Calculation of the hyperfine constants for the low-lying excited ^2S states of the lithium atom

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Hylleraas-type calculations of the hyperfine constants for the four lowest excited $3\,^2S$, $4\,^2S$, $5\,^2S$, and $6\,^2S$ states of the lithium atom are reported. Hyperfine constants are determined for the stable isotopes ^{6}Li and ^{7}Li and for the unstable isotopes ^{8}Li, ^{9}Li, and ^{11}Li for each state. Finite-nuclear-mass, lowest-order relativistic, quantum electrodynamic, Bohr-Weisskopf, Breit-Rosenthal, and Sushkov corrections are incorporated.

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I. INTRODUCTION

The determination of the hyperfine constants for the lithium atom and members of its isoelectronic series has attracted considerable theoretical and experimental attention [1–7]. The hyperfine structure of the ground state of Li has been the focus of most of the attention [1–4,8–12].

The nonrelativistic component of the calculation is now well understood. For example, for the ground state of Li, several methods have produced results in close agreement with the experimental derived value for this quantity: see Refs. [1,2] for a summary of a number of accurate calculations. The Hylleraas approach has been applied to the Li ground state over a number of years [8,3,9,10] and has produced the best converged nonrelativistic value for the hyperfine constant of the ground state of Li [4]. A complete match with experiment is limited by the necessity to determine a number of small corrections. Two issues arise: the first is that the exact form of the many-electron nature of the corrections is not fully resolved. The common approach is to employ one-electron treatments of the valence electron. The second issue concerns the use of one-electron models, which depend on parameters that are not accurately known. For example, the root-mean-square radius of the nuclear magnetization density distribution is known either with limited precision or, for some isotopes of Li, is unknown.

There has been recent experimental and theoretical interest in the hyperfine structure of the $3\,^2S$ state of lithium for both the stable isotopes ^{6}Li and ^{7}Li [13,14] and the unstable isotopes ^{8}Li and ^{9}Li [14]. This work was done as part of a program to ascertain the root-mean-square nuclear radius of these isotopes [13,14]. The isotope ^{11}Li has been of particular focus because of the halo structure of the nucleus for this system [15]. The measurements of Bushaw *et al.* [13] were carried out by two-photon excitation of the $2S$-$3S$ transition for the isotopes ^{6}Li and ^{7}Li. The experimental approach of Ewald *et al.* [14] also involved two photon excitation of the $2S$-$3S$ transition and included an investigation of the four isotopes ^{6}Li, ^{7}Li, ^{8}Li, and ^{9}Li. The results reported by these authors indicated a discrepancy with the earlier measurement of the $3\,^2S$ state of ^{7}Li carried out by Stevens *et al.* [16]. Both Bushaw *et al.* [13] and Ewald *et al.* [14] carried out a comparison with theoretical results based on the Hylleraas approach.

In addition to the Hylleraas approach, other theoretical methods have yielded results for various states of Li. These include the multiconfiguration Hartree-Fock approach [11,17] and a full-core multiconfiguration-interaction approach [18].

The purpose of this work is to report the results of precise calculations of the hyperfine constants for the $3\,^2S$, $4\,^2S$, $5\,^2S$, and $6\,^2S$ states of the two stable isotopes of Li, as well as the three aforementioned short-lived isotopes. A number of small corrections to the hyperfine constants are considered: these include the effects of finite nuclear mass, the effects of finite nuclear size: the Bohr-Weisskopf and the Breit-Rosenthal corrections, lowest-order relativistic, quantum electrodynamic (QED), and Sushkov corrections.

II. COMPUTATIONAL APPROACH

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

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

where $\mathcal{A}$ is the three-electron antisymmetrizer, c_κ denotes the expansion coefficients, χ_κ is a spin eigenfunction, r_i designates the electron-nuclear separation distance for electron i, r_{ij} is the interelectronic separation distance, and N represents the number of terms in the expansion. The nonlinear exponents α_κ, β_κ, and γ_κ are each >0 and the integer indices $\{i_\kappa,j_\kappa,k_\kappa,l_\kappa,m_\kappa,n_\kappa\}$ are each $\geqslant 0$. Extensive optimization of the nonlinear exponents was carried out for the separate excited states considered in the present investigation. The infinite-nuclear-mass nonrelativististic approximation was employed.

The Fermi contact operator is given by

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

where μ_0 is the vacuum permeability, g_J is the electronic g factor, g_I is the nuclear g factor, μ_B and μ_N are the Bohr and nuclear magnetons, respectively, $\boldsymbol{I}$ is the nuclear spin operator, $\boldsymbol{s}_i$ 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

TABLE I. Convergence behavior of the nonrelativistic energies for the excited $n\,^2S$ states of Li. The number of basis functions employed is denoted by N.

