term energy was used). The relativistic corrections were taken from the references cited in Section V and the mass corrections (the E_{sms} component) were taken from Table 6. The QED corrections were estimated from the one-electron formula, Eq. (50), with Z_{eff} determined from

$$Z_{\text{eff}} = n[2\{E_{\text{NR}}(1s^2, Li^+) - E_{\text{NR}}(1s^2nx, {}^2X)\}]^{1/2} \quad (64)$$

TABLE 8

TABLE 8
LEVEL ENERGIES ABOVE THE GROUND STATE FOR THE
LOW-LYING DOUBLET STATES OF ^7Li.

State	Team energy (cm^{-1})	
	Experimental[a,b]	Theoretical[c]
$2s\,^2S_{1/2}$	0.0000	
$3s\,^2S_{1/2}$	27206.0952(10)	27206.09(5)
$4s\,^2S_{1/2}$	35012.0326(10)	35012.05(5)
	35012.0337(7)[d]	
$5s\,^2S_{1/2}$	38299.4627(10)	38299.6(2)
$6s\,^2S_{1/2}$	39987.586(3)	39994(7)
$2p\,^2P_{1/2}$	14903.648130(14)[e]	
$2p\,^2P_{3/2}$	14903.983468(14)[e]	
	[14903.871689(20)]	14903.86(11)
$3p\,^2P_{1/2}$	[30925.5530(10)	
$3p\,^2P_{3/2}$	30925.6494(10)	
	[30925.6173(14)]	30925.60(11)
$4p\,^2P_{1/2}$	36469.7542(15)	
$4p\,^2P_{3/2}$	36469.7943(15)	
	[36469.7809(21)]	36469.76(12)
$5p\,^2P_{1/2}$	39015.6988(20)	
$5p\,^2P_{3/2}$	39015.7199(20)	
	[39015.7129(28)]	39015.89(25)
$6p\,^2P_{1/2}$	40391.283(10)	
$6p\,^2P_{3/2}$	40391.295(10)	
	[40391.291(14)]	
$3d\,^2D_{3/2}$	31283.0505(10)	
	31283.0496(7)[d]	
$3d\,^2D_{5/2}$	31283.0866(10)	
	31283.0856(7)[d]	
	[31283.0722(14)]	31283.05(11)
$4d\,^2D_{3/2}$	36623.3360(10)	
	36623.3444(7)[d]	
$4d\,^2D_{5/2}$	36623.3511(10)	
	36623.3596(7)[d]	
	[36623.3451(14)]	36623.2(2)
$5d\,^2D_{3/2}$	39094.861(10)	
$5d\,^2D_{5/2}$	39094.869(10)	
	[39094.866(14)]	39094.8(2)
$6d\,^2D_{3/2,5/2}$	40437.220(20)	
$4f\,^2F_{5/2}$	36628.329(3)	
$4f\,^2F_{7/2}$	36628.336(3)	
	[36628.333(4)]	36627.9(7)
$5f\,^2F_{5/2}$	39097.499(15)	
$5f\,^2F_{7/2}$	39097.503(15)	
	[39097.501(21)]	39097.2(7)
$6f\,^2F_{5/2,7/2}$	40438.90(5)	

[a] Experimental data from Radziemski et al. (1995), except where noted.

[b] Level values are determined from the center of gravity of the hyperfine structure of the ground state. Center of gravity estimates are given in [ ].

[c] Theoretical values are calculated from Eq. (59) or Eq. (63).

[d] From Lorenzen and Niemax (1983).

[e] From Sansonetti et al. (1995).

For the P, D, and F states, the quantity to compare with the theoretical result is the center of gravity of the two level energies, that is

$$E_{\text{CG}} = \frac{\sum_{j=1}^{2}(2J_j + 1)E_j}{\sum_{j=1}^{2}(2J_j + 1)} \tag{65}$$

The agreement between theory and the recent experimental results (Windholz and Umfer, 1994; Sansonetti *et al.*, 1995; Radziemski *et al.*, 1995) is, in general, rather good. Because there are often no published uncertainties for $E_{\text{REL}}(^2X)$, we have made rough estimates of the errors, based on the numbers of digits the authors have quoted. The uncertainties for ΔE_{QED} for the lowest lying ^2X states are also very difficult to gauge, and an error estimate based on the difference between the result calculated using a one-electron approximation and more precise results for the ^2S ground state has been employed. The uncertainties for the other quantities that determine $T(^2X)$ are much less important, and do not have an impact on the final error estimates. The final error estimates reported in Table 8 are believed to be generous, but do involve some rough estimation.

