

# High-Precision Calculations of the Hyperfine Constants and Some Selected Transition Energies for the Low-Lying $^4S$ Levels of the Lithium Atom

Frederick W. King

High-precision Hylleraas-type calculations of the hyperfine constants for the four lowest excited  $1s2sns\ ^4S^e$  ( $n = 3-6$ ) levels of the lithium atom are reported. The transition energies from the lowest  $^4P^o$  term to the  $1s2sns\ ^4S^e$  ( $n = 3-6$ ) levels for the stable isotopes  $^6\text{Li}$  and  $^7\text{Li}$  are evaluated. A number of addition expectation values for the four levels

studied are also reported, including some moments of the electron–nuclear separation, the electron–electron separation, and the specific mass-shift operator. © 2013 Wiley Periodicals, Inc.

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## Introduction

The excited quartet levels of the lithium atom have attracted considerable experimental<sup>[1–7]</sup> and theoretical attention,<sup>[8–30]</sup> though these levels have been studied significantly less extensively than both the ground state and some of the low-lying excited levels of various symmetries for this atomic system.<sup>[26,31]</sup>

The lowest excited  $1s2sns\ ^4S^e$  ( $n = 3, 4, \dots$ ) levels of the lithium atom lie energetically well above the lithium ground state, and this has probably contributed to the absence of experimental studies of the hyperfine structure of these levels. A focus of this study is the accurate calculation of the nonrelativistic contributions to the hyperfine constants for the four levels  $1s2sns\ ^4S^e$  ( $n = 3-6$ ) of the two stable isotopes  $^6\text{Li}$  and  $^7\text{Li}$ .

The  $1s2s2p\ ^4P^o$  configuration is the lowest lying quartet level for the lithium atom.<sup>[2,8]</sup> The transition energy from this level to the lowest  $1s2s3s\ ^4S^e$  level has been of interest for some time.<sup>[1,2,6–8,11,12,16,21,23]</sup> One of the early accurate observations of this transition was an unassigned line in the study of the electronic spectrum of  $\text{Li}^+$  by Herzberg and Moore.<sup>[1]</sup> In this study, the transition energies from  $1s2s2p\ ^4P^o$  to the four levels  $1s2sns\ ^4S^e$  ( $n = 3-6$ ) are evaluated and compared with both other theoretical determinations of these transition energies as well as some of the available experimental results.

The quartet  $S$  levels of lithium are attractive computational targets because the few-electron nature of the system makes it amendable to high-precision calculations. For the different computational approaches that have been used to study Li, the reader is referred to the reviews.<sup>[26,31]</sup> Transition energies between different core excited states of few-electron systems are also a feature of interest, and this has attracted a good deal of attention.<sup>[7]</sup>

## Theoretical Approach

The nonrelativistic portion of the variational calculations was carried using trial Hylleraas-type wave functions of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = A \sum_{\kappa=1}^N c_{\kappa} r_1^{i_{\kappa}} r_2^{j_{\kappa}} r_3^{k_{\kappa}} r_{12}^{l_{\kappa}} r_{13}^{m_{\kappa}} r_{23}^{n_{\kappa}} e^{-\alpha_{\kappa} r_1 - \beta_{\kappa} r_2 - \gamma_{\kappa} r_3} \chi_{\kappa}, \quad (1)$$

where  $A$  is the three-electron antisymmetrizer,  $c_{\kappa}$  denotes the expansion coefficients,  $\chi_{\kappa}$  is the spin eigenfunction, in this work taken to be  $\alpha(1)\alpha(2)\alpha(3)$ ,  $r_i$  designates the electron–nuclear separation distance for electron  $i$ ,  $r_{ij}$  is the interelectronic separation distance between electrons  $i$  and  $j$ , and  $N$  represents the number of terms in the expansion. The nonlinear exponents  $\alpha_{\kappa}$ ,  $\beta_{\kappa}$ , and  $\gamma_{\kappa}$  are each  $>0$ , and the integer indices  $\{i_{\kappa}, j_{\kappa}, k_{\kappa}, l_{\kappa}, m_{\kappa}, n_{\kappa}\}$  are each  $\geq 0$ . Extensive optimization of the nonlinear exponents was carried out for each of the separate excited levels considered in the present investigation. As each term was added to build the basis set, a stochastic optimization approach was used on a grid that encompassed the expected exponent sizes. The standard infinite nuclear mass nonrelativistic approach was used.