	E_{NR} (hartree)			
N	$3\,^2S$	$4\,^2S$	$5\,^2S$	$6\,^2S$
100	−7.353 802 490	−7.317 628 263	−7.300 437 837	−7.289 470 369
300	−7.354 093 640	−7.318 520 044	−7.303 528 946	−7.295 806 310
600	−7.354 097 872	−7.318 530 128	−7.303 549 737	−7.295 855 045
1000	−7.354 098 164	−7.318 530 696	−7.303 551 363	−7.295 859 124
1600	−7.354 098 333	−7.318 530 802	−7.303 551 534	−7.295 859 255
1900	−7.354 098 355	−7.318 530 816	−7.303 551 551	−7.295 859 384

$$H_F = hA_J \boldsymbol{I}\cdot\boldsymbol{J}, \tag{3}$$

where h denotes Planck's constant, $\boldsymbol{J}$ is the total electronic angular momentum operator, and A_J is the hyperfine constant (in Hz). We drop the subscript J on A in the sequel. For the ^2S states of Li, the energy splitting occurs between the $I+\frac{1}{2}$ and $I-\frac{1}{2}$ levels for $J=\frac{1}{2}$. In terms of the experimental hyperfine frequency $\Delta\nu$,

$$A = \frac{2}{2I+1}\Delta\nu. \tag{4}$$

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

$$f = \langle\psi|4\pi\sum_{i=1}^{3}\delta(\mathbf{r}_i)\sigma_{z_i}|\psi\rangle, \tag{5}$$

where the operator σ_{z_i} acts on the electron spin states $\alpha(i)$ 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 can be expressed as

$$A_{NR} = \frac{\mu_0\mu_B\mu_N}{2\pi h a_0^3}\frac{g_J\mu_I}{3I}f \equiv C\frac{g_J\mu_I}{3I}f, \tag{6}$$

where a_0 is the Bohr radius. The collection of constants denoted by C can be rewritten in terms of fundamental constants that collectively are known with greater accuracy, so that

$$C = \frac{\mu_0\mu_B\mu_N}{2\pi h a_0^3} = \alpha^2 cR_\infty(m_e/m_p) = 95.41066116(63)\ \text{MHz}, \tag{7}$$

where α is the fine structure constant, c is the speed of light, R_∞ is the Rydberg constant, and m_e and m_p are the mass of the electron and proton, respectively. Employing the most recent CODATA values [19] for the various contributions yields the value of C given in Eq. (7). The nuclear moments needed to evaluate Eq. (6) were taken from [20]. The corrections for diamagnetic shielding for isotopes 6 and 7 were reevaluated as discussed in [1]. The experimental value of g_J for the ground state of ^{6}Li is 2.002 301 9(24) [21], and to within experimental uncertainty ^{7}Li has the same value. Yan [22] has determined g_J theoretically for the ground state of ^{7}Li and his result agrees with the experimental determination. Yan has also determined g_J for the $3\,^2S$ of ^{7}Li to be 2.002 313 1. We have used this value for the calculations on the $3\,^2S$ state. It is expected that the change in the value of g_J for the higher $n\,^2S$ states will be very small, and accordingly, we have employed the value $g_J=2.002\,313\,1$ for the higher $n\,^2S$ states studied.

III. NONRELATIVISTIC RESULTS

The convergence behavior of the nonrelativistic energy (E_{NR}) for each of the states studied is shown in Table I. A comparison of the E_{NR} values with previous theoretical work is displayed in Table II. For the $4\,^2S$, $5\,^2S$, and $6\,^2S$ states, the results obtained for E_{NR} improve upon previously published work. For the $3\,^2S$ state the most accurate result available for E_{NR} is due to Puchalski *et al.* [33]. Their result is 66.38 nhartree below the result of the present calculations and was obtained using a wave function with approximately 5 times more basis functions than were employed in the present study.

The values for the expectation value f calculated using Eq. (5) are given in Table III along with other theoretical results for this quantity. For the $3\,^2S$ state the present result is approximately 0.025% above the result of Yan *et al.* [4] and 0.036% above the result of Jönsson *et al.* [30]. For the $4\,^2S$ state the present result for f is slightly higher (about 0.096%) than the result of Godefroid *et al.* [17]. The result of the present calculation for the $5\,^2S$ state agrees to within approximately 0.8% with the theoretical result of Guan and Wang [18]. No other accurate theoretical values are available for comparison for the 6^2S state.

