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Z. C. Yan

Gordon W. F. Drake
University of Windsor

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Lithium transition energies and isotope shifts: QED recoil corrections

Zong-Chao Yan[1] and G. W. F. Drake[2]
[1]*Department of Physics, University of New Brunswick, P. O. Box 4400, Fredericton, New Brunswick, Canada E3B 5A3*
[2]*Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4*

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A QED recoil correction of order $(\mu/M)\alpha^5mc^2$ recently derived by Pachucki [J. Phys. B **31**, 5123 (1998)] is evaluated for lithium in the $1s^22s\,^2S_{1/2}$, $1s^23s\,^2S_{1/2}$, and $1s^22p\,^2P$ states, and its contribution to the isotope shift is calculated. The new term is shown to be equivalent to the recoil term included in our previous work in a hydrogenic approximation. Total energies are calculated for each of the states in question, including screening corrections to the Bethe logarithm estimated from the two-particle parent states. The results for the total transition frequencies are shown to be in good agreement with experiment, but there are surprisingly large discrepancies between theory and experiment for the isotope shift in the fine structure splitting (SIS) for the $1s^22p\,^2P$ state. The ionization potential of ^{7}Li is calculated to be 43 487.1520(40) cm^{-1}. The estimated accuracy is about the same as the experimental value. A recent measurement of the ^{7}Li–^{6}Li isotope shift for the $2\,^2P_{1/2}-2\,^2S_{1/2}$ transition determines the difference of the squares of the nuclear radii to be 0.84(6) fm^2, which is a factor of 4 more accurate than the value 0.79(25) fm^2 derived from nuclear scattering data.

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I. INTRODUCTION

High-precision spectroscopy of lithium continues to be of interest both theoretically and experimentally, especially concerning the possibility of using the isotope shift to determine the nuclear charge radius of various lithium isotopes. The basic principle is that if all other contributions to the isotope shift can be calculated to sufficient accuracy, then a comparison between theory and experiment determines the nuclear charge radius from the residual discrepancy. The method, as originally proposed in Ref. [1], has been applied with success to helium [2] and Li$^+$ [3], and the theory for neutral lithium has been discussed previously [4] (referred to as paper I).

The purpose of the present paper is to discuss the contribution from a mass-dependent recoil correction to the quantum electrodynamic (QED) shift recently derived by Pachucki [5] and calculated by Pachucki and Sapirstein [6] for the case of helium. Their derivation of the complete expression for the leading QED recoil terms of order $(\mu/M)\alpha^5mc^2$ contains a new term of the form (in atomic units a.u.)

$$\Delta E_{Q_1}=-\frac{14}{3}Z^2\alpha^3\frac{m}{M}Q_1, \tag{1}$$

where Z is the nuclear charge, m is the electron mass, M is the nuclear mass, and Q_1 is defined by

$$Q_1=(1/4\pi)\lim_{\epsilon\to 0}\langle r_i^{-3}(\epsilon)+4\pi(\gamma_{\rm eu}+\ln\epsilon)\delta(\mathbf{r}_i)\rangle. \tag{2}$$

In the above, $\gamma_{\rm eu}$ is Euler's constant, ϵ is the radius of a sphere about $r_i=0$ excluded from the integration, and a summation over i from 1 to 3 is assumed for lithium. What is not clear from Ref. [6] is that the contribution from ΔE_{Q_1} corresponds to a well-known term in the one-electron Lamb shift, and so it is only the difference between the exact ΔE_{Q_1} and the one-electron approximation used in previous work [1–4] that should be added as a correction. Since the one-electron approximation turns out to be quite accurate, the correction is considerably smaller than the total ΔE_{Q_1} term.

In paper I, we calculated isotope shifts for the $2\,^2P_J-2\,^2S_{1/2}$ and $3\,^2S_{1/2}-2\,^2S_{1/2}$ transition energies in lithium, including nonrelativistic and relativistic terms of orders $O(\mu/M)$, $O(\mu/M)^2$, and $O(\alpha^2\mu/M)$ a.u., and the lowest-order finite nuclear size correction. The QED recoil corrections of order $O(\alpha^3\mu/M)$ were also included, with the Q_1 term estimated in a one-electron approximation. The purpose of this paper is to evaluate definitively the Q_1 term for lithium in the $2\,^2S_{1/2}$, $3\,^2S_{1/2}$, and $2\,^2P_J$ states and then to examine the impact of Q_1 on the lithium isotope shifts. The notations of paper I are followed.