Using Table 8, the theoretically determined transition energies between different levels—actually, between center of gravity estimates—are found to be in very close agreement with experimental results. To progress beyond the current precision levels will require a high-precision determination of E_{REL} for the states involved. Progress on this front has been limited by mathematical difficulties, a topic addressed earlier in Section V. Further progress on the calculation of ΔE_{QED} for systems beyond the two-electron level will also be required.

IX. Hyperfine Coupling Constants

The lithium atom has long served as a benchmark for testing various theoretical methodologies for calculating precise hyperfine coupling constants. High-precision experimental data are available for the coupling constants of the ground states of both ^6Li and ^7Li, and this serves as a valuable comparison point for the theoretical work.

The principal part of the magnetic Hamiltonian describing hyperfine interactions is

$$H_{\text{hfs}} = H_c + H_d + H_o + H_Q = H_{\text{mhfs}} + H_Q \tag{66}$$

where

$$H_c = \frac{8\pi}{3}\, g_J g_I \mu_{\text{B}} \mu_{\text{N}}\, \mathbf{I} \cdot \sum_{i=1}^{3} \mathbf{s}_i \delta(\mathbf{r}_i) \tag{67}$$

$$H_d = g_J g_I \mu_B \mu_N \mathbf{I} \cdot \sum_{i=1}^{3} [3(\mathbf{s}_i \cdot \mathbf{r}_i)\mathbf{r}_i - r_i^2 \mathbf{s}_i] r_i^{-5} \qquad (68)$$

$$H_o = 2g_I \mu_B \mu_N \mathbf{I} \cdot \sum_{i=1}^{3} \boldsymbol{\ell}_i r_i^{-3} \qquad (69)$$

$$H_Q = -\sum_{p=1}^{3} \sum_{i=1}^{3} (r_p^2 r_i^{-3}) P_2(\cos\theta_{ip}) \qquad (70)$$

In Eqs. (67–70), g_J is the electronic g-factor, g_I is the nuclear g-factor, μ_B is the Bohr magneton, μ_N is the nuclear magneton, $\mathbf{I}$ is the nuclear spin operator, $\mathbf{s}_i$ is the electron spin operator for electron i, $\delta(\mathbf{r}_i)$ is a Dirac delta function, $\boldsymbol{\ell}_i$, is the orbital angular momentum operator for electron i, P_n is a Legendre polynomial, and the p-summation is over protons. Equations (67–70) represent the Fermi contact hyperfine interaction, the spin dipolar hyperfine term, the orbital contribution, and the electric quadrupole interaction, respectively.

For a given J, it is possible to write effective operator forms:

$$H_c = a_{cJ} \mathbf{I} \cdot \mathbf{J} \qquad (71)$$

$$H_o = a_{oJ} \mathbf{I} \cdot \mathbf{J} \qquad (72)$$

$$H_d = a_{dJ} \mathbf{I} \cdot \mathbf{J} \qquad (73)$$

with an effective magnetic hyperfine operator defined by

$$H_m = A_J \mathbf{I} \cdot \mathbf{J} \qquad (74)$$

where

$$A_J = a_{cJ} + a_{oJ} + a_{dJ} \qquad (75)$$

To match up with theoretical calculations, the following connections to the various expectation values are employed:

$$f = \left\langle \Psi \left| 4\pi \sum_{i=1}^{3} \sigma_{zi} \delta(\mathbf{r}_i) \right| \Psi \right\rangle \qquad (76)$$

$$d = \left\langle \Psi \left| \sum_{i=1}^{3} \sigma_{zi} r_i^{-3} P_2(\cos\theta_i) \right| \Psi \right\rangle \qquad (77)$$

$$\ell = \left\langle \Psi \left| \sum_{i=1}^{3} r_i^{-3} \ell_{zi} \right| \Psi \right\rangle \qquad (78)$$

$$q = 2\left\langle \Psi \left| \sum_{i=1}^{3} r^{-3} P_2(\cos\theta_i) \right| \Psi \right\rangle \qquad (79)$$

with

$$a_{cJ} = \gamma_I \frac{\langle \mathbf{S} \cdot \mathbf{J} \rangle}{SJ(J + 1)} \left(\frac{g_J}{6}\right) f \tag{80}$$

$$a_{dJ} = \gamma_I \frac{[3\langle \mathbf{S} \cdot \mathbf{L}\rangle\langle \mathbf{L} \cdot \mathbf{J}\rangle - L(L + 1)\langle \mathbf{S} \cdot \mathbf{J}\rangle]}{SL(2L - 1)J(J + 1)} \left(\frac{g_J}{2}\right) d \tag{81}$$