IV. SMALL CORRECTIONS

There are a number of small corrections to the hyperfine constant that arise from the finite nuclear mass, relativistic effects, QED corrections, and nuclear effects. Detailed many-electron theory for all these corrections is currently not fully developed, and it is rather common to resort to approximate one-electron models or simple nuclear models to estimate some of these corrections. We employ a similar approach in this work. The uncertainties in the application of these approximate models lead to fairly obvious difficulties in assigning meaningful error estimates. There is a good deal of cancellation among these small corrections.

TABLE II. Comparison of different literature values for E_{NR} for the $n\,^2S$ states of Li. The number of basis functions employed by each author is indicated in the size column.

State	Nonrelativistic energy (hartree)	Size	Author, year, and reference
$3\,^2S$	−7.353 5	22	Perkins (1972) [23]
	−7.353 917	59	Larsson (1972) [24]
	−7.354 030	170	Pipin and Woźnicki (1982) [25]
	−7.354 076	447	King (1991) [26]
	−7.354 098 0		Wang, Zhu, and Chung (1992) [27]
	−7.354 097 8	898	Lüchow and Kleindienst (1992) [28]
	−7.354 098 369	1398	Lüchow and Kleindienst (1994) [29]
	−7.354 014	13306	Jönsson, Fischer, and Bieroń (1995) [30]
	−7.354 098 04	392	Pestka and Woźnicki (1996) [31]
	−7.354 098 421 082[a]	3502	Yan and Drake (2000) [32]
	−7.354 098 421 380	9576	Puchalski, Moro, and Pachucki (2006) [33]
	−7.354 098 355	1900	Present work
$4\,^2S$	−7.317 5	18	Perkins (1972) [23]
	−7.318 366	59	Larsson (1972) [24]
	−7.318 491	501	King (1991) [26]
	−7.318 530 3		Wang, Zhu, and Chung (1992) [27]
	−7.318 525	898	Lüchow and Kleindienst (1992) [28]
	−7.318 530 665	1398	Lüchow and Kleindienst (1994) [29]
	−7.318 451	13306	Jönsson, Fischer, and Bieroń (1995) [30]
	−7.318 529 38	241	Pestka and Woźnicki (1996) [31]
	−7.318 530 816	1900	Present work
$5\,^2S$	−7.303 392	59	Larsson (1972) [24]
	−7.303 439	450	King (1991) [26]
	−7.303 550 8		Wang, Zhu, and Chung (1992) [27]
	−7.303 547	898	Lüchow and Kleindienst (1992) [28]
	−7.303 551 551	1900	Present work
$6\,^2S$	−7.295 83	898	Lüchow and Kleindienst (1992) [28]
	−7.295 859 38	1900	Present work

[a]Extrapolated energy estimate given as −7.354 098 421 149 (18) hartree.

A. Finite-nuclear-mass corrections

The effects of finite nuclear mass enter the calculations in three ways. There are two ways to determine the nonrelativistic mass corrections to the hyperfine constant. One approach to the calculation of mass effects is to replace ψ in Eq. (1) by ψ_M, which is obtained in a standard variational approach using the Hamiltonian

$$H = -\frac{1}{2\mu}\sum_{i=1}^{3}\nabla_i^2 - \frac{1}{M}\sum_{i=1}^{3}\sum_{j>i}^{3}\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j - Z\sum_{i=1}^{3}\frac{1}{r_i} + \sum_{i=1}^{3}\sum_{j>i}^{3}\frac{1}{r_{ij}}, \quad (8)$$

where Z is the nuclear charge; μ is the reduced mass, $\mu = M/(1+M)$; and M is the nuclear mass of the particular lithium isotope of interest in a.u. The second term in this Hamiltonian takes account of mass polarization effects. The Fermi contact term in Eq. (5) is then evaluated with ψ replaced by ψ_M.

The second and simpler approach to obtain the principal mass correction to the hyperfine constant is to multiply f in Eq. (6) by a factor of $(1-\mu/M)^3$. This leads to a mass correction to the hyperfine constant of the form

$$\delta A_{mass} = -3\frac{\mu}{M}\left\{1 - \frac{\mu}{M} + \frac{1}{3}\left(\frac{\mu}{M}\right)^2\right\}A_{NR}. \quad (9)$$

For the calculation of δA_{mass} the nuclear masses for the isotopes 6, 8, 9, and 11 were taken from [34] and isotope 7 was taken from a recent determination [35].

