Isotope shifts and transition frequencies for the S and P states of lithium: Bethe logarithms and second-order relativistic recoil

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Isotope shifts and total transition frequencies are calculated for the $2\,^2S$-$3\,^2S$ transition of the lithium isotopes ^{6}Li, ^{7}Li, ^{8}Li, ^{9}Li, and the halo nucleus ^{11}Li. The accuracy is improved for previously calculated relativistic and quantum electrodynamic corrections, and in particular a disagreement for the Bethe logarithm is resolved for the ground ^2S state. Our previous result is confirmed for the $2\,^2P$ state. We use the pseudostate expansion method to perform the sum over virtual intermediate states. Results for the second-order relativistic recoil term of order $\alpha^2(\mu/M)^2$ Ry are shown to make a significant contribution relative to the theoretical uncertainty, but because of accidental cancellations the final result for the isotope shift is nearly unchanged. However, the spin-orbit term makes an unexpectedly large contribution to the splitting isotope shift (SIS) for the $2\,^2P_{1/2}$-$2\,^2P_{3/2}$ fine structure, increasing the theoretical value for the ^{6}Li-^{7}Li isotopes to $0.556\,31(7) \pm 0.001$ MHz. A comparison is made with high-precision measurements and other calculations for the SIS and for the total $2\,^2S$-$3\,^2S$ transition frequency.

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I. INTRODUCTION

The isotope shift method is well established as an effective method for the accurate determination of relative nuclear sizes for different isotopes of light atomic systems such as helium and lithium [1]. The method was proposed by Drake [2], and early applications were made to isotope shifts in ^{3}He-^{4}He [3] and ^{6}Li-^{7}Li [4] (see also Ref. [5] for a recent review). The method relies upon accurate and reliable calculations of the mass-dependent parts of the isotope shift so that the rms nuclear radius can be determined from the residual difference between theory and experiment. The method has been made possible by recent advances in calculations for two- and three-electron atomic systems such as helium and lithium. Essentially exact calculations are now possible for all practical purposes for the nonrelativistic energies and leading relativistic and quantum electrodynamic corrections. As a consequence, for example, comparisons with experiment for the hyperfine structure and isotope shift can be used to probe the properties of the nucleus and provide constraints on models for nuclear structure.

One of the most difficult quantities to calculate is the Bethe logarithm part of the quantum electrodynamic (QED) shift (Lamb shift) arising from the emission and reabsorption of virtual photons. Previous work resulted in a significant disagreement in value of the Bethe logarithm for the ground ^2S state of lithium [6,7]. The purpose of the present paper is to provide results of improved accuracy for this quantity in order to resolve the discrepancy. We also provide results for the second-order relativistic recoil corrections of order $\alpha^2(\mu/M)^2$ Ry, where α is the fine-structure constant, and $\mu/M = m_e/(M + m_e)$ is the ratio of the reduced electron mass to the nuclear mass. The result significantly changes the theoretical isotope shift. A theoretical value is also obtained for the $2\,^2S$-$3\,^2S$ transition frequency of lithium and compared with high-precision experiments.

The remainder of the paper is organized as follows. In Secs. II and III we briefly outline the calculation of the nonrelativistic energies, leading-order relativistic corrections, and the correlated Hylleraas wave functions used. This section includes the calculation of both the first- and second-order relativistic recoil corrections of order $\alpha^2\mu/M$ and $\alpha^2(\mu/M)^2$ Ry. This part has been extensively discussed in previous publications, and so the reader is referred to previous work for further details. Section IV then describes in greater detail the calculation of the leading-order QED corrections, and in particular the Bethe logarithm. The results demonstrate that the variational pseudostate expansion method is capable of high accuracy for the summation over virtual intermediate states. The results are presented in Sec. V for both the isotope shifts and the total transition frequencies. It is shown here that the second-order relativistic recoil term makes a significant contribution relative to the theoretical uncertainty, but for the $2\,^2S$-$3\,^2S$ transition the final result is nearly unchanged due to accidental cancellation. However, there is no such cancellation for the $2\,^2P_{1/2}$-$2\,^2P_{3/2}$ fine-structure splitting, resulting in a substantial change in the splitting isotope shift (SIS). Finally, Sec. VI provides some concluding remarks on the significance of the results and the need for future work on the QED terms to reduce the theoretical uncertainties.

II. NONRELATIVISTIC WAVE FUNCTIONS AND ENERGIES

Our aim throughout is to extract expansion coefficients for the energy in terms of powers of $\lambda = -\mu/M$. We begin with the Schrödinger equation for lithium $H\Psi_J = E_J\Psi_J$ with the

TABLE I. Nonrelativistic energy coefficients ε_0, ε_1, ε_2, and ε_3 due to mass polarization (specific isotope shift) for $1s^2 2s\,^2S$, $1s^2 3s\,^2S$, and $1s^2 2p\,^2P$ states of lithium. The coefficients $\tilde{\varepsilon}_0$, $\tilde{\varepsilon}_1$, $\tilde{\varepsilon}_2$, and $\tilde{\varepsilon}_3$ include the additional mass scaling contribution (normal isotope shift) such that the total energy is $E = \tilde{\varepsilon}_0 + \lambda\tilde{\varepsilon}_1 + \lambda^2\tilde{\varepsilon}_2 + \lambda^3\tilde{\varepsilon}_3 + \cdots$ in atomic units e^2/a_0, and $\lambda = -\mu/M$.

Coefficient	$1s^2 2s\,^2S$	$1s^2 3s\,^2S$	$1s^2 2p\,^2P$
ε_0	−7.478 060 323 910 150(5)	−7.354 098 421 444 367(3)	−7.410 156 532 652 41(3)
ε_1	−0.301 842 780 680 0(1)	−0.292 039 841 237 6(5)	−0.246 738 645 80(2)
ε_2	−1.499 788 835 879(6)	−1.385 931 956 9(3)	−1.559 764(2)
ε_3	−0.381 960 7(3)	−0.309 688(4)	−0.261 77(3)
$\tilde{\varepsilon}_0$	−7.478 060 323 910 150(5)	−7.354 098 421 444 367(3)	−7.410 156 532 652 41(3)
$\tilde{\varepsilon}_1$	−7.779 903 104 590 2(1)	−7.646 138 262 682 0(5)	−7.656 895 178 45(2)
$\tilde{\varepsilon}_2$	−1.801 631 616 559(6)	−1.677 971 798 1(3)	−1.806 503(2)
$\tilde{\varepsilon}_3$	−1.881 749 6(3)	−1.695 620(4)	−1.821 54(3)

nonrelativistic Hamiltonian

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

in reduced mass atomic units $(\mu/m_e)e^2/a_0 = (1+\lambda)e^2/a_0$, and Z is the nuclear charge. The factor $(1+\lambda)$ accounts for the normal isotope shift. The solution Ψ_J is expressed as linear combinations of antisymmetrized products of the form [8]

$$\phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \mathcal{A} r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1-\beta r_2-\gamma r_3} \times \mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\chi_1, \quad (2)$$

where $\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ is a vector-coupled product of spherical harmonics to form a state of total angular momentum L and z component M and