For the evaluation of the hyperfine constants in this work, the following background will be useful for the reader. The Fermi contact operator is given by

$$H_F = \frac{2}{3} \mu_0 g_e g_I \mu_B \mu_N \mathbf{I} \cdot \sum_{i=1}^3 \delta(\mathbf{r}_i) \mathbf{s}_i, \quad (2)$$

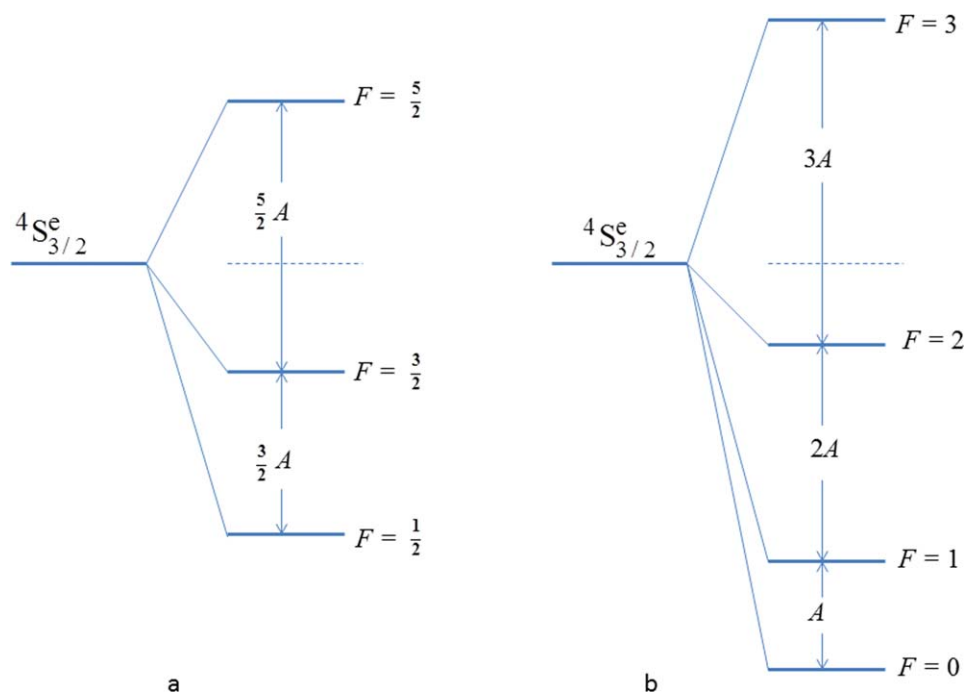
where  $\mu_0$  is the vacuum permeability,  $g_e$  is the electronic  $g$  factor which includes the electron magnetic moment anomaly,  $g_I$  is the nuclear  $g$  factor,  $\mu_B$  and  $\mu_N$  are the Bohr and nuclear magneton, respectively,  $\mathbf{I}$  is the nuclear spin operator,  $\mathbf{s}_i$  is the electron spin operator for electron  $i$ , and  $\delta(\mathbf{r}_i)$  is the Dirac delta distribution. The effective operator form is given by

F. W. King

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

E-mail: fking@uwec.edu

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**Figure 1.** Hyperfine intervals for the  $4S_{3/2}$  levels for  ${}^6\text{Li}$  (Fig. 1a) and for  ${}^7\text{Li}$  (Fig. 1b) with the numerical values of the hyperfine constants given in Table 5. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$$H_F = hA_J \mathbf{I} \cdot \mathbf{J}, \quad (3)$$

where  $h$  denotes Planck's constant,  $\mathbf{J}$  is the total angular momentum operator, and  $A_J$  is the hyperfine constant (in Hz). The subscript  $J$  on  $A$  is dropped in the sequel. Writing  $F = I + J$  and squaring allows the hyperfine energy levels to be written as:

$$W(F) = \frac{hA}{2} \{F(F+1) - I(I+1) - J(J+1)\}, \quad (4)$$

and the energy separation between adjacent hyperfine levels can be expressed as

$$W(F) - W(F-1) = hAF. \quad (5)$$

For the two naturally occurring isotopes of Li, the nuclear spins are: for  ${}^6\text{Li}$ ,  $I = 1$  and for  ${}^7\text{Li}$ ,  $I = 3/2$ . The hyperfine structure for the  $4S$  levels for  ${}^6\text{Li}$  and  ${}^7\text{Li}$  is shown in Figure 1. The center of gravity of the hyperfine structure is such that

$$\sum_F (2F+1) W(F) = 0, \quad (6)$$

and the spacing in the separate Figures 1a and 1b are shown approximately to scale.