The organization of the paper is as follows. In Sec. II we summarize the various QED contributions to the energies of lithium, and then show how the Q_1 term is related to the hydrogenic approximation used in paper I. In this section, we also make use of the two-electron Bethe logarithms that are now available for Li$^+$ to estimate the screening correction to the Bethe logarithm for the $3\,^2S_{1/2}$ state. Section III then presents the results for the mass-independent contributions to the transition frequencies, as well as corrected values for the mass-dependent terms discussed previously in paper I. This section also discusses the comparison with experiment for both total transition frequencies and isotope shifts, and the use of the results to extract relative nuclear radii from measured isotope shifts. The paper concludes with a discussion of the results and the remaining sources of uncertainty in Sec. IV. The values of the physical constants used are summarized in Table I.

II. CALCULATIONS

As discussed in paper I, the nonrelativistic variational wave functions are constructed from fully correlated basis sets in Hylleraas coordinates, and the total energy written in the form

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TABLE I. Values of physical constants used.

Constant	Value
R_∞	$109\,737.315\,685\,49(83)$ cm^{-1}
α	$1/137.035\,999\,76(50)$
$\mu/M(^6\mathrm{Li})$	$9.121\,676\,23(76)\times10^{-5}$
$\mu/M(^7\mathrm{Li})$	$7.820\,202\,24(56)\times10^{-5}$
$R_{\mathrm{rms}}(^6\mathrm{Li})$	2.55(4) fm
$R_{\mathrm{rms}}(^7\mathrm{Li})$	2.39(3) fm

$$E_{\mathrm{tot}}=E_{\mathrm{NR}}+E_{\mathrm{rel}}+E_{\mathrm{anom}}+E_{\mathrm{QED}}, \tag{3}$$

where E_{NR} is the nonrelativistic energy, E_{rel} is the $O(\alpha^2)$ a.u. relativistic correction from matrix elements of the Breit interaction, E_{anom} is the anomalous magnetic moment correction of $O(\alpha^3)$ a.u. for states with angular momentum $L>0$, and E_{QED} represents the sum of other QED corrections of $O(\alpha^3)$ a.u. and higher. Each term has an expansion in powers of μ/M, where μ/M is the ratio of the reduced electron mass to the nuclear mass. There are contributions to the expansion from both the mass scaling of the individual terms, and from the mass polarization operator $(1/M)\Sigma_{i>j}\mathbf{p}_i\cdot\mathbf{p}_j$ in the nonrelativistic Hamiltonian, which can be treated either as a perturbation, or included explicitly in the Hamiltonian.

All terms up to E_{QED} in Eq. (3) are the same as tabulated in paper I and their discussion need not be repeated here (note that in paper I, the notation $\lambda=-\mu/M$ is used). However, the E_{QED} term must be modified in order to accommodate the new Q_1 contribution. We also take this opportunity to include new screening and mass polarization corrections to the Bethe logarithm. Following our previous work, terms in the one-electron QED shift can be simply generalized to the lithium case if their sole dependence on the quantum numbers n and L has the form

$$\frac{Z^3}{\pi n^3}\delta_{L,0}=\langle\delta(\mathbf{r})\rangle. \tag{4}$$

One then simply replaces factors of $Z^3/(\pi n^3)$ by the expectation value $\langle\Sigma_i\delta(\mathbf{r}_i)\rangle$ for lithium to obtain the main $E_{\mathrm{L},1}$ term. Terms with a more complicated dependence on n and L must be calculated separately, and there are additional electron-electron contributions denoted by $E_{\mathrm{L},2}$. With the notation

$$\langle\delta(\mathbf{r}_i)\rangle=\langle\delta(\mathbf{r}_i)\rangle^{(0)}+(\mu/M)\langle\delta(\mathbf{r}_i)\rangle^{(1)}+\cdots \tag{5}$$

the QED shift for a $1s^2nL\,^2L$ state of lithium then has the form

$$E_{\mathrm{QED}}=E_{\mathrm{L},1}+E_{\mathrm{M},1}+E_{\mathrm{R},1}+E_{\mathrm{L},2} \tag{6}$$