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \quad (3)$$

is the spin function with the total spin 1/2, and

$$\mathcal{A} = (1) - (12) - (13) - (23) + (123) + (132) \quad (4)$$

is the three-particle antisymmetrizer. The quantities r_i, $i = 1,2,3$ are the radial coordinates for the three electrons, and the $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ are the interparticle coordinates. As described previously [9], all terms in Eq. (2) are nominally included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega \quad (5)$$

and the convergence studied as the integer Ω is progressively increased up to $\Omega = 15$. In addition, the basis set is expanded into six sectors for S states and seven sectors for P states with different values of the nonlinear parameters α, β, and γ in each sector (see [8] for further details), resulting in basis sets with up to 33 600 terms for the $2\,^2P$ state. We also performed several calculations with basis sets that included the second spin function (i.e., with intermediate coupling to form a triplet state), and found no significant differences in the final results. All calculations were performed with octuple precision (approximately 64 decimal digit) arithmetic.

For convenience in extracting the isotope shift for different isotopes, the nonrelativistic energies were expanded in the form

$$E = \varepsilon_0 + \lambda\varepsilon_1 + \lambda^2\varepsilon_2 + \lambda^3\varepsilon_3 + \cdots, \quad (6)$$

where ε_0 is the energy for infinite nuclear mass ($\lambda = 0$), and the ε_i, $i = 1,2,3$ are calculated by perturbation theory with the mass polarization operator $\lambda\sum_{i>j}^{3}\nabla_i\cdot\nabla_j$ as the perturbation. The calculated ε_i coefficients are listed in Table I. The $\tilde{\varepsilon}_i = \varepsilon_i + \varepsilon_{i-1}$, $i = 1,2,3$ include the additional overall multiplying factor of $1+\lambda$ due to the normal isotope shift, and $\tilde{\varepsilon}_0 = \varepsilon_0$.

III. LEADING-ORDER RELATIVISTIC CORRECTIONS

The leading-order relativistic corrections of order α^2 Ry, including the relativistic recoil correction of order $(m_e/M)\alpha^2$ Ry, are calculated by first-order perturbation theory,

$$\Delta E_{\rm rel} = \langle\Psi_J|H_{\rm rel}|\Psi_J\rangle, \quad (7)$$

where Ψ_J is an eigenfunction of the nonrelativistic Hamiltonian (1) and $H_{\rm rel}$ is the relativistic correction operator defined by

$$H_{\rm rel} = B_1 + B_2 + B_4 + B_{3Z} + B_{3e} + B_{ss} + \frac{m_e}{M}(\tilde{\Delta}_2 + \tilde{\Delta}_{3Z}) + \gamma\left(2B_{3Z} + \frac{4}{3}B_{3e} + \frac{2}{3}B_{3e\gamma} + 2B_{ss}\right) + \gamma\frac{m_e}{M}\tilde{\Delta}_{3Z}, \quad (8)$$

with $\gamma = \alpha/(2\pi) - 0.328\,47(\alpha/\pi)^2 + \cdots$. The terms containing γ are the corrections due to the electron anomalous magnetic moment. In the above equation,

$$B_1 = -\frac{\alpha^2}{8}\left(\nabla_1^4 + \nabla_2^4 + \nabla_3^4\right), \quad (9)$$

$$B_2 = \frac{\alpha^2}{2}\sum_{i>j}^{3}\left[\frac{1}{r_{ij}}\nabla_i\cdot\nabla_j + \frac{1}{r_{ij}^3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\nabla_i)\nabla_j\right], \quad (10)$$

$$B_4 = \pi\alpha^2\left[\frac{Z}{2}\sum_{i=1}^{3}\delta(\mathbf{r}_i) - \sum_{i>j}^{3}\left(1 + \frac{8}{3}\mathbf{s}_i\cdot\mathbf{s}_j\right)\delta(\mathbf{r}_{ij})\right], \quad (11)$$

$$B_{3Z} = \frac{Z\alpha^2}{2}\sum_{i=1}^{3}\frac{1}{r_i^3}\mathbf{r}_i\times\mathbf{p}_i\cdot\mathbf{s}_i, \quad (12)$$

$$B_{3e} = \frac{\alpha^2}{2}\sum_{i\neq j}^{3}\frac{1}{r_{ij}^3}\mathbf{r}_{ji}\times\mathbf{p}_i\cdot(\mathbf{s}_i + 2\mathbf{s}_j), \quad (13)$$

$$B_{\rm ss} = \alpha^2 \sum_{i>j}^{3} \left[\frac{1}{r_{ij}^3}(\mathbf{s}_i \cdot \mathbf{s}_j) - \frac{3}{r_{ij}^5}(\mathbf{r}_{ij} \cdot \mathbf{s}_i)(\mathbf{r}_{ij} \cdot \mathbf{s}_j) \right], \tag{14}$$

$$\tilde{\Delta}_2 = \frac{iZ\alpha^2}{2} \sum_{j=1}^{3} \left[\frac{1}{r_j}\mathbf{p} \cdot \nabla_j + \frac{1}{r_j^3}\mathbf{r}_j \cdot (\mathbf{r}_j \cdot \mathbf{p})\nabla_j \right], \tag{15}$$

$$\tilde{\Delta}_{3Z} = Z\alpha^2 \sum_{i=1}^{3} \frac{1}{r_i^3}\mathbf{r}_i \times \mathbf{p} \cdot \mathbf{s}_i, \tag{16}$$

$$B_{3e\gamma} = \frac{\alpha^2}{2} \sum_{i\neq j}^{3} \frac{1}{r_{ij}^3}\mathbf{r}_{ji} \times \mathbf{p}_i \cdot (\mathbf{s}_i - \mathbf{s}_j), \tag{17}$$

with $\mathbf{p} = \mathbf{p_1} + \mathbf{p_2} + \mathbf{p_3}$. These operators can be interpreted as follows. B_1 is the correction due to the variation of mass with velocity, B_2 is the correction to the interaction between electrons due to retardation effect, B_4 is the contact interactions between the electron and the nucleus and between the electrons, which is also named the Darwin term, B_{3Z}, B_{3e}, and $B_{\rm ss}$ are, respectively, the spin-orbit, spin-other-orbit, and spin-spin interactions due to magnetic dipole moments. $B_{\rm ss}$ does not contribute for spin-1/2 states. The operators $\tilde{\Delta}_2$ and $\tilde{\Delta}_{3Z}$ associated with m_e/M in (8) are relativistic recoil effects coming from the transformation of the Breit interaction from inertial coordinates to center-of-mass plus relative coordinates [10].