The expectation value of the Fermi contact term is most commonly reported in the form:

$$f = \left\langle \psi \left| 4\pi \sum_{i=1}^3 \delta(\mathbf{r}_i) \sigma_{z_i} \right| \psi \right\rangle \quad (7)$$

where the operator  $\sigma_{z_i}$  acts on the electron spin levels  $\alpha(i)$  and  $\beta(i)$  in the following manner:  $\sigma_{z_i} \alpha(i) = \alpha(i)$  and  $\sigma_{z_i} \beta(i) = -\beta(i)$ . The connection between  $f$  and the

nonrelativistic contribution to the hyperfine constant, denoted as  $A_{\text{NR}}$ , can be expressed as

$$A_{\text{NR}} = \frac{\mu_0 \mu_B \mu_N \mu_I}{2\pi h a_0^3 I} \frac{g_e \langle \mathbf{S} \cdot \mathbf{J} \rangle}{6 SJ(J+1)} f, \quad (8)$$

where  $a_0$  is the Bohr radius and  $\mathbf{S}$  is the total spin operator. This result can be rewritten for the  $4S_{3/2}$  levels as

$$A_{\text{NR}} = \frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} \frac{g_e \mu_I}{9I} f \equiv C \frac{g_e \mu_I}{9I} f. \quad (9)$$

The collection of constants denoted by  $C$  can be rewritten in terms of fundamental constants that collectively are known with greater accuracy, so that

$$C = \frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} = \alpha^2 c R_\infty (m_e/m_p) = 95.410\,660\,37(10) \text{ MHz}, \quad (10)$$

where  $\alpha$  is the fine structure constant,  $c$  is the speed of light,  $R_\infty$  is the Rydberg constant, and  $m_e$  and  $m_p$  are the mass of the electron and proton, respectively. Using the most recent CODATA values<sup>[32]</sup> for the various contributions yields the value of  $C$  given in eq. (10). The error estimate is indicated in parenthesis. The nuclear moments needed to evaluate eq. (2) were taken from Ref. [33]. The corrections for diamagnetic shielding for the lithium isotopes 6 and 7 were re-evaluated as discussed in Ref. [31].

## Nonrelativistic Results

The convergence behavior of the nonrelativistic energy ( $E_{\text{NR}}$ ) for each of the levels studied is shown in Table 1. A comparison of the  $E_{\text{NR}}$  values with previous theoretical work is

**Table 1.** Convergence behavior of the nonrelativistic energies for the excited  $1s2sns\ ^4S$  levels of Li. The number of basis functions used is denoted by  $N$ .

$N$	$E_{NR}$ (hartree)			
	$(1s2s3s)\ ^4S$	$(1s2s4s)\ ^4S$	$(1s2s5s)\ ^4S$	$(1s2s6s)\ ^4S$
100	-5.212 722 620 9	-5.158 351 849	-5.138 141 687	-5.128 127 5
300	-5.212 747 264 4	-5.158 392 140	-5.138 457 577	-5.128 823 6
600	-5.212 748 191 8	-5.158 393 411	-5.138 462 224	-5.128 878 1
1000	-5.212 748 241 2	-5.158 393 464	-5.138 462 451	-5.128 880 5
1144				-5.128 880 7
1600	-5.212 748 246 1		-5.138 462 512	
1620		-5.158 393 471 89		
1904	-5.212 748 246 6			

displayed in Table 2. For the  $1s2sns\ ^4S$  levels, our results are 0.625 nanohartree ( $n = 3$ ), 1.31 nanohartree ( $n = 4$ ), 23 nanohartree ( $n = 5$ ), and 479 nanohartree ( $n = 6$ ), respectively, above the most accurate results available in the literature due to Yan.<sup>[28,30]</sup> Each of the wavefunctions used by Yan uses a much larger basis set than used in this study.

As a focus of the present investigation is the evaluation of the hyperfine coupling, the convergence of the calculated expectation value for  $f$  is shown in Table 3. For the  $1s2s3s\ ^4S$ ,

one-electron operators is:

$$\langle O_i \rangle \equiv \left\langle \psi \left| \sum_{i=1}^3 O_i \right| \psi \right\rangle, \quad (11)$$

and for two-electron operators, it is:

$$\langle O_{ij} \rangle \equiv \left\langle \psi \left| \sum_{i=1}^3 \sum_{j>i}^3 O_{ij} \right| \psi \right\rangle. \quad (12)$$

To monitor significant figure loss for each expectation value, the sum of all the positive components and the sum of all the negative components are computed separately, and then the significant figure loss that occurs when these two sums are combined is evaluated. Usually this loss is no more than a couple of digits. In the case of the  $1s2s6s\ ^4S$  level, the loss amounted to seven to eight digits for a number of expectation values.