$$a_{oJ} = \gamma_I \frac{\langle \mathbf{L} \cdot \mathbf{J} \rangle}{LJ(J + 1)} \left(\frac{g_J}{6}\right) \ell \tag{82}$$

and

$$\gamma_I = \frac{2\mu_B \mu_N \mu_I}{h a_0^3 I} \tag{83}$$

In Eq. (83), h is Planck's constant, a_0 is the Bohr radius, I is the nuclear spin, and μ_I is the nuclear magnetic moment. The expectation values in Eqs. (76–78) are also sometimes identified notationally with a_c, a_d, and a_o, respectively. In Eq. (76), σ_{zi} is the Pauli spin operator and satisfies $\sigma_{zi}\alpha(i) = \alpha(i)$ and $\sigma_{zi}\beta(i) = -\beta(i)$.

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

$$A_{1/2} = a_{c1/2} \tag{84}$$

It is convenient to simplify the notation by dropping the J dependence of a_λ, and express $A_{1/2}$ and $A_{3/2}$ in terms of $a_{\lambda 3/2}$. For the state $^2P_{3/2}$

$$A_{3/2} = a_c + a_o + a_d \tag{85}$$

and for the $^2P_{1/2}$ state

$$A_{1/2} = -a_c + 2a_o - 10a_d \tag{86}$$

The connection between $a_{\lambda 3/2}$ and $a_{\lambda 1/2}$ can be obtained directly from Eqs. (80–82). A third hyperfine coupling parameter, $A_{3/2,1/2}$, arises as an off-diagonal component,

$$A_{J,J-1} = \langle JI, M_J I | H_{\text{mhfs}} | (J - 1)I, M_J I \rangle, \tag{87}$$

leading to

$$A_{3/2,1/2} = -a_{c3/2} + \frac{1}{2} a_{o3/2} + \frac{5}{4} a_{d3/2} \tag{88}$$

Slightly different definitions of a_λ can be found in the literature (see, for example, Lindgren and Rosén, 1974), with the result that Eqs. (85, 86, 88) will also appear in a slightly different form.

The electric quadrupole constant is defined by

$$b_q = \langle LSI, \ LSI | H_Q | LSI, \ LSI \rangle \tag{89}$$

The determination of the hyperfine constant for the $^2S_{1/2}$ state of Li has attracted extensive theoretical attention (Larsson, 1968; Lindgren, 1985; King and Shoup, 1986; King, 1989; Panigrahy *et al.* 1989; Blundell *et al.*, 1989; King and Bergsbaken, 1990; Mårtensson-Pendrill and Ynnerman, 1990; Sundholm and Olsen, 1990; Esquivel *et al.*, 1991; Carlsson *et al.*, 1992; Tong *et al.*, 1993; Shabaev *et al.*, 1995; Bieroń *et al.*, 1996; Yan *et al.*, 1996b; King, 1998b). A collection of references to earlier work on the Li ground state is given by King (1997). For the excited S states of Li, the most precise theoretical values available have been determined by Blundell *et al.* (1989), King (1991), Jönsson *et al.* (1995), and Yan *et al.* (1996b). There has been considerable interest in the theoretical determination of the hyperfine coupling constants of the $^2P_{1/2}$ and $^2P_{3/2}$ states (Ahlenius and Larsson, 1973, 1978; Garpman *et al.*, 1975, 1976; Glass and Hibbert, 1976; Lindgren, 1985; Johnson *et al.*, 1987; Blundell *et al.*, 1989; Mårtensson-Pendrill and Ynnerman, 1990; Sundholm and Olsen, 1990; Carlsson *et al.*, 1992; Tong *et al.*, 1993; Bieroń *et al.*, 1996; Yan *et al.*, 1996b). Other excited states of Li have received far less attention; with only more approximate results being available (Goddard, 1968; Ladner and Goddard, 1969; Lunell, 1973).

The availability of a number of experimental hyperfine coupling constants has undoubtedly been a stimulus for theoretical developments. A good review of the earlier experimental work has been given by Arimondo *et al.* (1977). Experimental results are available for the $2\ ^2S_{1/2}$, $3\ ^2S_{1/2}$, and $4\ ^2S_{1/2}$ states (Beckmann *et al.*, 1974, Vadla *et al.*, 1987; Stevens *et al.*, 1995; Kowalski *et al.*, 1978), and the $2\ ^2P_{1/2}$, $2\ ^2P_{3/2}$, $3\ ^2P_{1/2}$, $3\ ^2P_{3/2}$, and $4\ ^2P_{3/2}$ states (Ritter, 1965; Brog *et al.*, 1967; Budick *et al.*, 1966; Isler *et al.*, 1969; Orth *et al.*, 1975 ; Nagourney *et al.*, 1978; Shimizu *et al.*, 1987; Carlsson and Sturesson, 1989). The high precision measurement of $A_{1/2}$ for the ground state of Li presents a significant computational challenge. For the ground state of the isoelectronic ion Be^+, the experimental precision is higher still, and the difference between experiment (Wineland *et al.*, 1983) and theory (King, 1988; Yan *et al.*, 1996b) is even more pronounced.