The expectation values of the leading-order relativistic correction operators (Breit operators) are calculated with high precision nonrelativistic wave functions as described in our previous work [8,11]. Since the basis sets for these wave functions contain up to 30 000 terms, it was necessary to invoke programs with parallel processing to calculate the expectation values of the various relativistic correction operators. The computational methods to evaluate the matrix elements of these operators are described by Yan and Drake [9] and Yan [12]. With careful programming, the matrix elements can be calculated to enough accuracy by using these methods, especially for singular cases such as $\langle r_{ij}^{-2}\rangle$, $\langle r_{ij}^{-3}\rangle$, and $\langle r_i^{-3}\rangle$. Additionally, to improve the convergence of the expectation values of the operators $\delta(\mathbf{r}_i)$ and $\delta(\mathbf{r}_{ij})$, we used Drachman's global operator method [13] in the calculations of the matrix elements. The main idea of Drachman's method is the use of the two identities

$$\begin{aligned}\langle\psi|\delta(\mathbf{r}_i)|\psi\rangle &= -\frac{1}{\pi}\langle\psi|\frac{1}{r_i}(V_d - E)|\psi\rangle \\ &\quad - \frac{1}{2\pi}\sum_{s=1}^{N}\langle\nabla_s\psi|\frac{1}{r_i}|\nabla_s\psi\rangle, \end{aligned}\tag{18}$$

$$\begin{aligned}\langle\psi|\delta(\mathbf{r}_{ij})|\psi\rangle &= -\frac{1}{2\pi}\langle\psi|\frac{1}{r_{ij}}(V_d - E)|\psi\rangle \\ &\quad - \frac{1}{4\pi}\sum_{s=1}^{N}\langle\nabla_s\psi|\frac{1}{r_{ij}}|\nabla_s\psi\rangle, \end{aligned}\tag{19}$$

where E and ψ are the energy and wave function of the state of interest, and $V_d = -\sum_{i=1}^{N}\frac{Z}{r_i} + \sum_{i>j}\frac{1}{r_{ij}} - \frac{\mu}{M}\sum_{i>j}\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j$. For B_1, the following identity is used to improve the convergence of the expectation value:

$$\begin{aligned}\langle\psi|B_1|\psi\rangle &= \frac{\alpha^2}{4}\sum_{i>j}\left\langle p_i^2\psi\middle|p_j^2\psi\right\rangle - \frac{\alpha^2}{2}\langle\psi|(E-V)^2|\psi\rangle \\ &\quad - \frac{\alpha^2}{2}\frac{\mu}{M}\langle\psi|(E-V)\sum_{i>j}\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j \\ &\quad + \sum_{i>j}\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j(E-V)|\psi\rangle \\ &\quad - \frac{\alpha^2}{2}\left(\frac{\mu}{M}\right)^2\langle\psi|\left(\sum_{i>j}\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j\right)^2|\psi\rangle \end{aligned}\tag{20}$$

with $V = -\sum_{i=1}^{N}\frac{Z}{r_i} + \sum_{i>j}\frac{1}{r_{ij}}$. For the case of finite nuclear mass, we included the last term in Eq. (20), which is order of $(\frac{\mu}{M})^2$. The expectation values of the various relativistic correction operators are listed in Tables II and III for the S and P states respectively. The first-order mass polarization coefficients of these operators, except for B_1, are calculated by perturbation methods [14]. For B_1, the first- and second-order mass polarization coefficients are calculated indirectly by fitting a quadratic polynomial to values of $\langle B_1\rangle$ for $\mu/M = 0$, $(\mu/M)_{^7\rm Li}$, and $2(\mu/M)_{^7\rm Li}$. The results are also listed in Tables II and III.

Finite mass and relativistic recoil corrections

Our objective is to include finite mass corrections of order $\alpha^2\lambda$ and $\alpha^2\lambda^2$ Ry. Each term B_i in the Breit interaction (8) has a mass polarization expansion due to the perturbing effect of the mass polarization operator $\lambda\sum_{i>j}\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j$ in the Schrödinger Hamiltonian (1). The result is a perturbation expansion of the form

$$B_i(\lambda) = B_i^{(0)} + \lambda B_i^{(1)} + \lambda^2 B_i^{(2)} + \cdots. \tag{21}$$

In addition, each term $B_i^{(k)}$ has a mass scaling contribution of the form

$$\begin{aligned}B_i^{(k)}(\lambda) &= (1+\lambda)^n B_i^{(k)}(0) \\ &= \left(1 + n\lambda + \frac{n(n-1)}{2}\lambda^2 + \cdots\right)B_i^{(k)}(0), \end{aligned}\tag{22}$$

where $n = 4$ for B_1 and $n = 3$ for all the other terms, according to their dependence on inverse powers of r. Combining the two expansions results in the total mass dependence

$$\begin{aligned}B_i(\lambda) &= B_i^{(0)}(0) + \left[B_i^{(1)}(0) + nB_i^{(0)}(0)\right]\lambda \\ &\quad + \left[B_i^{(2)}(0) + nB_i^{(1)}(0) + \frac{n(n-1)}{2}B_i^{(0)}(0)\right]\lambda^2 + \cdots. \end{aligned}\tag{23}$$

The coefficients of λ and λ^2 will be referred to as the first- and second-order relativistic recoil terms respectively. The one additional consideration is that the factor $m_{\rm e}/M$ multiplying the terms $\tilde{\Delta}_2 + \tilde{\Delta}_{3Z}$ in Eq. (8) is equivalent to

$$\frac{m_{\rm e}}{M} = -\frac{\lambda}{1+\lambda} \tag{24}$$

TABLE II. Total Breit interaction expansion coefficients $B^{(0)}$, $\tilde{B}^{(1)}$, and $\tilde{B}^{(2)}$ in powers of $\lambda = -\mu/M$ for $1s^2 2s\ ^2S$ and $1s^2 3s\ ^2S$ states of lithium. The coefficients include the mass-scaling corrections as shown in Eq. (22) such that the total matrix element for each operator is of the form $B_i = B_i^{(0)} + \lambda\tilde{B}_i^{(1)} + \lambda^2\tilde{B}_i^{(2)}$, in atomic units of $2R_\infty$.

Operator	$B_i^{(0)}$	$\tilde{B}_i^{(1)}$	$\tilde{B}_i^{(2)}$
		$1s^2 2s\ ^2S_{1/2}$	
B_1/α^2	−78.556 122 8(1)	−319.371 572(3)	−538.499(8)
B_2/α^2	−0.435 597 832 4(3)	−4.383 945 07(1)	−11.362 3(5)
$\tilde{\Delta}_2/\alpha^2$	−130.915 112 22(4)	−304.443 028 70(9)	
$\sum_i\langle\delta(\mathbf{r}_i)\rangle$	13.842 610 859(2)	42.012 422 9(7)	47.988(9)
$\sum_{i>j}\langle\delta(\mathbf{r}_{ij})\rangle$	0.544 324 632 88(5)	1.550 966 3(4)	1.80(2)
Q	0.021 766 3(1)	−0.064 215 17(5)	
Q_1	−24.534 879(2)		
		$1s^2 3s\ ^2S_{1/2}$	
B_1/α^2	−77.857 416(1)	−316.508 278 1(2)	−531.818(8)
B_2/α^2	−0.429 908 605(3)	−4.212 140 20(1)	−10.776 219(1)
$\tilde{\Delta}_2/\alpha^2$	−129.433 834 41(8)	−299.347 561 89(7)	
$\sum_i\langle\delta(\mathbf{r}_i)\rangle$	13.736 502 928(4)	41.697 404 8(5)	47.512(7)
$\sum_{i>j}\langle\delta(\mathbf{r}_{ij})\rangle$	0.536 168 417 8(2)	1.530 101 39(2)	1.778(1)
Q	0.015 769 6(5)	−0.083 653(2)	
Q_1	−24.345 861(1)		