## Determination of the Hyperfine Constants

There are a number of small corrections to the hyperfine constant that arise from the finite nuclear mass, relativistic effects, quantum electrodynamic (QED) corrections, and nuclear effects. Detailed many-electron theory for all these corrections is currently not fully developed. All these corrections are fairly small, for example, for Li and  $\text{Be}^+$ , these corrections in total amount to significantly less than 1% of the hyperfine constant value for the low-lying  $S$  levels of these three electron systems: see for example, Refs. [34–36]. For further theoretical refinements, see the work of Pachucki<sup>[37]</sup> and the recent article of Pachucki, Yerkhin

**Table 2.** Comparison of different literature values for  $E_{NR}$  for the  $1s2sns\ ^4S$  ( $n = 3$ –6) levels of Li. The number of basis functions used by each author is indicated in the size column.

Level	Nonrelativistic energy (hartree)	Size	Reference	
$(1s2s3s)\ ^4S$	-5.211 0	30	Holøien and Geltman <sup>[8]</sup>	
	-5.212 396	44	Larsson <sup>[9]</sup>	
	-5.212 59	73	Larsson et al. <sup>[14]</sup>	
	-5.212 59	50	Larsson and Crossley <sup>[16]</sup>	
	-5.212 737	200	Bunge and Bunge <sup>[11]</sup>	
	-5.212 741	170	Bunge <sup>[15]</sup>	
	-5.212 739	571	Hsu et al. <sup>[19]</sup>	
	-5.212 748 24	956	Lüchow et al. <sup>[22]</sup>	
	-5.212 748 246	2780	Barrois et al. <sup>[23]</sup>	
	-5.212 742 5		Qu et al. <sup>[25]</sup>	
	-5.212 748 247 217(3)	4213	Yan <sup>[28]</sup>	
	-5.212 748 247 225(5)	5005	Yan <sup>[30]</sup>	
$(1s2s4s)\ ^4S$	-5.212 748 246 6	1904	Present work	
	-5.156 2	30	Holøien and Geltman <sup>[8]</sup>	
	-5.154 90		Lunell and Beebe <sup>[10]</sup>	
	-5.158 23	74	Larsson and Crossley <sup>[16]</sup>	
	-5.158 393 45	1049	Lüchow et al. <sup>[22]</sup>	
	-5.158 393 45	1049	Barrois et al. <sup>[23]</sup>	
	-5.158 412 8	2015	Qu et al. <sup>[25]</sup>	
	-5.158 393 473 12(5)		Yan <sup>[28]</sup>	
	-5.158 393 473 2(2)		Yan <sup>[30]</sup>	
	-5.158 393 471 89	1620	Present work	
	$(1s2s5s)\ ^4S$	-5.136 14		Lunell and Beebe <sup>[10]</sup>
		-5.138 16	74	Larsson and Crossley <sup>[16]</sup>
-5.138 462 4		1049	Lüchow et al. <sup>[22]</sup>	
-5.138 430 4			Qu et al. <sup>[25]</sup>	
-5.138 462 531 6(5)			Yan <sup>[28]</sup>	
-5.138 462 535(4)			Yan <sup>[30]</sup>	
$(1s2s6s)\ ^4S$	-5.138 462 512	1600	Present work	
	-5.126 98		Lunell and Beebe <sup>[10]</sup>	
	-5.128 29	74	Larsson and Crossley <sup>[16]</sup>	
	-5.128 880	1049	Lüchow et al. <sup>[22]</sup>	
	-5.128 901 2		Qu et al. <sup>[25]</sup>	
	-5.128 881 179(1)		Yan <sup>[30]</sup>	
	-5.128 880 7	1144	Present work	

**Table 3.** Convergence behavior of the Fermi contact expectation value for the excited  $1s2sns\ ^4S$  levels of Li. The number of basis functions used is denoted by  $N$ .

$N$	$f$ (nonrelativistic) a.u.			
	$(1s2s3s)\ ^4S$	$(1s2s4s)\ ^4S$	$(1s2s5s)\ ^4S$	$(1s2s6s)\ ^4S$
100	114.95454	114.70847	114.6338	114.650
300	114.94328	114.75591	114.7163	114.676
600	114.94528	114.75447	114.7118	114.710
1000	114.94598	114.75657	114.7134	114.701
1100				114.699
1300	114.94565	114.75636	114.7134	
1600	114.94579		114.7131	
1620		114.75612		
1904	114.94579			

**Table 4.** Expectation values for the infinite nuclear mass model for different excited  $1s2sns\ ^4S$  levels of Li. The estimated uncertainty for each expectation value is expected to be in the last digit reported.