Table 9 presents a summary of some of the high-precision values of the Fermi contact term (Eq. (76)) and the hyperfine coupling constants for the ^2S states of Li. These values are mostly based on nonrelativistic calculations in the infinite nuclear mass approximation. To determine the coupling constant $A_{1/2}$ for the $^2S_{1/2}$ states, the following relationship is employed:

$$A_{1/2} = \left(\frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} \right) \left(\frac{g_J \mu_I}{3I} \right) f \tag{90}$$

TABLE 9

EXPECTATION VALUES AND HYPERFINE COUPLING CONSTANTS FOR THE
LOW-LYING ^2S STATES OF ^7Li.

State	f_{NR} (a.u.)	f (a.u.)	$A_{1/2}$ (MHz)	Reference
$2\,^2S$	2.906	2.907	401.9	Larsson (1968)
	2.9041	2.905	401.6	King and Shoup (1986)
	2.9064	2.9072	401.91	King (1989)
	2.9071	2.9079	402.01	King and Begrsbaken (1990)
	2.9039	2.9047	401.56	Sundholm and Olsen (1990)
	2.9047	2.9055	401.67	Carlsson et al. (1992)
	2.9051	2.9059	401.73	Tong et al. (1993)
		2.904	401.5	Shabaev et al. (1995)
		2.90578	401.714	Bieroń et al. (1996)
	2.905922(50)	2.90575(22)	401.71(3)	Yan et al. (1996b)
		expt.	401.7520433(5)	Beckmann et al. (1974)
$3\,^2S$			93.24(2)	Blundell et al. (1989)
	0.670	0.670	92.7	King (1991a)
	0.67335	0.67372	93.139	Jönsson et al. (1995)
	0.673405(50)	0.673368(86)	93.091(12)	Yan et al. (1996b)
		expt.	94.68(22)	Stevens et al. (1995)
$4\,^2S$	0.254	0.254	35.	King (1991a)
	0.25327	0.25336	35.026	Jönsson et al. (1995)
		expt.	36.4(40)	Kowalski et al. (1978)
$5\,^2S$	0.11	0.11	16	King (1991a)

where

$$C = \left(\frac{\mu_0\mu_B\mu_N}{2\pi h a_0^3}\right)$$

$$= \alpha^2 c R_\infty (m_e/m_p)$$

$$= 95.410673(9) \text{ MHz} \tag{91}$$

In Eq. (91), m_p is the proton mass, c is the speed of light, and μ_0 is the vacuum permeability.

Using the most recent estimates for the fundamental constants (Cohen and Taylor, 1987), and the revised values for the nuclear moments of ^6Li and ^7Li (King, 1997), Eqs. (80–82) can be expressed for the $^2P_{3/2}$ state of ^7Li as,

$$a_c = 69.123175(44)f/J \tag{92}$$

$$a_d = 207.36953(13)d/J \tag{93}$$

$$a_o = 207.13122(11)\ell/J \tag{94}$$

and for $^2P_{3/2}$ state of ^6Li:

$$a_c = 26.174020(20)f/J \qquad (95)$$

$$a_d = 78.522059(60)d/J \qquad (96)$$

$$a_o = 78.431823(53)\ell/J \qquad (97)$$

In Eqs. (92–97), f, d, and ℓ are in a.u. and a_c, a_d and a_o are in MHz.

To employ Eq. (90), the f value must be corrected for the finite nuclear mass, for relativistic effects and for quantum electrodynamic corrections, that is

$$f = f_{NR} + \Delta f_{MASS} + \Delta f_{REL} + \Delta f_{QED} \qquad (98)$$

The correction for finite nuclear mass is handled by multiplying f_{NR} by $(1 - \mu/M)^3$, leading to the result

$$\Delta f_{MASS} = -\frac{3\mu}{M}\left[1 - \frac{\mu}{M} + \frac{1}{3}\left(\frac{\mu}{M}\right)^2\right]f_{NR} \approx -\frac{3\mu}{M}f_{NR} \qquad (99)$$