and so only the λ^0 and λ^1 terms in (23) should be kept, with $n = 3$ and $1/(1+\lambda) = 1 - \lambda + \cdots$. The overall expansion is thus

$$\frac{m_e}{M}\tilde{\Delta}_2 = -\lambda\tilde{\Delta}_2^{(0)} + \lambda^2\left(\tilde{\Delta}_2^{(1)} + 2\tilde{\Delta}_2^{(0)} + \cdots\right) \tag{25}$$

and similarly for $\tilde{\Delta}_{3Z}$.

IV. LEADING-ORDER QED CORRECTIONS

As discussed in detail in previous papers [1,15], the QED contribution to the energy, and its finite mass correction, can be expressed in the form

$$E_{\rm QED} = E_{\rm L,1} + E_{\rm M,1} + E_{\rm R,1} + E_{\rm L,2}, \tag{26}$$

where $E_{\rm L,1}$ is the mass-independent part of the electron-nucleus Lamb shift (the Kabir-Salpeter term [16]), $E_{\rm M,1}$ contains mass scaling and mass polarization corrections, $E_{\rm R,1}$ contains recoil corrections (including radiative recoil), and $E_{\rm L,2}$ is the electron-electron term originally obtained by Araki [17] and Sucher [18]. We are concerned here primarily with the terms $E_{\rm L,1}$ and $E_{\rm M,1}$. With the notation $\langle\sum_i\delta(\mathbf{r}_i)\rangle = \langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)} + \lambda\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(1)} + \cdots$ to express the mass dependence of this and other similar matrix elements, they are given by

$$\begin{aligned} E_{\rm L,1} = {}& \frac{4Z\alpha^3\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}}{3}\left\{\ln(Z\alpha)^{-2} - \beta(n^2L) + \frac{19}{30}\right. \\ & + (3\pi\alpha Z)0.765\,405\,577 \\ & + \frac{\alpha}{\pi}[0.404\,17 - (3\alpha Z/4)21.556\,85] \\ & + (Z\alpha)^2\left[-\frac{3}{4}\ln^2(Z\alpha)^{-2} + C_{61}(1s^2\,nL)\ln(Z\alpha)^{-2}\right. \\ & \left.\left. + C_{60}(1s^2\,nL)\right]\right\}, \end{aligned} \tag{27}$$

$$\begin{aligned} E_{\rm M,1} = {}& \frac{\mu\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(1)}}{M\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}}E_{\rm L,1} \\ & + \frac{4Z\alpha^3\mu\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}}{3M}[1 - \Delta\beta_{\rm MP}(n^2L)], \end{aligned} \tag{28}$$

and

$$\begin{aligned} E_{\rm R,1} = {}& \frac{4Z^2\alpha^3\mu\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}}{3M}\left[\frac{1}{4}\ln(Z\alpha)^{-2} - 2\beta(n^2L) - \frac{1}{12}\right. \\ & - \frac{7}{4}a(1s^2\,nL) - \frac{3}{4}(\pi\alpha)1.364\,49 \\ & \left. + \frac{3}{4}\pi Z\alpha D_{50}(1s^2\,nL) + \frac{1}{2}\alpha^2 Z\ln^2(Z\alpha)^{-2}\right]. \end{aligned} \tag{29}$$

These terms closely resemble the corresponding terms in the hydrogenic Lamb shift [19], except that an overall multiplying factor of $\langle\delta(\mathbf{r})\rangle = Z^3\delta_{L,0}/(\pi n^3)$ for the hydrogenic case is replaced by the correct expectation value $\langle\sum_{j=1}^N\delta(\mathbf{r}_j)\rangle$ for the multielectron case, summed over the N electrons. The term $a(1s^2\,nL)$ corresponds to a well-known term in the hydrogenic Lamb shift. Its three-electron generalization is [20,21]

$$a(1s^2\,nL) = \frac{2Q_1}{\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}} + 2\ln Z - 3, \tag{30}$$

where

$$Q_1^{(0)} = \frac{1}{4\pi}\lim_{\epsilon\to 0}\sum_i\left\langle r_i^{-3}(\epsilon) + 4\pi(\gamma_{\rm eu} + \ln\epsilon)\delta(\mathbf{r}_i)\right\rangle \tag{31}$$

and $\gamma_{\rm eu}$ is Euler's constant. The residual state dependence due to other terms such as the Bethe logarithm discussed below is then relatively weak. The state-dependent coefficients $C_{61}(1s^2\,nL)$, $C_{60}(1s^2\,nL)$, and $D_{50}(1s^2\,nL)$ are approximated by the generic formula [20]

$$X(1s^2\,nL) = \frac{2X(1s) + X(nL)/n^3}{2 + \delta_{L,0}/n^3}, \tag{32}$$

TABLE III. Total Breit interaction expansion coefficients $B^{(0)}$, $\tilde{B}^{(1)}$, and $\tilde{B}^{(2)}$ in powers of $\lambda = -\mu/M$ for the $1s^2 2p\,^2P_{1/2}$ state of lithium. The spin-dependent terms B_{3Z}, B_{3e}, and $B_{3e\gamma}$ differ by a factor of $-1/2$ for the $1s^2 2p\,^2P_{3/2}$ state. The coefficients include the mass-scaling corrections as shown in Eq. (22) such that the total matrix element for each operator is of the form $B_i = B_i^{(0)} + \lambda \tilde{B}_i^{(1)} + \lambda^2 \tilde{B}_i^{(2)}$, in atomic units of $2R_\infty$.

Operator	$B_i^{(0)}$	$\tilde{B}_i^{(1)}$	$\tilde{B}_i^{(2)}$
	$1s^2 2p\ ^2P_{1/2}$		
B_1/α^2	−77.505 616 73(9)	−315.883 643(9)	−532.21(8)
B_2/α^2	−0.396 425 741 7(4)	−4.190 763(1)	−11.2(6)
$\tilde{\Delta}_2/\alpha^2$	−128.614 890 332(1)	−300.579 56(3)	
$\sum_i \langle\delta(\mathbf{r}_i)\rangle$	13.676 197 050 58(6)	41.676 52(2)	47.6(2)
$\sum_{i>j} \langle\delta(\mathbf{r}_{ij})\rangle$	0.532 274 099 91(4)	3.126 917(5)	7.96(6)
Q	0.023 050 7(1)	−0.081 72(4)	
Q_1	−24.232 722 36(3)		
B_{3e}/α^2	0.075 396 972 7(30)	−0.023 177 7(1)	0.14(3)
B_{3Z}/α^2	−0.094 459 765 48(4)	0.000 531(1)	20.37(5)
$B_{3e\gamma}/\alpha^2$	0.046 541 795 29(7)	−0.025 148(2)	
$\tilde{\Delta}_{3Z}/\alpha^2$	0.033 787 593(4)	−0.154 402(9)	

where $X(1s)$ and $X(nL)$ are the corresponding hydrogenic coefficients [19] evaluated directly for $L = 0$, and in a fully screened hydrogenic approximation for $L > 0$. The above formula leaves the coefficients unchanged if they are in fact state independent (other than the overall factor of $1/n^3$), and it reproduces the leading term in a $1/Z$ expansion if the coefficients are state dependent.