where the main one-electron part is (in atomic units throughout)

$$\begin{aligned}E_{\mathrm{L},1}=\frac{4Z\alpha^3\langle\delta(\mathbf{r}_i)\rangle^{(0)}}{3}\Big\{&\ln(Z\alpha)^{-2}-\beta(n\,^2L)+\frac{19}{30}\\&+(3\pi\alpha Z)0.765\,405\,577+\frac{\alpha}{\pi}[0.404\,17\\&-(3\alpha Z/4)21.556\,85]+(Z\alpha)^2\Big[-\frac{3}{4}\ln^2(Z\alpha)^{-2}\\&+C_{61}(n\,^2L)\ln(Z\alpha)^{-2}\\&+C_{60}(n\,^2L)\Big]\Big\},\end{aligned} \tag{7}$$

the mass scaling and mass polarization corrections are

$$\begin{aligned}E_{\mathrm{M},1}=&\frac{\mu\langle\delta(\mathbf{r}_i)\rangle^{(1)}}{M\langle\delta(\mathbf{r}_i)\rangle^{(0)}}E_{\mathrm{L},1}\\&+\frac{4Z\alpha^3\mu\langle\delta(\mathbf{r}_i)\rangle^{(0)}}{3M}[1-\Delta\beta_{\mathrm{MP}}(n\,^2L)],\end{aligned} \tag{8}$$

and the recoil corrections (including radiative recoil) are given by

$$\begin{aligned}E_{\mathrm{R},1}=\frac{4Z^2\alpha^3\mu\langle\delta(\mathbf{r}_i)\rangle^{(0)}}{3M}\Big[&\frac{1}{4}\ln(Z\alpha)^{-2}-2\beta(n\,^2L)-\frac{1}{12}\\&-\frac{7}{4}a(n\,^2L)-\frac{3}{4}(\pi\alpha)1.364\,49+\frac{3}{4}\pi Z\alpha D_{50}(n\,^2L)\\&+\frac{1}{2}\alpha^2Z\ln^2(Z\alpha)^{-2}\Big].\end{aligned} \tag{9}$$

These equations involve contributions to the hydrogenic Lamb shift obtained by many authors, as summarized by Eides *et al.* [7]. The quantity $\beta(n\,^2L)=\ln(k_0/Z^2R_\infty)$ is the three-electron Bethe logarithm, and the two terms $1-\Delta\beta_{\mathrm{MP}}(n\,^2L)$ in Eq. (8) account for the mass scaling and mass polarization corrections to $\beta(n\,^2L)$, respectively. These terms are further discussed below. The orders of magnitude for the other state-dependent coefficients $C_{61}(n\,^2L)$, $C_{60}(n\,^2L)$, and $D_{50}(n\,^2L)$ are all estimated from the generic formula

$$X(1s^2nL\,^2L)=\frac{2\tilde{X}(1s)+\tilde{X}(nL)/n^3}{2+\delta_{L,0}/n^3}, \tag{10}$$

where $\tilde{X}(nL)$ is the corresponding one-electron coefficient, evaluated directly for $L=0$ and in a fully screened hydrogenic approximation for $L>0$ [8]. Since these terms have been discussed before for the case of helium [8], we simply list the numerical values used in Table II, and take their contribution to the transition energy as the uncertainty.

The crucial term connected with the Q_1 contribution is $a(n\,^2L)$ in Eq. (9). In the hydrogenic case, the corresponding $\tilde{a}(nL)$ is given by

TABLE II. Data to calculate the QED shift for the $2\,^2S_{1/2}$, $3\,^2S_{1/2}$, and $2\,^2P_J$ states of lithium, and the $1\,^1S$ state of Li$^+$. Finite nuclear mass corrections are expressed in the form $X = X^{(0)} + (\mu/M)X^{(1)}$ for each quantity. Units are atomic units.