For ^7Li this correction is -0.000682 a.u. Δf_{REL} has been estimated in several ways. One approach involves a comparison of MCHF and MCDF calculations using different basis sets, and then estimating Δf_{REL} using an extrapolation procedure (Tong *et al.*, 1993). An alternative approach is based on a one-electron relativistic correction to $|\Psi(0)|^2$ (Yan *et al.*, 1996b). For the $^2S_{1/2}$ ground state of *Li*, several estimates of Δf_{REL} lead to approximately 0.0017 a.u., with the error in the second significant digit being roughly estimated as ±3, based on the spread of the calculated values. Relatively little work is available on the determination of Δf_{QED}. Three rather different estimates for the ground state of *Li* are available: -0.0002 a.u. (Panigrahy *et al.*, 1989), 0.00336 a.u. (Bieroń *et al.*, 1996), and $-0.000918(47)$ (Yan *et al.*, 1996b). It should be clear from the preceding remarks on Δf_{REL} and Δf_{QED} that these two contributions are the principal factors that prevent a more precise theoretical determination of the hyperfine coupling constants from being made.

A list of calculated $A_{1/2}$ values for the ^2S states of *Li* is presented in Table 9. For the ^2S ground state, the corrections $\Delta f_{REL} = 0.0017$ a.u., $\Delta f_{QED} = -0.0002$ a.u., and the mass correction given above have been applied, unless the authors included values for these contributions. For the excited ^2S states, the Δf_{QED} correction was ignored, and $\Delta f_{REL} \approx 0.0006$ a.u. (Yan *et al.*, 1996b) was employed for the 3 ^2S state and ignored for the 4 ^2S state. The precision of the experimental results for the excited ^2S states is not sufficiently high to provide a test of the calculated relativistic and QED corrections to f. Only modest agreement between theory and experiment is found for the hyperfine constants of the low-lying excited doublet S states.

In Table 10 a summary is presented for some of the higher precision theoretical

TABLE 10

EXPECTATION VALUES (EQS. (76–79)) AND HYPERFINE COUPLING CONSTANTS FOR THE LOW-LYING ^2P STATES OF ^7Li.

State	f (a.u.)	d (a.u.)	ℓ (a.u.)	q (a.u.)	$A_{1/2}$ (MHz)[a]	$A_{3/2}$ (MHz)[a]	$A_{3/2,1/2}$ (MHz)[a]	Reference
$2\,^2P$	−0.214619	−0.013525	0.063218	−0.022824	45.667	−2.992	11.965	Nesbet (1970)
	−0.2162	−0.0134	0.0634	−0.0202	46.0	−3.07	12.0	Ahlenius and Larsson (1973)
	−0.2086	−0.0135	0.0628	−0.0224	45.6	−2.81	11.6	Ahlenius and Larsson (1978)
	−0.2210(3)[b]	−0.013476(2)[b]	0.06308(1)[b]	−0.022664(4)[b]	46.24	−3.337	12.21	Lindgren (1985)
					45.96(1)	−3.03		Blundell et al. (1989)
	−0.2158(15)	−0.01346(2)	0.06304(8)	−0.02253(8)	45.96	−3.100	11.97	Sundholm and Olsen (1990)
	−0.2159(15)[b]	−0.01346(2)[b]	0.06303(8)[b]	−0.02253(8)[b]	45.96	−3.106	11.98	Sundholm and Olsen (1990)
					45.789	−2.879		Mårtensson-Pendrill and Ynnerman (1990)
	−0.2155	−0.01346	0.06305	−0.02255	45.95	−3.085	11.96	Carlsson et al. (1992)
	−0.21705	−0.01341	0.06308	−0.02187	45.96	−3.145	12.040	Tong et al. (1993)
					45.989[c]	−3.1060[c]		Bieroń et al. (1996)
					45.977[b]	−3.058[b]		Godefroid et al. (1996)
								Yan et al. (1996b)
	−0.214860 (extrapolated estimate)							
	−0.214783(50)							Yan et al. (1996b)
				expt.	45.914(25)	−3.055(14)	11.85(35)	Orth et al. (1975)
$3\,^2P$	−0.0677	−0.00354	0.0177	−0.00708	12.9	−1.16	3.73	Lunell (1973)
		−0.003988	0.01868	−0.006832				Garpman et al. (1975)
				expt.	13.5(2)	−0.96(13)		Budick et al. (1966)
				expt.		−0.965(20)		Isler et al. (1969)
				expt.	13.7(12)	−1.036(16)		Nagourney et al. (1978)
$4\,^2P$	−0.0289	−0.00149	0.00746	−0.00298	5.45	−0.51	1.59	Lunell (1973)
		−0.001682	0.007858	−0.002892				Garpman et al. (1975)
				expt.		−0.41(2)		Isler et al. (1969)

[a] Hyperfine coupling constants have been recomputed using Eqs. (85, 86, 88, 92–94).