The electron-electron QED shift $E_{L,2}$ can similarly be separated into mass-independent and mass dependent parts according to

$$E_{L,2} = E_{L,2}^{(0)} + \frac{\mu}{M} E_{L,2}^{(1)} + \cdots , \tag{33}$$

where [17,18,22]

$$E_{L,2}^{(0)} = \alpha^3 \left(\frac{14}{3} \ln\alpha + \frac{164}{15} - \pi\alpha \ln\alpha \right) \sum_{i>j} \langle\delta(\mathbf{r}_{ij})\rangle^{(0)} - \frac{14}{3}\alpha^3 Q^{(0)} \tag{34}$$

and the mass scaling and mass polarization corrections are

$$E_{L,2}^{(1)} = \alpha^3 \left(\frac{14}{3} \ln\alpha + \frac{164}{15} \right) \sum_{i>j} \langle\delta(\mathbf{r}_{ij})\rangle^{(1)} - \frac{14}{3}\alpha^3 \left(Q^{(1)} + \sum_{i>j} \langle\delta(\mathbf{r}_{ij})\rangle^{(0)} \right). \tag{35}$$

Following our notation, the $Q^{(0)}$ term for infinite mass is given by

$$Q^{(0)} = \frac{1}{4\pi} \lim_{\epsilon\to 0} \sum_{i>j} \left\langle r_{ij}^{-3}(\epsilon) + 4\pi(\gamma_{eu} + \ln\epsilon)\delta(\mathbf{r}_{ij}) \right\rangle. \tag{36}$$

The $Q^{(1)}$ term is the correction due to the mass polarization correction to the wave function and mass scaling. As a word of explanation, the infinitesimal limiting quantity ϵ has dimensions of distance, and so it generates the additional term $\sum_{i>j} \langle\delta(\mathbf{r}_{ij})\rangle^{(0)}$ in (35) when distances are rescaled for the finite mass case according to $\epsilon \to (\mu/m_e)\epsilon$.

The calculations of the leading-order QED corrections involve the expectation values of the operators $\sum_i \delta(\mathbf{r}_i)$, $\sum_{i>j} \delta(\mathbf{r}_{ij})$, Q and Q_1, and the Bethe logarithm. The expectation values of $\sum_i \delta(\mathbf{r}_i)$, $\sum_{i>j} \delta(\mathbf{r}_{ij})$, and the coefficients $Q^{(0)}$, $Q^{(1)}$, and $Q_1^{(0)}$ can be calculated to high precision, as shown in Tables II and III; but the coefficients $Q^{(n)}$ and the Bethe logarithm converge very slowly. We use the variational pseudostate method to calculate the Bethe logarithm. This method was discussed by Drake and Goldman [23] for helium and was used to calculate the Bethe logarithm for lithium by Yan and Drake [6,24]. Very large exponential parameters need to be included in the variational basis sets to get good convergence. But unfortunately, these large parameters make one subsidiary integral (W function as it called in [25]) used in the calculation of matrix elements converge very slowly. This obstacle limited the accuracy of Bethe logarithms of lithium in the previous implement of the variational method. But it was overcome recently by Li *et al.* [26]. In Ref. [26], the subsidiary integral was expressed in terms of either a finite series or a finite recursion relation, which are both computationally efficient and numerically stable. Without the basic integral problem, the variational basis sets are enlarged to 6809 terms for $1s^2 2s\,^2S$ and $1s^2 3s\,^2S$ states, and 18 708 terms (including S, P, and D symmetries) for the $1s^2 2p\,^2P$ state. As a consequence, the accuracies of the Bethe logarithms and their mass dependent coefficients for these states are improved significantly. The results are listed in Table IV and compared with those of other authors. For the $1s^2 2s\,^2S$ state, our result is consistent with and has a similar accuracy to that calculated recently by Puchalski and Pachucki [7], and consistent with that calculated by Yan and Drake [24] in 2003, but inconsistent with that calculated by Yan *et al.* [6] in 2008. For $1s^2 3s\,^2S$ state, our result is more accurate than those of others by at least two orders of magnitude. For $1s^2 2p\,^2P$ state, our result is consistent with those of others but more accurate by one order of magnitude.

V. RESULTS AND DISCUSSION

A. Isotope shifts

It is conventional to express the total isotope shift for an atomic transition $a \to b$ between isotopes A and A'

TABLE IV. Bethe logarithms for $1s^2 2s\,^2S$, $1s^2 3s\,^2S$, and $1s^2 2p\,^2P$ states of lithium, expressed in the form $\beta = \beta^{(0)} + (\mu/M)\beta^{(1)} + \ln(Z^2\mu/m_e)$.

N_1	N_2	$\beta^{(0)}$	$R(\Omega)$	$\beta^{(1)}$	$R(\Omega)$
		$1s^2 2s\,^2S$			
3910	1452	2.980 833 469	9.587	0.113 790 737	15.526
3910	2445	2.980 923 592	8.791	0.113 793 610	17.772
3910	4109	2.980 937 643	6.414	0.113 801 327	0.372
3910	6809	2.980 941 416	3.724	0.113 809 084	0.995
∞		2.980 943(1)		0.113 81(1)	
Yan *et al.* [24]		2.980 925(3)		0.113 6(2)	
Yan *et al.* [6]		2.981 06(1)		0.113 05(5)	
Puchalski *et al.* [7]		2.980 944(4)		0.113 81(3)	
Stanke *et al.* [27]		2.980 93			
		$1s^2 3s\,^2S$			
3910	2445	2.982 187 350	8.908	0.110 628 587	–0.1989
3910	4109	2.982 209 101	10.29	0.110 549 049	2.372
3910	6809	2.982 210 691	13.68	0.110 520 286	2.764
∞		2.982 210(1)		0.110 50(2)	
Yan *et al.* [24]		2.982 40(4)		0.111(1)	
Yan *et al.* [6]		2.982 36(6)		0.110 5(3)	
Stanke *et al.* [27]		2.982 12			
		$1s^2 2p\,^2P$			
4172	6070	2.982 243 400	5.902	0.111 183 023	3.726
4172	10735	2.982 549 536	6.435	0.111 118 489	6.697
4172	18708	2.982 565 711	7.142	0.111 109 241	6.978
∞		2.982 568(3)		0.111 107(2)	
Yan *et al.* [6]		2.982 57(6)		0.111 08(5)	
Puchalski *et al.* [7]		2.982 58(7)		0.111 3(5)	

in the form

$$\delta\nu^{A,A'}_{a\to b} = \delta\nu^{A,A'}_{a\to b}(0) + C_{a\to b}\left[\left(\bar{r}_c^{A'}\right)^2 - \left(\bar{r}_c^{A}\right)^2\right], \qquad (37)$$

where $\delta\nu^{A,A'}_{a\to b}(0)$ is the mass-dependent part coming from atomic structure, $(\bar{r}_c^A)^2$ is the rms nuclear charge radius for isotope A, and $C_{a\to b}$ is a constant determined primarily by the change in electron density at the nucleus with small corrections due to finite mass and relativistic effects (see Ref. [15] for a detailed discussion).