Subtracting the mass-corrected hyperfine constant based on the factor $(1-\mu/M)^3$ from the hyperfine constant calculated based on the wave function ψ_M allows the mass polar-

TABLE III. Comparison of different literature values for the Fermi contact expectation value for the $n\,^2S$ states of Li. The number of basis functions employed by each author is indicated in the size column.

State	f (nonrelativistic) a.u.	Size	Author, year, and reference
$3\,^2S$	0.670 256	447	King (1991) [26]
	0.673 33	13306	Jönsson, Fischer, and Bieroń (1995) [30]
	0.673 405 (50)		Yan, McKenzie, and Drake (1995) [4]
	0.674 51	488	Guan and Wang (1998) [18]
	0.673 104 4		Godefroid, Fischer, and Jönsson (2001) [17]
	0.673 57	1900	Present work
$4\,^2S$	0.254 397	447	King (1991) [26]
	0.253 26	13306	Jönsson, Fischer, and Bieroń (1995) [30]
	0.253 66	575	Guan and Wang (1998) [18]
	0.253 754 2		Godefroid, Fischer, and Jönsson (2001) [17]
	0.253 998	1900	Present work
$5\,^2S$	0.113 116	501	King (1991) [26]
	0.121 00	399	Guan and Wang (1998) [18]
	0.121 94	1900	Present work
$6\,^2S$	0.067 671	1900	Present work

ization correction to the hyperfine constant to be obtained. For the $3\,^2S$ state of ^{7}Li, the mass polarization contribution affects [4] the first digit beyond what we retain for significant digits in the calculation. The impact for higher $n\,^2S$ states will be even less significant. For this reason, the mass polarization correction is not incorporated in the calculations of the total hyperfine constants.

There are, in addition, some relativistic and QED contributions having a mass dependence [36–38]. These are at least an order of magnitude smaller than the least significant digits we retain and are ignored in the calculations.

B. Lowest-order relativistic corrections

Pachucki [37] has recently considered a general theoretical treatment of the relativistic corrections to the lithium hyperfine splitting through order α^6. The singular-like structure of the resulting formulas have, however, not yet been evaluated.

In place of the Pachucki analysis, a one-electron model is employed to treat the valence electron [39–41]. Defining the parameters

$$\kappa = (-1)^{j+l+1/2}\left(j+\tfrac{1}{2}\right), \quad \gamma = \sqrt{\kappa^2 - \alpha^2 Z^2}, \tag{10}$$

$$d = \sqrt{n^2 + 2(|\kappa| - n)(|\kappa| - \gamma)}, \tag{11}$$

where j, l, and n are the total angular momentum, orbital angular momentum, and principal quantum numbers, respectively, the relativistic correction to the hyperfine constant is obtained from

$$\delta A_{rel} = \left\{ \frac{n^3\left(l+\frac{1}{2}\right)(2j+1)|2\kappa(n-|\kappa|+\gamma)-d|}{d^4\gamma(4\gamma^2-1)} - 1 \right\} A_{NR}. \tag{12}$$

The series expansion of the preceding formula for an ns electron ($l=0$, $j=1/2$, $\kappa=-1$) in terms of αZ takes the form

$$\delta A_{rel} = \left[\frac{11n^2+9n-11}{6n^2}(\alpha Z)^2 + \left(\frac{189-330n-134n^2+225n^3+203n^4}{72n^4} \right)(\alpha Z)^4 + O(\alpha^6 Z^6) \right] A_{NR}. \tag{13}$$

To evaluate the relativistic correction, some authors [4] have replaced Z by an effective nuclear charge Z_{eff}, where $Z_{eff}=Z-\sigma$ and σ denotes a suitable screening factor. Other authors—for example, [6,7]—have not included a screening constant. Unfortunately, it is not clear how this constant should be selected. In the present work, a screening constant has not been employed. The amount of screening in the vicinity of the nucleus is likely to be small. Introducing a small amount of screening into the Breit model leads to fairly small changes to the relativistic correction to the hyperfine constant, which would be about 1–4 in the fifth significant figure for the hyperfine constant. This may be smaller than the error arising from the application of the Breit model. The definitive answer on this issue awaits further theoretical developments in the *many-electron* relativistic corrections to the hyperfine constants along the lines of Pachucki [37].