[b] Includes relativistic and mass corrections.

[c] Includes QED, relativistic, and mass corrections.

results for the terms f, d, ℓ, and q, along with the hyperfine coupling constants $A_{1/2}$, $A_{3/2}$, $A_{3/2,1/2}$, computed from Eqs. (85, 86, 88) . The precision of the experimental results for the P-states is currently not very high, and as a consequence, the relativistic and QED corrections to the hyperfine constants of these excited states have received less attention, relative to the efforts expended on the ^2S ground state.

The quadrupole moment, Q, is related to the electric field gradient (q) at the nucleus. There is a scatter of the computed results derived from different theoretical approaches: see Diercksen *et al.*, (1988) for a tabulation of results. Precise theoretical estimates for Q in barns (1 b = 1 $\times$ 10^{-28} m^2) are: $Q(^7Li)$ = $-0.04055(80)$ b (Diercksen *et al.*, 1988) and $Q(^6Li)$ = -0.00083 b (Sundholm *et al.*, 1984). The result for ^7Li is in good agreement with the experimental result $Q(^7Li)$ = $-0.041(6)$ b (Orth *et al.*, 1975). Unfortunately, the uncertainty in the experimental result is too large to provide a severe test for different computational approaches.

X. Other Properties

Space limitations do not allow us to discuss all the recent progress on calculating the different properties of the lithium atom. There are, however, three areas where very significant progress has been made, and these are discussed briefly next.

A. POLARIZABILITIES

The static dipole polarizability of the ground state of Li has been of theoretical interest for a long time. A summary of the more significant calculations performed over the past thirty years is given by King (1997). Several relatively recent calculations (Pipin and Bishop, 1992; Wang and Chung, 1994; Yan *et al.*, 1996a) settle on the value of 164.1 a.u. (Yan *et al.* 1996a quote a value 164.116(2) a.u.). This result is in agreement with the best experimental value available, 164.0(34) a.u. (Molof *et al.*, 1974); unfortunately, the error associated with this experimental work is too large to provide a severe test for the theoretical calculations. A significant reduction in the error of the experimental measurement will be needed to induce theoretical developments beyond the nonrelativistic level.

There has been continuing interest in the calculation of the quadrupole polarizability and the hyperpolarizability for the ground state of Li (for a recent summary of progress see King, 1997). Unfortunately, there are no experimental measurements for Li to compare with the results of calculations. The hyperpolarizability is a particularly difficult property to determine. It is only recently (Pipin and Bishop, 1992; Kassimi and Thakkar, 1994; Jaszunski and Rizzo, 1996) that both the correct sign and the magnitude have been determined.

There has been some theoretical attention directed at evaluating the polariza-
bilities of some of the excited states of Li, including high-lying Rydberg states
(Schmieder et al., 1971; Shestakov et al., 1972; Adelman and Szabo, 1973; Man-
akov et al., 1975; Sims et al., 1976b; Beck and Nicolaides, 1977; Redmon and
Browne, 1977; Davydkin and Zon, 1982; Davydkin and Ovsiannikov, 1986;
Chung, 1992; Pipin and Bishop, 1993; Themelis and Nicolaides, 1992, 1995;
Ponomarenko and Shestakov, 1993; Mérawa et al., 1994). The principal experi-
mental result available is a measurement of the Stark shift of the lithium D_1
line $(1s^2 2s\ ^2S_{1/2} - 1s^2 2p\ ^2P_{1/2})$ (Hunter et al., 1991; Windholz et al., 1992),
which is directly related to the difference in the scalar polarizabilities (α_0) of the
two states involved in the transition. This experimental result offers a valuable
check on the theoretically determined $\alpha_0(^2P)$. The Stark shift of the D_2 line
$(1s^2 2s\ ^2S_{1/2} - 1s^2 2p\ ^2P_{3/2})$ has also been measured (Windholz et al., 1992) and this
allows the tensor polarizability, α_2, for the $^2P_{3/2}$ state to be determined. The best
calculations of α_0 and α_2 (Pipin and Bishop, 1993) are found to be in very good
agreement with the experimental results.