The primary motivation for this work is to improve the accuracy of the mass-dependent part $\delta\nu^{A,A'}_{a\to b}(0)$ from atomic structure. As emphasized previously [2–4], the accuracy of $\delta\nu^{A,A'}_{a\to b}(0)$ is much higher than for the atomic energies themselves because the mass-independent part of the energy cancels when taking differences between isotopes. For example, the leading QED uncertainties for the total energy come from terms of order α^4 Ry, but these cancel, leaving much smaller uncertainties of order $\alpha^4\lambda$ Ry $\sim$ 20 kHz.

The various calculated contributions to $\delta\nu^{A,A'}_{a\to b}(0)$ for the Li isotopes relative to ^{6}Li are summarized in Table V, with the assumed nuclear masses as listed at the head of each column. There is close agreement for all entries with the previous calculations of Puchalski and Pachucki [15,31]. The main potentially important difference is the additional contribution from the second-order relativistic recoil term of order $\alpha^2\lambda^2$. As shown in Table VI for the ^{6}Li-^{7}Li isotope shift, there are individual contributions as large as -5.1 kHz from the $\lambda^2 B_1^{(2)}$ term. However, there is a great deal of accidental cancellation, leaving a net contribution of only 0.12 kHz. The changes are more than an order of magnitude smaller than the uncertainties in the measured isotope shifts ($\pm$34 kHz or larger [15]), and so they do not significantly change the previously obtained nuclear charge radii. The theoretical uncertainty comes almost entirely from the estimated radiative recoil contribution of order $\alpha^4\lambda$. The uncertainty is taken to be 25% of this term.

B. Total $2\,^2S$-$3\,^2S$ transition frequency

We summarize in Table VII the contributions to the total $2\,^2S$-$3\,^2S$ transition frequency, for which there are earlier calculations [6,31] and high precision measurements [32,33] available for comparison. Just as for the isotope shift, the second-order relativistic recoil term of order $\lambda^2\alpha^2$ is abnormally small because the positive contribution of 19.5 kHz from the $\lambda^2 B_1^{(2)}$ term is almost exactly canceled by the other contributions, leaving a net contribution of only $-0.44(22)$ kHz for ^{6}Li. The higher accuracy of the relativistic corrections in the present work now brings our results into essentially exact agreement with those of Puchalski and Pachucki [31], but the uncertainties due to the QED terms of order α^4 and α^5 Ry make the final results much less accurate ($\pm$18 MHz) than the measurements ($\pm$0.09 MHz). Further progress on the theoretical side must await calculations of these higher-order QED terms. The main significance of the results in Table VII is that all other lower-order contributions are known to sufficiently high accuracy that an experimental value for the higher-order terms is clearly defined.

TABLE V. Theoretical isotope shifts of ^{A}Li ($A = 7, 8, 9, 11$) relative to ^{6}Li in the $2\,^2S_{1/2} \rightarrow 3\,^2S_{1/2}$ transition. Contributions of the mass-dependent terms to $\delta\nu^{A,A'}_{2s\rightarrow 3s}$ with $A = {}^6$Li are calculated using the masses listed in the first row. The mass of the reference isotope ^{6}Li is 6.015 122 794(16) u [28]. The coefficient $C_{A,A'}$ for the field shift is in units of MHz/fm^2. All other values are in MHz.

Term	^{7}Li	^{8}Li	^{9}Li	^{11}Li
M (amu)	7.016 003 4256(45) [29]	8.022 486 24(12) [30]	9.026 790 20(21) [30]	11.043 723 61(69) [30]
λ[a]	11 454.655 1(2)	20 090.837 3(9)	26 788.479 1(13)	36 559.175 4(27)
λ^2	−1.794 03	−2.964 4	−3.764 16	−4.761 89
λ^3	0.000 34	0.000 54	0.000 65	0.000 78
$\alpha^2\lambda$	0.017 20(5)	0.030 2(1)	0.040 2(1)	0.054 9(2)
$\alpha^2\lambda^2$	0.000 12(6)	0.000 20(10)	0.000 25(12)	0.000 31(15)
$\alpha^3\lambda$	−0.050 08	−0.087 84(1)	−0.117 12(1)	−0.159 84(1)
$\alpha^4\lambda$	−0.008 4(28)	−0.014 7(50)	−0.019 6(66)	−0.026 8(90)
$\nu_{\rm pol}$				0.039(4)[b]
Total	11 452.820 4(28)	20 087.801 3(50)	26 784.619 5(66)	36 554.322(9)
	11 452.820 7(24)[c]	20 087.801 9(42)[c]	26 784.620 2(66)[c]	36 554.323(9)[c]
	11 452.821 1(28)[d]	20 087.802 6(50)[d]	26 784.621 3(67)[d]	36 554.325(9)[d]
$C_{A,A'}$[e]	−1.571 9(16)	−1.571 9(16)	−1.572 0(16)	−1.570 2(16)

[a]Uncertainties for this line are dominated by the nuclear mass uncertainty.
[b]Nuclear polarization correction calculated by Puchalski and Pachucki [15].
[c]Calculation by Puchalski and Pachucki [31].
[d]Calculation by Yan and Drake [15].
[e]Uncertainty in $C_{A,A'}$ is from the known error in the corresponding relativistic correction for hydrogenic systems based on the behavior of the Dirac wave function at the origin.

C. $2\,^2S_{1/2}$-$2\,^2P_J$ transition frequency and fine structure

The $2\,^2S_{1/2}$-$2\,^2P_J$ transitions (the D lines) and fine structure have recently been calculated to high precision by Puchalski and co-workers [7,34], including corrections of order α^4 and $\alpha^5\ln(\alpha)$ Ry, but not the $\lambda^2\alpha^2$ terms evaluated in the present work. The two sets of results are compared in Table VIII for the $2\,^2S_{1/2}$-$2\,^2P_J$ centroid (i.e., center of gravity). The agreement is excellent for all the contributions with the exception of the leading QED term of order α^3 Ry. After correcting what is evidently a misprint in Ref. [7] there is a significant discrepancy of 15 MHz between their corrected value of −8870(8) MHz and our value of −8885(3) MHz. This discrepancy accounts for most of the difference in the final transition frequencies quoted in the table. A possible explanation is that our old value of 2.981 06(1) for the $2\,^2S$ Bethe logarithm was used in Ref. [7] in place of the new value 2.980 943(1).