C. QED corrections

The QED correction is commonly split into two parts. One contribution is the Schwinger correction to the electronic g factor, which takes the form $\alpha/(2\pi)$ [42]. Additional small corrections are incorporated in the electronic g factor. The remaining QED contributions to the hyperfine constant are based on a one-electron model and are given by [43,44]

$$\delta A_{QED} = \left(c_1 \alpha (Z\alpha) + \frac{\alpha (Z\alpha)^2}{\pi} [c_{22} \{\ln (Z\alpha)^{-2}\}^2 + c_{21}(n) \ln (Z\alpha)^{-2} + c_{20}(n)] \right) A_{NR}, \tag{14}$$

where the state-independent constants are given by

$$c_1 = \ln 2 - \frac{5}{2}, \quad c_{22} = -\frac{2}{3}, \tag{15}$$

and the state-dependent term $c_{21}(n)$ is given for nS states by [38]

$$c_{21}(n) = -\frac{8}{3} \ln (2n) + \frac{1001}{360} - \frac{8}{3n} + \frac{2}{3n^2} + \frac{8}{3} \sum_{k=1}^{n-1} \frac{1}{k}, \tag{16}$$

where the empty sum $\Sigma_{k=1}^{0}$ is assigned the value zero. The state-dependent terms $c_{20}(n)$ are available as numerical values [38]. The results employed for $c_{20}(n)$ for the present calculations are 10.417 048, 9.719 388, 9.312 703, and 9.045 565 for $n=3$, 4, 5, and 6, respectively.

D. Bohr-Weisskopf correction

The adjustment of the hyperfine constant for the effect of finite nuclear structure is obtained by multiplying A_{NR} by the factor C_{NS}, given by [45]

$$C_{NS} = (1 - \delta)(1 - \varepsilon), \tag{17}$$

where δ is a correction arising from the finite nuclear size, often referred to as the Breit-Rosenthal correction [46], and is treated in the following subsection, and ε is the Bohr-Weisskopf [47–49] correction to the hyperfine constant arising from the distribution of the magnetization density in the nucleus.

The simplest and most commonly employed approach to account for nuclear-size effects is to use a result of Zemach [50], where the atom is approximated as a one-electron system and the correction to the hyperfine constant obtained as $-2a_0^{-1}\langle r \rangle_{em}$ where $\langle r \rangle_{em}$ is the first statistical moment of the convolution of the nuclear electric and magnetic distributions. The difficulty in this approach is assigning accurate values to the quantity $\langle r \rangle_{em}$. In this and the following subsection, we take a different approach to deal with the nuclear-size contributions to the hyperfine constant.

The correction ε can be determined in a single-particle model, using

$$\varepsilon = \alpha_S \langle K_S \rangle + \alpha_L \langle K_L \rangle + \alpha_S \zeta (\langle K_S \rangle - \langle K_L \rangle), \tag{18}$$

where α_S and α_L are the fractional spin and orbital contributions to the magnetic moment,

$$\alpha_S = \frac{g_S (g_I - g_L)}{g_I (g_S - g_L)}, \quad \alpha_L = 1 - \alpha_S, \tag{19}$$

and the spin distribution asymmetry is described by the parameter ζ [48]:

$$\zeta = \begin{cases} \dfrac{2I-1}{4(I+1)}, & \text{for } I = l + \dfrac{1}{2}, \\ \dfrac{2I+3}{4I}, & \text{for } I = l - \dfrac{1}{2}. \end{cases} \tag{20}$$

The expectation values $\langle K_S \rangle$ and $\langle K_L \rangle$ are determined from [51]

$$\langle K_S \rangle = \int_0^\infty K_S(R) |u(R)|^2 R^2 dR \tag{21}$$

and

$$\langle K_L \rangle = \int_0^\infty K_L(R) |u(R)|^2 R^2 dR, \tag{22}$$

where the radial part of the probability density of the odd nucleon is assumed homogeneously distributed over the nuclear volume, with

$$|u(R)|^2 = \frac{3}{R_0^3} H(R_0 - R), \tag{23}$$

where $H(R)$ is a Heaviside step function. The functions $K_S(R)$ and $K_L(R)$ are determined from integrals of the radial parts of the Dirac wave function for the electron. Shabaev [51] gives the approximate expressions for S states in the nonrelativistic limit:

$$K_S(R) = \frac{\alpha Z R_0}{\lambda\!\!\!^{-}_C} \left[\left(\frac{R}{R_0} \right)^2 - \frac{1}{10} \left(\frac{R}{R_0} \right)^4 \right] \tag{24}$$

and

$$K_L(R) = \frac{3 \alpha Z R_0}{5 \lambda\!\!\!^{-}_C} \left[\left(\frac{R}{R_0} \right)^2 - \frac{1}{14} \left(\frac{R}{R_0} \right)^4 \right], \tag{25}$$