Expectation value	$(1s2s3s)\ ^4S$	$(1s2s4s)\ ^4S$	$(1s2s5s)\ ^4S$	$(1s2s6s)\ ^4S$
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	5.212748250	5.158393478	5.13846250	5.128884
$\langle \frac{1}{r_i} \rangle$	0.749737861	0.616275947	0.55741706	0.5267216
$\langle \frac{Z}{r_i} \rangle$	-11.175 234 357	-10.933 062 897	-10.834 342 08	-10.784 489
$\langle \nabla_i \cdot \nabla_j \rangle$	-0.019098695	-0.018619484	-0.01791604	-0.0175855
$\langle r_i \rangle$	10.71579088	18.9084529	30.12958	44.3503
$\langle r_i^2 \rangle$	74.834463	292.072882	832.543	1920.2
$\langle r_i^3 \rangle$	669.3602	5510.146	26798.3	93939.
$\langle r_{ij} \rangle$	18.97725486	34.8241086	57.0694	85.423
$\langle r_{ij}^2 \rangle$	158.034044	589.33664	1668.544	3842.9
$\langle r_{ij}^3 \rangle$	$1.5408370 \times 10^3$	$1.135847 \times 10^4$	$5.41132 \times 10^4$	$1.886 \times 10^5$
$\langle \delta(\mathbf{r}_i) \rangle$	9.147096	9.132 002	9.12858	9.1275

and Cancio Pastor gives a detailed treatment of hyperfine structure corrections.<sup>[38]</sup> It should be noted that some of the corrections arise with opposite signs, and there is a major cancellation between some of these corrections. In this study, only the effect of finite nuclear mass will be considered.

The simplest approach to obtain the principal mass correction to the hyperfine constant is to multiply  $f$  in eq. (7) by a factor of  $(1 - \frac{\mu}{M})^3$ , where  $M$  is the nuclear mass and  $\mu$  is the reduced mass with respect to the nucleus and the electron mass. This leads to a mass correction to the hyperfine constant of the form

$$\delta A_{\text{mass}} = -3 \frac{\mu}{M} \left\{ 1 - \frac{\mu}{M} + \frac{1}{3} \left( \frac{\mu}{M} \right)^2 \right\} A_{\text{NR}}. \quad (13)$$

For the calculation of the mass correction to the hyperfine constants, the nuclear masses for the lithium isotopes used are 10,961.898 a.u. for  $^6\text{Li}$  and 12,786.3919 a.u. for  $^7\text{Li}$ . These values are derived from the atomic mass values given in Refs. [[39] and [40]] and the electronic mass reported in Ref. [32]. Equation (13) includes only the mass scaling correction. An alternative approach, which incorporates both the mass scaling and the much smaller correction due to the mass polarization contribution, is to replace  $\psi$  in eq. (7), which is based on the infinite nuclear mass Hamiltonian, by  $\psi_M$ , which is obtained in a standard variational approach using the following Hamiltonian in a.u.:

$$H = -\frac{1}{2\mu} \sum_{i=1}^3 \nabla_i^2 - \frac{1}{M} \sum_{i=1}^3 \sum_{j>i}^3 \nabla_i \cdot \nabla_j - Z \sum_{i=1}^3 \frac{1}{r_i} + \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}}, \quad (14)$$

where  $Z$  is the nuclear charge. The second term in this Hamiltonian takes account of mass polarization effects. The difference between the two approaches can be ignored because the mass polarization correction to the hyperfine constant is very small and note that small relativistic and QED contributions to the hyperfine constants are also ignored.

The hyperfine constants for  $^6\text{Li}$  and  $^7\text{Li}$  determined using eqs. (7–10) are reported in Table 5. The mass corrected hyperfine coupling constants, denoted  $A_{\text{mc}}$ , are also reported in

Table 5. The uncertainty estimates are based on the convergence pattern indicated by the results in Table 3.