For the ^{6}Li-^{7}Li isotope shift in the $2\,^2S_{1/2}$-$2\,^2P_J$ transitions and the fine structure, the $\lambda^2\alpha^2$ term plays a significant role. As shown in Table IX, it contributes -17.3 ± 2.0 kHz for $J = 1/2$ and 6.7 ± 2.0 kHz for $J = 3/2$. The effect comes primarily from the spin-orbit term, and so it almost exactly cancels from the $2\,^2S_{1/2}$-$2\,^2P_J$ centroid. However, it makes a significant contribution to the fine-structure splitting and the splitting isotope shift (SIS). Beginning with the fine-structure splittings, Table X shows the results for ^{6}Li and ^{7}Li. For ^{6}Li as an example, the leading mass-independent term agrees well with the calculations of Puchalski *et al.* [7], but the first-order recoil correction of −2.701 02(7) MHz

TABLE VI. ^{7}Li-^{6}Li isotope shift: contributions to the second-order relativistic recoil of order $\lambda^2\alpha^2$ Ry for the $3\,^2S$-$2\,^2S$ transition. Units are kHz.

Term	$2\,^2S$	$3\,^2S$	$3\,^2S$-$2\,^2S$
$\lambda^2 B_1^{(2)}$	416.022(6)	410.862(6)	−5.161(8)
$\lambda^2 B_2^{(2)}$	8.777 861	8.325 276	−0.452 585(1)
$\lambda^2\tilde{\Delta}_2^{(1)}$	−235.200 520	−231.263 966	3.936 554
$\lambda^2\alpha^2\pi\langle\delta(\mathbf{r}_{ij})\rangle^{(2)}$	−4.375(39)	−4.314 8(31)	0.060(39)
$\lambda^2\alpha^2\pi Z\langle\delta(\mathbf{r}_i)\rangle^{(2)}/2$	−174.707(33)	−172.972(24)	1.73(4)
Total	10.52(5)	10.636(25)	0.12(6)

TABLE VII. Contributions to the total $2\,^2S_{1/2} \rightarrow 3\,^2S_{1/2}$ transition frequency. All values are in GHz.

Term	^{6}Li	^{7}Li
Infinite mass	815 630.136 435	815 630.136 435
λ	−80.282 635	−68.827 980
λ^2	0.006 770	0.004 976
λ^3	−0.000 000 93	−0.000 000 59
α^2	62.630 04(14)	62.630 04(14)
$\alpha^2\lambda$	−0.000 121	−0.000 103
$\alpha^2\lambda^2$	−0.000 000 4(2)	−0.000 000 3(2)
α^3	−5.602 8(6)	−5.602 8(6)
$\alpha^3\lambda$	0.000 351	0.000 301
α^4 (est.)	−0.175(12)	−0.175(12)
α^5 (est.)	0.013(5)	0.013(5)
$(\bar{r}_c)^2$	−0.010 1(3)	−0.008 9(2)
$(\bar{r}_c)^2\lambda$	0.000 003	0.000 002
Total	815 606.717(18)	815 618.171(18)
Other theory		
Yan *et al.* [6]	815 606.712(30)	815 618.171(30)
Puchalski *et al.* [31]	815 606.717(19)	815 618.170(19)
Experiment		
Lien *et al.* [32]	815 606.727 46(18)	815 618.181 45(9)
Sánchez *et al.* [33]	815 606.727 59(18)	815 618.181 57(18)

TABLE VIII. Contributions to the total $2\,^2S_{1/2} \rightarrow 2\,^2P_{\text{cent.}}$ transition frequency centroid for ^{6}Li. All values are in MHz.

Term	Present work	Puchalski *et al.* [7]
Infinite mass	446785483.5(1)	446785483.5(1)
λ	−73826.577	−73826.6
λ^2	−0.267	
λ^3	0.000	
α^2	93765.69(4)	93765.1(2)
$\alpha^2\lambda$	8.57(4)	8.6
α^3	−8885.(3)	−8870.(8)[a]
$\alpha^3\lambda$	−0.257	−0.265
α^4	−272.(26)	−269.(26)
α^5	21.(7)	30.(7)
$\bar{r}_c^2$	−16.0	−16.0
Total	446796278.(28)	446796306.(28)

[a]Misprint corrected from −8850.(8) MHz in Ref. [7].

does not agree with their value −2.7861(5) MHz. The agreement considerably improves when the second-order recoil correction of −0.090 35(27) is added, but there remain discrepancies of −5.3(5) kHz for ^{6}Li and 6.6(5) kHz for ^{7}Li. These discrepancies are small compared with the ±0.09 MHz uncertainties in the higher-order (mass independent) QED corrections of order α^4 and $\alpha^5 \ln\alpha$ Ry corrections recently evaluated by Puchalski and co-workers [34,35], but they are significant compared with other uncertainties in the calculation. It is interesting that the large second-order contribution comes primarily from the $\lambda^2 B_{3Z}^{(2)}$ term. In fact, because of accidental cancellation between mass scaling and mass polarization for the first-order term, $\lambda^2 B_{3Z}^{(2)}$ is actually larger than $\lambda B_{3Z}^{(1)}$.

D. The $2\,^2P_{1/2}$-$2\,^2P_{3/2}$ splitting isotope shift (SIS)

As pointed out previously for the cases of Li^+ [4] and Li [20], the SIS provides a valuable check of the consistency of experimental data because on the theoretical side it is insensitive to higher-order QED corrections or the finite nuclear size, and so a reliable theoretical value can be calculated for comparison. In particular, the ±90-kHz uncertainties [34,35] in the higher-order QED corrections shown in Table X cancel from the SIS because they are mass independent, leaving a theoretical prediction with an estimated uncertainty of less than ±1 kHz. Results for the SIS and comparisons with experiment are shown in Table XI. Our results disagree with those of Puchalski *et al.* [7] largely because of the second-order recoil terms included in the present work, and the degree to which they may have been partially included in Ref. [7]. For the experimental values, the older measurements shown in Table X are in poor agreement with each other or with theory. The situation is considerably improved with the two most recent measurements [36,42]. The smaller value of 0.531 ± 0.024 MHz [42] includes the effects of interference between unresolved lines and laser polarization, and so should be taken in preference. Our older value of 0.397(9) MHz [6] did not include the hyperfine mixing correction of 0.146 99 MHz [7]. When this is added, the result 0.544(9) comes into agreement with the present work. The present theoretical value 0.556 31(7) MHz has an additional theoretical uncertainty of approximately ±1 kHz due to uncalculated higher-order terms of order $\alpha^4\lambda$ Ry. It is substantially larger than the previous theoretical value 0.5447(6) MHz of Puchalski *et al.* [7] because of the large second-order contribution from the $\lambda^2 B_{3Z}^{(2)}$ spin-orbit term.