and $R_0 = \sqrt{5/3} \langle r^2 \rangle_M^{1/2}$, where $\langle r^2 \rangle_M^{1/2}$ is the root-mean-square radius of the nuclear magnetization density distribution and $\lambda\!\!\!^{-}_C$ is the Compton wavelength: $\lambda\!\!\!^{-}_C = \hbar/(m_e c)$. One approximation is to assume that the root-mean-square radius of the nuclear magnetization density distribution is the same as the root-mean-square radius of the nuclear charge distribution, $\langle r^2 \rangle^{1/2}$. For the calculations of this correction, we have used the values of $\langle r^2 \rangle_M^{1/2}$ taken from Ref. [52] for ^{6}Li and ^{7}Li. The values reported spread over a range, and there is potentially an error of approximately 10% for ^{6}Li and approximately 5% for ^{7}Li, for these factors. For the isotopes ^{8}Li, ^{9}Li, and ^{11}Li, we are not aware of any published values for $\langle r^2 \rangle_M^{1/2}$. In view of the absence of experimental data, the aforementioned approximation might be satisfactory; however, a slightly better result might be obtained in the following manner. A comparison of the results for $\langle r^2 \rangle^{1/2}$ and $\langle r^2 \rangle_M^{1/2}$ for ^{6}Li and ^{7}Li shows there is an increase in the magnetization root-mean-square radius of approximately a factor of 1.1. We used this factor

TABLE IV. Input values used to determine the Bohr-Weisskopf correction to the hyperfine constants of Li.

	^{6}Li	^{7}Li	^{8}Li	^{9}Li	^{11}Li
Nuclear spin	1	3/2	2	3/2	3/2
Nuclear moment (nm) [20]	0.82204454	3.2564159	1.653560	3.4391	3.6678
$\langle r^2\rangle^{1/2}$ fm	2.517 [15]	2.39 [52]	2.299 [15]	2.217 [15]	2.467 [15]
$\langle r^2\rangle_M^{1/2}$ fm	2.81 [52]	2.69 [52]	2.53	2.44	2.71
Spin g value (proton)	0.64408908	4.5128318	0.3071200	4.8782	5.3356
Asymmetry parameter ζ	1/8	1/5	1/4	1/5	1/5
α_S	0.39176045	0.69291392	0.0928663	0.70923	0.72736
α_L	0.60823955	0.30708608	0.9071337	0.29077	0.27264
$\langle K_S\rangle$	0.000115	0.000110	0.000103	0.0000994	0.000111
$\langle K_L\rangle$	0.0000703	0.0000673	0.0000632	0.0000610	0.0000679
ε	0.0000898	0.000103	0.0000679	0.0000937	0.000105

and the corresponding values of $\langle r^2\rangle^{1/2}$, which have been recently reported [14,15], to estimate the values for $\langle r^2\rangle_M^{1/2}$ for the isotopes ^{8}Li, ^{9}Li, and ^{11}Li. The results are given in Table IV. The values for g_S were determined from the result

$$g_I = g_L \pm \frac{(g_S - g_L)}{(2l+1)}, \quad \text{for } I = l \pm \frac{1}{2}. \tag{26}$$

If the odd nucleon is a proton, which is the case for Li, then g_L is commonly assigned the value 1. The calculated values of g_S are given in Table IV, and the values determined for α_S and α_L from Eq. (19) are also given in this table. The values of $\langle K_S\rangle$ and $\langle K_L\rangle$ determined from Eqs. (21)–(25) are presented in Table IV, and the final values of the Bohr-Weisskopf correction obtained from Eq. (18) are presented in the same table. The corrections to the hyperfine constant are determined as $\delta A_{BW} = \varepsilon A_{NR}$.

E. Breit-Rosenthal corrections

The other part of the correction for finite nuclear size is the Breit-Rosenthal correction δ, given for low Z for S states by Shabaev [51] as

$$\delta = \frac{3}{2}\alpha Z \frac{R_0}{\lambda\!\!\!^{-}_C}, \tag{27}$$

where a homogeneously charged sphere is assumed to model the nuclear charge distribution and R_0 is given in terms of the root-mean-square nuclear charge radius as $R_0 = \sqrt{5/3}\langle r^2\rangle^{1/2}$. For a discussion of nuclear charge density distribution models, see Andrae [53]. There is a spread in the available values for $\langle r^2\rangle^{1/2}$ for the isotopes of Li. The values employed in the present calculations are indicated in Table IV.

The Breit-Rosenthal correction to the hyperfine constant is given by

$$\delta A_{BR} = \delta\, A_{NR}, \tag{28}$$

and the value of δ is given in Eq. (27). The values obtained for this correction are small but typically affect the fourth or fifth significant digit for the states considered in this work.