## Some Quartet Transition Energies

In this section, evaluation of the transition energies for  $1s2s2p\ ^4P^o \rightarrow 1s2sns\ ^4S^e$  ( $n = 3-6$ ) is discussed. The configuration  $1s2s2p\ ^4P^o_{3/2}$  is the lowest of the quartet levels for the lithium atom and the term energy is determined without regard to a particular  $J$  value in the following way. The most accurate nonrelativistic calculation of this level is due to Yan,<sup>[30]</sup> who gives the value  $E_{\text{NR}} = -$

5.368 010 1539(2) from a large-scale Hylleraas calculation. The two mass corrections to this value are the normal mass shift given by

$$\Delta E_{\text{NMS}} = -\frac{1}{M+1} E_{\text{NR}}, \quad (15)$$

and

$$\Delta E_{\text{SMS}} = -\frac{1}{M+1} \left\langle \psi \left| \sum_{i=1}^3 \sum_{j>i}^3 \nabla_i \cdot \nabla_j \right| \psi \right\rangle \quad (16)$$

where the nuclear mass  $M$  is in atomic units. The mass factors could be handled in a nonperturbation fashion by using the Hamiltonian given in eq. (14), but the available accuracy for some of the small corrections does not at present necessitate this refinement. The most accurate calculations of the relativistic corrections for the  $1s2s2p\ ^4P^o$  level are due to Hsu et al.<sup>[19]</sup> They give the result  $-0.0005948$  a.u. for the sum of the relativistic kinetic energy correction, the electron–nuclear Darwin correction, and the electron–electron orbit correction (retardation correction). The QED correction for the  $1s2s3s\ ^4S$  level has been estimated by Hsu et al.<sup>[21]</sup> at  $0.6(2)\text{ cm}^{-1}$  relative to the  $1s2s2p\ ^4P^o$  level. Combining these results together leads to the result for  $^6\text{Li}$ :

$$E(1s2s2p\ ^4P^o) = -5.368 133 3\text{ a.u.} = -1, 178, 169.1\text{ cm}^{-1}, \quad (17)$$

and for  $^7\text{Li}$ :

$$E(1s2s2p\ ^4P^o) = -5.368 200 6\text{ a.u.} = -1, 178, 183.9\text{ cm}^{-1}. \quad (18)$$

**Table 5.** Nonrelativistic hyperfine constants,  $A_{\text{NR}}$ , and mass-corrected hyperfine constants,  $A_{\text{mc}}$ , for the  $1s2sns\ ^4S$  levels in  $^6\text{Li}$  and  $^7\text{Li}$  in units of MHz.

Level	$A_{\text{NR}}(^6\text{Li})$	$A_{\text{mc}}(^6\text{Li})$	$A_{\text{NR}}(^7\text{Li})$	$A_{\text{mc}}(^7\text{Li})$
$1s2s3s\ ^4S$	2005.7470(5)	2005.1982(5)	5296.9930(5)	5295.7503(5)
$1s2s4s\ ^4S$	2002.4373(16)	2001.8894(16)	5288.2527(16)	5287.0120(16)
$1s2s5s\ ^4S$	2001.687(7)	2001.139(7)	5286.270(7)	5285.030(7)
$1s2s6s\ ^4S$	2001.44(9)	2000.89(9)	5285.63(9)	5284.37(9)

**Table 6.** Contributions to the transition energies from the lowest quartet level of Li to the  $1s2sns\ ^4S$  levels in a.u.