Quantity	$1s^2 2s\,^2S$	$1s^2 3s\,^2S$	$1s^2 2p\,^2P_J$	$1s^2\,^1S$
$\langle\delta(\mathbf{r}_i)\rangle^{(0)}$	13.842 609 64(5)	13.736 509 6(9)	13.676 195 49(13)	13.704 018 869
$\langle\delta(\mathbf{r}_i)\rangle^{(1)}$	−42.012 42(3)	−41.697 3(3)	−41.672 5(24)	−41.602 401
$\langle\delta(\mathbf{r}_{ij})\rangle^{(0)}$	0.544 329 8(3)	0.536 175 2(5)	0.532 281 4(5)	0.533 722 537
$\langle\delta(\mathbf{r}_{ij})\rangle^{(1)}$	−1.550 974(9)	−1.530 15(4)	−1.530 11(10)	−1.523 97
$Q^{(0)}$	0.021 778(21)	0.015 79(9)	0.022 998(9)	0.014 232 18
$Q^{(1)}$	0.065(5)	0.084(6)	0.079 5(20)	0.088 55
$Q_1^{(0)}$	−24.534 8(2)	−24.345 6(6)	−24.232 66(3)	−24.287 724 58
β_0	2.973 989 8	2.980 192 8	2.982 252 5	2.984 128 556
σ	−0.008 42	−0.001 38	0.001 61	0.002 255[a]
$\Delta\beta_{\mathrm{MP}}$	0.110 4	0.101 3	0.109 4	0.109 6
C_{61}	3.987 1	3.970 8	3.964 7	3.964 5
C_{60}	−23.191 0	−23.164 4	$-23.151\,2_{1/2}, -23.150\,9_{3/2}$	−23.150 6
D_{50}	−0.727 4	−0.727 4	−0.727 9	−0.727 4

[a] Reproduces the exact $\beta(1s^2\,^1S) = 2.982\,624\,555(4)$ for Li$^+$ [10].

$$\tilde{a}(nL) = -2\left(\ln\frac{2}{n} + \sum_{q=1}^{n} q^{-1} + 1 - \frac{1}{2n}\right)\delta_{L,0} + \frac{1-\delta_{L,0}}{L(L+1)(2L+1)}. \tag{11}$$

Since Q_1 in the hydrogenic case is given by [5]

$$Q_1 = \frac{Z^3}{2\pi n^3}[\tilde{a}(nL) + (3 - 2\ln Z)\,\delta_{L,0}] \tag{12}$$

[the extra $2\ln(Z)\delta_{L,0}$ term comes from the Z-scaling of $\ln\epsilon$ in Eq. (2)], it is clear that the Q_1 contribution is already included in the $a(nL)$ term for lithium in our previous one-electron approximation, and the effectively corrected $a_{\mathrm{c}}(n\,^2L)$ term for lithium can be written in the form

$$a_{\mathrm{c}}(n\,^2L) = \frac{2Q_1}{\langle\delta(\mathbf{r}_i)\rangle^{(0)}} + 2\ln Z - 3. \tag{13}$$

With this substitution, Eq. (9) for $E_{\mathrm{R},1}$ agrees with Eq. (15) of Pachucki and Sapirstein [6] for their E_{R2}. It is therefore only the difference

$$\delta E_{Q_1} = -\frac{7Z^2\alpha^3\mu}{3M}[a_{\mathrm{c}}(n\,^2L) - a(n\,^2L)], \tag{14}$$

and not the full ΔE_{Q_1} given by Eq. (1), that should be added to our previous results in paper I.

Since $r_i^{-3}(\epsilon)$ is logarithmically divergent, it is necessary to extract the terms proportional to $(\gamma_{\mathrm{eu}} + \ln\epsilon)$ analytically and to cancel the corresponding term in the definition of Q_1. A procedure has been developed [9] to evaluate $r_i^{-3}(\epsilon)$, as well as $r_{ij}^{-3}(\epsilon)$ (associated with the two-electron QED terms), in Hylleraas coordinates. The numerical results for the $2\,^2S$, $3\,^2S$, and $2\,^2P_J$ states of lithium are listed in Table II. As an example, $a(2\,^2S) = -4.3930$ from Eq. (10), and the corrected value from Eq. (13) is $a_{\mathrm{c}}(2\,^2S) = -4.3476$. The total contribution for the $2\,^2S$ state of ^{7}Li is $\Delta E_{Q_1} = 206.0$ MHz, but the correction is only $\delta E_{Q_1} = -2.638$ MHz, and the corrections to the ^{7}Li–^{6}Li isotope shift for the $2\,^2S$, $3\,^2S$, and $2\,^2P$ states are 0.439, 0.397, and 0.376 MHz, respectively. Since it is the differences of these numbers that contribute to the isotope shifts in the transition frequences, the final corrections are of the order 0.05 MHz, as listed in Table III. This is the same order of magnitude as the higher order terms in Eq. (9), which were not included in paper I.