B. OSCILLATOR STRENGTHS

For an electric dipole transition, the oscillator strength is given by

$$f_{if,\ell} = \frac{2\Delta E}{3g_i} \left| \left\langle \Psi_i \left| \sum_{j=1}^{3} \mathbf{r}_j \right| \Psi_f \right\rangle \right|^2 \tag{100}$$

$$f_{if,\nu} = \frac{2}{3g_i \Delta E} \left| \left\langle \Psi_i \left| \sum_{j=1}^{3} \nabla_j \right| \Psi_f \right\rangle \right|^2 \tag{101}$$

$$f_{if,a} = \frac{2Z^2}{3g_i(\Delta E)^3} \left| \left\langle \Psi_i \left| \sum_{j=1}^{3} \frac{\mathbf{r}_j}{r_j^3} \right| \Psi_f \right\rangle \right|^2 \tag{102}$$

In Eqs. (100–102), ΔE denotes the transition energy between the initial and final
states expressed in a.u., and g_i is the statistical weight of the initial state. An im-
plicit summation over degeneracies is assumed for both states involved in the
transition. Equations (100–102) represent the dipole length, dipole velocity, and
dipole acceleration forms, respectively. These relationships are all mathematically
equivalent when exact eigenfunctions are employed. Refinements to Eqs. (100–
102) are necessary when the effects of finite nuclear mass are considered (Yan and
Drake, 1995b). When approximate wave functions are utilized, agreement be-
tween the different forms is sometimes taken as a sign of a better calculation, but
there are known risks associated with drawing this inference. The dipole accelera-
tion form is infrequently evaluated. The transition moment involved in the evalua-
tion of $f_{if,a}$ is sensitive to the near-nuclear region of configuration space, and this
is a region that is more difficult to account for theoretically in the standard varia-
tional approach.

The other property commonly reported is the multiplet line strength, S. This is connected to the oscillator strength by the relationship

$$f_{if} = \frac{2}{3g_i} \Delta E \, S_{if} \tag{103}$$

where ΔE and S_{if} are both expressed in a.u.

The calculation of a precise value for the $1s^2 2s \, {}^2 S_{1/2} - 1s^2 2p \, {}^2 P_{1/2}$ oscillator strength has attracted considerable attention. Gaupp *et al.* (1982) reported a measurement of this oscillator strength, $f = 0.7416(12)$, with an uncertainty of 0.16%, making it one of the most precise measurements of its kind. A number of theoretical results emerged shortly thereafter, using a diverse variety of techniques, including MBPT, CI, CI-HY, MCHF, HY (Fischer, 1988; Peach *et al.*, 1988; Blundell *et al.*, 1989; Mårtensson-Pendrill and Ynnerman, 1990; Weiss, 1992; Pipin and Bishop, 1992; Tong *et al.*, 1993; Chung, 1993; Liaw and Chiou, 1994; Brage *et al.*, 1994; Yan and Drake, 1995b), together with some earlier results (Ahlenius and Larsson, 1973; Sims *et al.*, 1976a), made it apparent that despite the quoted precision, the experimental result of Gaupp *et al.* was slightly low. Most of the theoretical results were in the range 0.7467–0.748, with the highest precision result being 0.7469572(10) in the infinite nuclear mass approximation, and 0.7467871(10) for ${}^7Li$ (Yan and Drake, 1995b). Two later measurements by Carlsson and Sturesson (1989) and McAlexander *et al.* (1995) gave results 0.7439(55) and 0.7502(44), respectively. These were in closer agreement with the theoretical results, but the larger uncertainties left the issue unresolved. The most recent measurement of Volz and Schmoranzer (1996) gives the value 0.7467(16), which is in excellent agreement with a number of the theoretical calculations. The outstanding work of Yan and Drake (1995b) and of the most recent experimental measurements will probably end discussion of this discrepancy between theory and experiment.

Quantum Monte Carlo (QMC) calculations by Barnett *et al.* (1992, 1995) were found to support the experimental result of Gaupp *et al.* The most recent result of these authors was 0.7431(6). The current applications of the QMC method do not reach the precision levels obtainable by the HY technique, so it appears that the error limit is too optimistic in these QMC calculations. Because the QMC approach is a useful computation technique, particularly for larger electronic systems, there should be some interest in using the D_1 line oscillator strength of Li as a test property to refine the technique.

Less attention has been directed at the calculation of oscillator strengths for other transitions of Li. The interested reader can pursue this topic with the following works (Lunell, 1975; Caves, 1975; Sims *et al.*, 1976a; Martin and Wiese, 1976; Pipin and Bishop, 1992; Yan and Drake, 1995b).

C. LIFETIMES

Closely tied to the previous discussion is the topic of lifetimes. The radiative life-time of an excited level k is given by

$$\tau_k = \left(\sum_n A_{kn} \right)^{-1} \tag{104}$$

where A_{kn} is a transition probability and the summation is over all levels of the atom that have an energy less than E_k. If only one decay channel is possible (say i), Eq. (104) simplifies to

$$\tau_k = A_{ki}^{-1} \tag{105}$$

The transition probability can be calculated from

$$A_{ki} = \frac{8\pi^2 \mu_0 e^2 c}{m_e \lambda^2} \frac{g_i}{g_k} f_{ik} \tag{106}$$

where e is the absolute value of the electronic charge, λ is the wavelength of the transition, and the other symbols have been introduced previously. Using values of the fundamental constants from Cohen and Taylor (1987), Eq. (106) can be simplified to

$$A_{ki} = 0.66702532(44)(\Delta E)^2 \frac{g_i}{g_k} f_{ik} \tag{107}$$

where ΔE is the transition energy expressed in cm^{-1}.