Level	$1s2s3s\ ^4S$	$1s2s4s\ ^4S$	$1s2s5s\ ^4S$	$1s2s6s\ ^4S$
<b>Isotope <math>^6\text{Li}</math></b>				
$E_{NR}$	-5.2127482466(6)	-5.1583934718(13)	-5.138462512(23)	-5.1288807(5)
$\Delta E_{NMS}$	$4.75489985(1) \times 10^{-4}$	$4.70531919(1) \times 10^{-4}$	$4.68713882(2) \times 10^{-4}$	$4.6783986(5) \times 10^{-4}$
$\Delta E_{SMS}$	$1.7421210(1) \times 10^{-6}$	$1.6984089(1) \times 10^{-6}$	$1.634243(1) \times 10^{-6}$	$1.60410(1) \times 10^{-6}$
$E_{rel}$	-0.0006210(50)	-0.0006176(50)	-0.0006166(50)	-0.0006156(50)
$\Delta E_{QED}$	0.0000030(10)	0.0000030(10)	0.0000030(10)	0.0000030(10)
$E_{total}$	-5.2128890(60)	-5.1585358(60)	-5.1386058(60)	-5.1290239(60)
$\Delta E(1s2sns\ ^4S - 1s2s2p\ ^4P)$	0.1552443(80)	0.2095975(80)	0.2295275(80)	0.2391094(80)
	$34,072.2(17)\ \text{cm}^{-1}$	$46,001.3(17)\ \text{cm}^{-1}$	$50,375.5(17)\ \text{cm}^{-1}$	$52,478.4(17)\ \text{cm}^{-1}$
<b>Isotope <math>^7\text{Li}</math></b>				
$E_{NR}$	-5.2127482466(6)	-5.1583934718(13)	-5.138462512(23)	-5.1288807(5)
$\Delta E_{NMS}$	$4.07647429(1) \times 10^{-4}$	$4.03396776(1) \times 10^{-4}$	$4.01838135(2) \times 10^{-4}$	$4.0108882(5) \times 10^{-4}$
$\Delta E_{SMS}$	$1.4935565(1) \times 10^{-6}$	$1.4560812(1) \times 10^{-6}$	$1.401070(1) \times 10^{-6}$	$1.37522(1) \times 10^{-6}$
$E_{rel}$	-0.0006210(50)	-0.0006176(50)	-0.0006166(50)	-0.0006156(50)
$\Delta E_{QED}$	0.0000030(10)	0.0000030(10)	0.0000030(10)	0.0000030(10)
$E_{total}$	-5.2129571(60)	-5.1586032(60)	-5.1386729(60)	-5.1290908(60)
$\Delta E(1s2sns\ ^4S - 1s2s2p\ ^4P)$	0.1552435(80)	0.2095974(80)	0.2295277(80)	0.2391098(80)
	$34,072.0(17)\ \text{cm}^{-1}$	$46,001.3(17)\ \text{cm}^{-1}$	$50,375.5(17)\ \text{cm}^{-1}$	$52,478.5(17)\ \text{cm}^{-1}$
Expt.	$34,071.91(05)\ \text{cm}^{-1(1,2)}$	$45,996(2)\ \text{cm}^{-1(6)}$	$50,381(2)\ \text{cm}^{-1(6)}$	$52,472(8)\ \text{cm}^{-1(6)}$
	$34,072.0\ \text{cm}^{-1(6)}$	$45,998(42)\ \text{cm}^{-1(3)}$		
	$34,083\ \text{cm}^{-1(5)}$	$46,019\ \text{cm}^{-1(5)}$		

Table 6 summarizes for the  $1s2sns\ ^4S^e$  ( $n = 3-6$ ) terms the values for  $E_{NR}$ ,  $\Delta E_{NMS}$ ,  $\Delta E_{SMS}$  computed in this work, along with the relativistic corrections from Qu et al.<sup>[25]</sup> For the  $1s2s3s\ ^4S^e$  level, Hsu et al.<sup>[19]</sup> have also calculated the relativistic correction, and their result agrees with the value used in Table 6 to within one in the last reported digit. A QED correction of  $0.6(2)\ \text{cm}^{-1}$ , based on the work of Hsu et al.,<sup>[21]</sup> has been included in the  $E_{total}$  entries in Table 6.

## Discussion

Two results in Table 2 require comment. The energy reported by Qu et al.<sup>[25]</sup> for the  $(1s2s4s)\ ^4S$  level is below the results of both the present calculation of this level and the result of Yan.<sup>[28,30]</sup> For the  $(1s2s6s)\ ^4S$  level, Qu et al. also report a non-relativistic energy below the results of this work and below the highly accurate value reported by Yan.<sup>[30]</sup> Yan<sup>[30]</sup> has commented that the result of Qu et al. is in error for the  $(1s2s6s)\ ^4S$  level. In the full core plus correlation (FCPC) approach used by Qu et al., it might be anticipated that the basis set truncation error had been misevaluated but the authors report no truncation error was included. As their  $1s2s\ ^3S$  core component is in very good agreement with accurate literature results, the source of the error presumably must lie in the noncore correlation component of their wave function.

The convergence of the calculated  $f$  values for the different levels reported in Table 3 is not monotonic increasing or decreasing as the basis set size is increased. Sometimes, this behavior explains the fact that basis sets of modest size can lead fortuitously to accurate values of the quantity  $f$ . A feature to be noted from the results of Table 3 is the strongly dominant nature of the contribution from the  $1s2s$  configuration. This leads to hyperfine constants (see Table 5) that are approximately constant across the four levels  $1s2sns\ ^4S^e$  ( $n = 3-6$ ).

Some comments on error assessment are appropriate. For the  $1s2sns\ ^4S^e$  ( $n = 3-5$ ), the error in  $E_{NR}$  occurs in a digit beyond those reported for the transition energy  $\Delta E(1s2sns\ ^4S - 1s2s2p\ ^4P)$ . For the  $1s2s6s\ ^4S^e$  level, the error is about four in the last quoted digit for the transition energy  $\Delta E(1s2s6s\ ^4S - 1s2s2p\ ^4P)$ , but this error could be reduced by a factor of about 400 by using the accurate value of Yan<sup>[30]</sup> for  $E_{NR}$ . For the corrections  $\Delta E_{NMS}$  and  $\Delta E_{SMS}$ , the errors reside in digits beyond those reported for the transition energies.