F. Sushkov correction

Sushkov [54] has considered the effect of the polarization of the paired electrons by the valence s electron via a Breit interaction. He gives the total Breit correction to the hyperfine constant arising from the electron-electron interaction as

$$\delta A_{pol} = 0.681 Z\alpha^2 A_{NR}. \tag{29}$$

Sushkov also derived a Coulomb correction to the hyperfine constant as

$$\delta A_C = -0.558 Z\alpha^2 A_{NR}. \tag{30}$$

This correction arises from the v/c (particle velocity to speed of light ratio) expansion of the electron-electron Coulomb interaction involving Dirac spinors and retaining only terms of order $(v/c)^2$. Combining Eqs. (29) and (30) gives the total Sushkov correction to the hyperfine constant:

$$\delta A_S = 0.123 Z\alpha^2 A_{NR}. \tag{31}$$

The values obtained for this correction are small but do have a minor impact on the final digit reported for some of the calculated hyperfine constants.

V. TOTAL HYPERFINE CONSTANT

The nonrelativistic component of the hyperfine constants, along with the small corrections of the previous six subsections, and the total hyperfine constants, calculated using

$$A_{total} = A_{NR} + \delta A_{mass} + \delta A_{rel} + \delta A_{QED} + \delta A_{BW} + \delta A_{BR} + \delta A_S, \tag{32}$$

are summarized in Table V.

VI. DISCUSSION

As indicated by the results of Table V, several of the published theoretical values for the hyperfine constant for the

TABLE V. Theoretical results for the nonrelativistic and small corrections to the hyperfine constants of the excited $n\,^2S$ states of Li. Other theoretical and experimental results are also given.

		A (MHz)				
State	Contribution	^{6}Li	^{7}Li	^{8}Li	^{9}Li	^{11}Li
$3\,^2S$						
	Nonrelativistic	35.260	93.119	35.463	98.343	104.88
	Finite mass	−0.0096	−0.0218	−0.0073	−0.0179	−0.016
	Relativistic	0.0360	0.0951	0.0362	0.1005	0.107
	QED	−0.0109	−0.0289	−0.0110	−0.0305	−0.033
	Bohr-Weisskopf	−0.0032	−0.0095	−0.0024	−0.0092	−0.011
	Breit-Rosenthal	−0.0097	−0.0244	−0.0090	−0.0239	−0.028
	Sushkov	0.0007	0.0018	0.0007	0.0019	0.002
	Total	35.263	93.131	35.471	98.364	104.90
	Other theory		93.24 [55]			
			92.7 [26]			
			93.139 [30]			
			93.09 [4,13]			
			93.250 [18]			
			93.055 [17]			
			93.084 [17]			
		35.250	93.09	35.453	98.31 [14][a]	
	Experimental	34(13)	95(10) [56]			
			94.68(22) [16]			
		35.263(15)	93.106(11) [13]			
		35.283(10)	93.117(25)	35.496(28)	98.39(12) [14]	
$4\,^2S$						
	Nonrelativistic	13.2964	35.1145	13.3730	37.084	39.551
	Finite mass	−0.00364	−0.00824	−0.00274	−0.0068	−0.0059
	Relativistic	0.01335	0.03526	0.01343	0.0372	0.0397
	QED	−0.00410	−0.01083	−0.00412	−0.0114	−0.0122
	Bohr-Weisskopf	−0.00119	−0.00306	−0.00091	−0.0035	−0.0042
	Breit-Rosenthal	−0.00367	−0.00921	−0.00338	−0.0090	−0.0107
	Sushkov	0.00026	0.00069	0.00026	0.0007	0.0008
	Total	13.2974	35.1186	13.3755	37.092	39.558
	Other theory		35 [26]			
			35.026 [30]			
			35.068 [18]			
			35.08 [17]			
			35.09 [17]			
	Experimental	13.1(13)	36.4(40) [57]			
		15(3)	38(3) [58]			
		13.5(8)	34.9(4) [59]			
$5\,^2S$						
	Nonrelativistic	6.3834	16.858	6.4201	17.804	18.988
	Finite mass	−0.00175	−0.0040	−0.00132	−0.0033	−0.0028
	Relativistic	0.00631	0.0167	0.00634	0.0176	0.0188
	QED	−0.00196	−0.0052	−0.00197	−0.0055	−0.0058
	Bohr-Weisskopf	−0.00057	−0.0017	−0.00044	−0.0017	−0.0020

TABLE V. (*Continued.*)