A number of theoretical and experimental lifetimes for various excited levels of Li have been tabulated by Theodosiou and coworkers (1984, 1991). The life-time of the $2\,{}^2P_{1/2}$ level of Li has been well studied experimentally and theoreti-cally. The most precise theoretical result for the $2\,{}^2P$ term is 27.117301(36) ns (Yan and Drake, 1995b), which is in excellent agreement with the very recent experimental measurement of Volz and Schmoranzer (1996), who find a value of 27.11(6) ns, and McAlexander *et al.* (1996) who obtained 27.102(7) ns. The latter results improve the earlier experimental value of Gaupp *et al.* (1982), who ob-tained 27.29(4) ns. Relativistic effects were not accounted for in the calculations of Yan and Drake, but this appears not to be an important issue given the present accuracy levels of the most recent experimental work.

XI. Outlook

The lithium atom will continue to play the role of a benchmark system in testing new computational methodologies. For many properties, there are now available

a number of high-precision estimates, which can serve as valuable reference points for testing different theoretical approaches. The precision level of the calculations for certain properties has progressed to the point where the theoretical results can serve as both a guide and a calibration marker for some experimental measurements.

The lithium atom will also continue to be studied for its own intrinsic interest. There are several areas where theoretical progress is desirable and likely to occur in the next few years. Improved precision determination of the relativistic corrections to the energy levels is a priority problem. Advances in this area will be directly tied to solving various recalcitrant integration problems. Resolution of these mathematical issues will improve the precision of a number of calculated ionization potentials, the accuracy of which is currently limited in part by the uncertainties associated with the relativistic corrections.

Improved calculations of the hyperpolarizability will pose a significant challenge. With the recent progress on high-precision calculations of the low-lying excited states, we might be optimistic that considerable progress can be made on the theoretical evaluation of several of the polarizabilities. There are a number of experimental opportunities available for these properties. An improved precision measurement of the static polarizability would provide an important check for some of the high-precision theoretical results of this property that have become available in the last few years.

Recently, there has been a substantial increase in the precision level for the experimental determination of some of the low-lying energy levels for ^6Li and ^7Li. These measurements provide a stimulus for a theoretical examination of some of the smaller contributions to the term energies. Currently, a significant fraction of the uncertainty for the theoretical determination of the first ionization potential arises from the correction ΔE_{QED}. There is a clear need for additional work by the QED theorists to improve the precision level of calculations of ΔE_{QED} for many-electron atoms. The nonrelativistic calculation of the low-lying energy levels has progressed significantly over the past ten years. There has been recent theoretical (Drachman and Bhatia, 1995; Bhatia and Drachman, 1997) and continuing experimental advances (Liang *et al.*, 1986; Day *et al.*, 1994; Rothery *et al.*, 1995; Hoogenraad *et al.*, 1995; Stevens *et al.*, 1996; Storry *et al.*, 1997) in the study of the Rydberg states of Li. The high-lying states will provide the next computational challenge. Brute force application of the standard variational technique is not likely to be very successful for the higher lying Rydberg levels.

Improved calculations of the hyperfine coupling constants for the ground and excited states will require combined efforts on several fronts. The determination of precise Fermi contact contributions requires wave functions of high quality in the near nuclear region. Improved procedures to build wave functions that are highly accurate in this region, rather than just relying on the output from the standard variational approach, appear to be needed. Improved ways to determine the

relativistic and QED contributions must be found. For the $2\,^2S_{1/2}$ ground state of ^6Li and ^7Li, the experimentalists have measured results of high precision; it is now up to the theorists to accept the challenge of calculating these constants to high precision. Two related properties, the hyperfine anomaly and the hyperfine pressure shift, have received very little theoretical attention for the lithium atom. A theoretical study of the hyperfine anomaly might provide an avenue for the determination of useful nuclear structure information.

Over the past twenty-five years there has been a close interplay between theoretical and experimental studies of the properties of the ground and excited states of atomic lithium. This trend will likely be maintained in the foreseeable future. Advances in computer technology have played a pivotal role in recent theoretical progress, and continued technological progress will be an integral component of the theoretical advances that occur in the future.

XII. Acknowledgments

XIII. References

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