To the best of the author's knowledge, no Hylleraas-type calculations of the relativistic corrections of the levels under discussion have been reported. Neither Qu et al.<sup>[25]</sup> nor Hsu et al.<sup>[19]</sup> provide any convergence data for the individual relativistic contributions that would allow an approximate assessment of the errors in the individual relativistic values reported. As some of the relativistic contributions are much more sensitive to the near-nuclear region of configuration space, convergence of these corrections can be much slower than the individual energy components. On the basis of a comparison of similar FCPC calculations carried out on the ground state of Li with more accurate Hylleraas calculations of the relativistic corrections, the observed change in the calculated relativistic expectation values amounts to slightly under a 1% difference. Using this figure as a rough estimate of the error would suggest that the error arising from the relativistic contribution is about 50 in the last two digits reported for the  $E_{total}$  ( $1s2sns\ ^4S$ ) values in a.u. The QED value used is based on a very rough estimate, and the error in this value could be significantly higher than the 33% figure quoted by Hsu et al.<sup>[21]</sup> At minimum, using the 33% estimate, would give an uncertainty of about 10 in the last two quoted digits of the transition energies. So at minimum, a very rough estimate of the uncertainty is around 60 for the last two quoted digits of the  $E_{total}$  energies in a.u. or around  $1.3\ \text{cm}^{-1}$ . For the transition energies  $\Delta E(1s2s3s\ ^4S - 1s2s2p\ ^4P)$ , the error would be approximately 80 in the last two quoted

digits in a.u. or around  $1.7 \text{ cm}^{-1}$ . There is the possibility of significant cancellation of errors in the relativistic and QED contributions when the energy difference between the different levels is calculated.

The calculated  $\Delta E(1s2s3s \ ^4S - 1s2s2p \ ^4P)$  is in close agreement with the accurate result of Barrois et al.<sup>[24]</sup> who report the value  $34,071.36(44) \text{ cm}^{-1}$  in comparison with the present calculation of  $34,072.0(17) \text{ cm}^{-1}$ . The error reported by Barrois et al.<sup>[24]</sup> makes no reference to assessment of the relativistic error and the QED contribution is not considered. Both these theoretical values are in close agreement to the experimental value of Levitt and Feldman<sup>[2]</sup> who report the value  $34,071.91(05) \text{ cm}^{-1}$ . For the transition  $1s2s2p \ ^4P^o \rightarrow 1s2s4s \ ^4S^e$ , the transition energy determined in this work is  $46,001.3(17) \text{ cm}^{-1}$  and this value is in fair agreement with the experimental results  $45,996(2) \text{ cm}^{-1[6]}$  and  $45,998(42) \text{ cm}^{-1[3]}$ . For the transitions  $1s2s2p \ ^4P^o \rightarrow 1s2s5s \ ^4S^e$  and  $1s2s2p \ ^4P^o \rightarrow 1s2s6s \ ^4S^e$ , the theoretical results  $50,375.5(17) \text{ cm}^{-1}$  and  $52,478.5(17) \text{ cm}^{-1}$  differ from the experimental results  $50,381(2) \text{ cm}^{-1[6]}$  and  $52,472(8) \text{ cm}^{-1[6]}$  by approximately  $6 \text{ cm}^{-1}$ . For the  $1s2s2p \ ^4P^o \rightarrow 1s2s5s \ ^4S^e$  transition, the difference between theory and experiment lies outside the range of values incorporating the error estimates.

From Table 6, it is clear that the accuracy of the calculations is not sufficient to resolve the isotope shifts for  $^6\text{Li}$  and  $^7\text{Li}$  for the transitions  $1s2s2p \ ^4P^o \rightarrow 1s2sns \ ^4S^e$  ( $n = 3-6$ ). The principal obstacle to resolve this theoretically is the limited accuracy available for the combined relativistic correction and in particular, the QED correction. Improved calculations of these two contributions would open up the possibilities to make accurate theoretical predictions of the transition energies for  $1s2s2p \ ^4P^o \rightarrow 1s2sns \ ^4S^e$  for the different isotopes of lithium.

Perhaps, the present theoretical determination of the hyperfine constants for the  $1s2sns \ ^4S^e$  ( $n = 3-6$ ) levels of the isotopes  $^6\text{Li}$  and  $^7\text{Li}$  will attract the interest of experimentalists to examine the hyperfine structure of these systems.

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