State	Contribution	A (MHz) ^{6}Li	^{7}Li	^{8}Li	^{9}Li	^{11}Li
	Breit-Rosenthal	−0.00176	−0.0044	−0.00162	−0.0043	−0.0051
	Sushkov	0.00013	0.0003	0.00013	0.0003	0.0004
	Total	6.3837	16.860	6.4213	17.807	18.991
	Other theory		16 [26]			
			16.728 [18]			
$6\,^2S$						
	Nonrelativistic	3.5425	9.3553	3.5629	9.8802	10.537
	Finite mass	−0.00097	−0.00219	−0.00073	−0.00180	−0.0016
	Relativistic	0.00345	0.00912	0.00347	0.00963	0.0103
	QED	−0.00109	−0.00287	−0.00109	−0.00303	−0.0032
	Bohr-Weisskopf	−0.00032	−0.00096	−0.00024	−0.00093	−0.0011
	Breit-Rosenthal	−0.00098	−0.00245	−0.00090	−0.00240	−0.0029
	Sushkov	0.00007	0.00018	0.00007	0.00019	0.0002
	Total	3.5426	9.3562	3.5635	9.8818	10.539

[a]Reference refers to all four results.

$3\,^2S$ state of ^{7}Li are in close agreement with the result of the present calculations. For the isotopes ^{6}Li, ^{7}Li, ^{8}Li, and ^{9}Li, the present calculations are in very close concurrence with the theoretical results reported by Ewald *et al.* [14]. The present theoretical result for the $3\,^2S$ state of ^{6}Li is in excellent agreement with the experimental measurement of Bushaw *et al.* [13], and the calculated hyperfine constant for the same state for ^{7}Li is approximately 0.027% above the reported experimental result by the same authors. The theoretical results of the present work are also in very close agreement with the experimental results reported in Ewald *et al.* [14] for the isotopes ^{6}Li, ^{7}Li, ^{8}Li, and ^{9}Li. The precision with which the magnetic moments for ^{9}Li and ^{11}Li are known restricts the accuracy with which the hyperfine constants can be obtained for these two isotopes. For example, for the $3\,^2S$ state, the theoretical results of the present calculations are for ^{9}Li, 98.364±0.017 MHz, and for ^{11}Li, 104.90±0.07 MHz. We stress that these errors are from the uncertainties in just the magnetic moments. Because of the approximate nature of the calculation of the small corrections, with the inherent neglect of the many-electron nature of some of the corrections, it is extremely difficult if not impossible to make meaningful estimates of the errors for these corrections. The absence of certain information on the nuclear structure compounds the difficulties. Even though the net result for the sum of the small corrections is an approximate cancellation, the accumulated uncertainty from the small corrections is obviously additive.

Yan *et al.* [4], Jönsson *et al.* [30], and Godefroid *et al.* [17] have indicated a discrepancy of the theoretical values for the $3\,^2S$ state of ^{7}Li compared with the experimental value, allowing for experimental uncertainty, of Stevens *et al.* [16]. The recent experimental measurements of this state for ^{7}Li by Bushaw *et al.* [13] and Ewald *et al.* [14] are in very close agreement with theoretical values, including the results of the present calculations. It appears that the error bounds for the result of Stevens *et al.* are underestimated by a factor of approximately 7.

For the $4\,^2S$ state of ^{7}Li our present result is in close agreement with several literature theoretical calculations. Unfortunately, the most accurate experimental result for the hyperfine constant of the $4\,^2S$ state of ^{7}Li has an associated error that is too large to provide a severe challenge for the present theoretical result. For the same state for ^{6}Li, the present calculation agrees with the available experimental results, and again, the reported experimental error values are too large to provide a severe test of the theoretical calculations. No experimental or previous theoretical results are available for the isotopes ^{8}Li, ^{9}Li, and ^{11}Li for the $4\,^2S$ state.

For the $5\,^2S$ state of ^{7}Li the present theoretical result is in close agreement with the theoretical calculation of Guan and Wang [18]. No experimental results appear to be available for the hyperfine constant of this state for any of the lithium isotopes. A similar situation prevails for the $6\,^2S$ state of Li. We hope the present results will provide motivation for experimental studies on these higher states.

A feature that occurs for each of the $n\,^2S$ states studied, for all the isotopes of Li, is the approximate cancellation of the sum of the small corrections to the hyperfine constant. This does provide a rationalization of why previous nonrelativistic calculations of these hyperfine constants tend to be in reasonable agreement with experimental results, provided the nonrelativistic calculations take full account of electron correlation effects.

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