VI. CONCLUSIONS

High-precision calculations for lithium and similar atomic systems, coupled with equally high-precision measurements, open the way to interesting techniques for measurements at the interface between atomic and nuclear physics and tests of fundamental QED theory. However, the calculations themselves are sufficiently demanding in terms of both mathematical analysis and computational technique that independent checks by more than one group play an important role. This paper has achieved our main goal of resolving discrepancies between our previous results [6,15] and those of Puchalski and Pachucki [15,31]. We have also verified that the pseudostate expansion method for calculating the sums over virtual intermediate states in the Bethe logarithm [6,23,24] is capable of the same or higher accuracy as obtained by Puchalski and Pachucki by use of the integral method developed by Schwartz [43].

For isotope shifts, we have obtained results for the second-order relativistic recoil term, and shown that, although individual contributions are large compared with the other uncer-

TABLE IX. Contributions to the ^{6}Li-^{7}Li isotope shift for the $2\,^2S_{1/2} \rightarrow 2\,^2P_J$ transition frequency. The term $\gamma\lambda$ is the anomalous magnetic moment contribution. All values are in MHz.

Term	$2\,^2S_{1/2}$-$2\,^2P_{1/2}$	$2\,^2S_{1/2}$-$2\,^2P_{3/2}$	Centroid	Puchalski *et al.* [7]
λ	10 533.510 55	10 533.510 55	10 533.510 55(20)	10 533.5105
λ^2	0.070 675	0.070 675	0.070 68(3)	0.0707
λ^3	0.000 111	0.000 111	0.000 111	
$\alpha^2\lambda$	−1.477 640	−1.091 623	−1.220 3(4)	−1.2202
$\alpha^2\lambda^2$	−0.017 3(20)	0.006 7(20)	−0.001 3(20)	
$\gamma\lambda$	−0.000 425	0.000 213	0.000 000	
$\alpha^3\lambda$	0.036 8	0.036 8	0.036 8	0.0377(1)
$\alpha^4\lambda + \cdots$	−0.010(3)	−0.010(3)	−0.010(3)	−0.011(3)
Total	10 532.112 9(20)	10 532.523 5(20)	10 532.386 6(20)	10 532.388(3)

TABLE X. Contributions to the $2\,^2P_{1/2}$-$2\,^2P_{3/2}$ fine-structure splitting for ^{6}Li and ^{7}Li. $B_{\rm Anom.}$ is the anomalous magnetic moment contribution. All values are in MHz.

Term	^{6}Li	^{7}Li
	Zero-order fine structure $\alpha^2\lambda^0$	
$B^{(0)}_{3e}$	−39 626.056 4(20)	−39 626.056 4(20)
$B^{(0)}_{3Z}$	49 644.804 88(2)	49 644.804 88(2)
$B^{(0)}_{\rm Anom.}$	34.960 394	34.960 394
Total	10 053.708 8(20)	10 053.708 8(20)
Puchalski *et al.* [7]	10 053.712 6(11)	10 053.712 6(11)
	First-order recoil $\alpha^2\lambda^1$	
$B^{(1)}_{3e}$	−1.111 147(7)	−0.952 609(6)
$B^{(1)}_{3Z}$	0.025 45(7)	0.021 82(6)
$\tilde{\Delta}^{(0)}_{3Z}$	−1.619 790	−1.388 680
$B^{(1)}_{\rm Anom.}$	0.004 469	0.003 832
Total 1st order	−2.701 02(7)	−2.315 64(6)
	Second-order recoil $\alpha^2\lambda^2$	
$B^{(2)}_{3e}$	−0.000 60(12)	−0.000 44(9)
$B^{(2)}_{3Z}$	−0.089 07(24)	−0.065 47(17)
$\tilde{\Delta}^{(1)}_{3Z}$	−0.000 6752	−0.000 4962
Total 2nd order	−0.090 35(27)	−0.066 40(20)
Total 1st + 2nd order	−2.791 37(27)	−2.382 04(20)
Puchalski *et al.* [7]	−2.786 1(5)	−2.388 6(5)
Difference	−0.005 3(5)	0.006 6(5)
Higher-order QED + $\delta E_{\rm fs}$[a]	1.63(5) + 0.15(7) + 0.01217	1.63(5) + 0.15(7) + 0.15916
Total fine structure	10 052.71±0.09[a]	100 53.27±0.09[a]
Puchalski and Pachucki [35]	10 052.72±0.09[a]	100 53.25±0.09[a]
	Experiment	
Brown *et al.* [36]	10 052.779(17)	10 053.310(17)
Brog *et al.* [37]	10 052.76(24)	10 053.24(22)
Orth *et al.* [38]		10 053.184(58)
Noble *et al.* [39]	10 052.964(50)	10 053.119(58)
Walls *et al.* [40]	10 052.044(91)	10 052.37(11)
Das and Natarajan [41]	10 052.862(41)	10 051.999(41)

[a]QED corrections and ±0.09 MHz uncertainty of order α^4 and $\alpha^5\ln\alpha$ Ry, and the hyperfine mixing correction $\delta E_{\rm fs}$ calculated by Puchalski and Pachucki [34,35].

TABLE XI. ^{6}Li-^{7}Li isotope shift in the $2\,^2P_{3/2}$-$2\,^2P_{1/2}$ finestructure splitting (SIS). Anom. is the anomalous magnetic moment contribution. All values are in MHz.

Term	Present work	Puchalski *et al.* [7]
$\alpha^2\lambda$	0.385 38(1)	0.397 5(6)
$\alpha^2\lambda^2$	0.023 94(7)	
Anom.	0.000 638	
Mixing [7]	0.146 99	0.146 99
Total	0.556 31(7)± 0.001[a]	0.544 7(1)± 0.001[a]
	Recent Experiment	
Sansonetti *et al.* [42]	0.594(30)	
Brown *et al.* [36]	0.531(24)[b]	

[a]Additional uncertainty due to higher-order QED terms of order $\alpha^4\lambda$ Ry is not included in the calculation.

[b]Includes the effects of quantum interference between unresolvable overlapping lines and laser polarization.

tainties, the final result is nearly unchanged for the $2\,^2S$-$3\,^2S$ transition. The remaining uncertainty is still dominated by QED corrections of order $\alpha^4\lambda$ Ry and higher. Spin-dependent contributions of this order have recently been calculated by Puchalski and Pachucki [34] for the fine-structure splittings of the $2\,^2P_J$ states, but the spin-independent part is more difficult and has not yet been evaluated. Similarly our results for the total $2\,^2S$-$3\,^2S$ transition frequency resolve previous discrepancies, but are less accurate than the measurements by a factor of about 100 due to the uncalculated QED terms of order α^4 Ry. These will remain important problems for the future. Recent progress for helium [44] provides an important indication of what can be achieved for terms of this order.

Finally, our results for the SIS in Table XI show that the second-order relativistic recoil makes a substantial contribution that significantly shifts the theoretical prediction. This remains an important consistency check for experimental measurements of fine-structure splittings and isotope shifts.

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