The largest remaining sources of uncertainty are the Bethe logarithm $\beta(n\,^2L)$ for lithium, and the mass polarization correction $\Delta\beta_{MP}(n\,^2L)$. Although direct calculations for these terms are not yet available, accurate results for the two-electron parent states [10], together with the two-particle coefficients of fractional parentage [11], can be used to calculate the leading two terms in a $1/Z$ expansion, applied separately to the numerator and denominator of the Bethe logarithm ratio [12]. For example, if the Bethe logarithm is written in the form $\beta = A/B$, then the coefficients in the expansion $A = A_0 + A_1 Z^{-1} + \cdots$ for the three-electron case are determined by the corresponding two-particle coefficients by the equations

$$A_0(1s^2nL\,^2L) = \tfrac{1}{2}[A_0(1s^2\,^1S) + \tfrac{1}{2}A_0(1snL\,^1L) + \tfrac{3}{2}A_0(1snL\,^3L)], \tag{15}$$

$$A_1(1s^2nL\,^2L) = [A_1(1s^2\,^1S) + \tfrac{1}{2}A_1(1snL\,^1L) + \tfrac{3}{2}A_1(1snL\,^3L)], \tag{16}$$

and similarly for B_0 and B_1. The results can be expressed in the form

$$\beta(n\,^2L) = \beta_0(n\,^2L) + \ln\{[Z - \sigma(n\,^2L)]/Z\}^2, \tag{17}$$

TABLE III. Mass-dependent expansion coefficients for contributions to the lithium $1s^23s\,^2S-1s^22s\,^2S$ and $1s^22p\,^2P_J-1s^22s\,^2S$ transition energies and $1s^22s\,^2S$ ionization potential. Quantities are expressed in the general form $X=X^{(0)}+(\mu/M)X^{(1)}+\cdots$. For the finite nuclear size correction, the form is $E_{\rm nuc}=[C^{(0)}_{r^2_{\rm rms}}+(\mu/M)C^{(1)}_{r^2_{\rm rms}}]r^2_{\rm rms}$ with $r_{\rm rms}$ in units of the Bohr radius. For the $2\,^2P_J$ state, the subscript indicates the value of J. Units are $2R_\infty$.

Term	$3\,^2S_{1/2}$–$2\,^2S_{1/2}$	$2\,^2P_J$–$2\,^2S_{1/2}$	$2\,^2S_{1/2}$ I.P.
$E^{(0)}_{\rm NR}$	0.123 961 902 501(19)	0.067 903 791 89(4)	0.198 146 910 981(7)
$E^{(1)}_{\rm NR}$	−0.133 764 851 4(3)	−0.123 007 687(7)	−0.211 013 907 61(25)
$E^{(2)}_{\rm NR}$	0.123 648 10(29)	−0.003 95(14)	0.235 286 29(17)
$E^{(0)}_{\rm rel}$	0.000 009 518 3(18)	0.000 013 235 66(11)$_{1/2}$	0.000 012 809 37(6)
		0.000 014 758 32(11)$_{3/2}$	
$E^{(1)}_{\rm rel}$	−0.000 002 2(6)	0.000 016 3(8)$_{1/2}$	−0.000 000 6(5)
		0.000 011 8(8)$_{3/2}$	
$E^{(0)}_{\rm anom}$		−0.000 000 003 542$_{1/2}$	
		0.000 000 001 771$_{3/2}$	
$E^{(1)}_{\rm anom}$		0.000 000 002 05(10)$_{1/2}$	
		−0.000 000 001 02(5)$_{3/2}$	
$E^{(0)}_{\rm L,1}$	−0.000 000 930(6)	−0.000 001 442(6)$_{1/2}$	−0.000 001 237(6)
		−0.000 001 442(6)$_{3/2}$	
$E^{(1)}_{\rm M,1}+E^{(1)}_{\rm R,1}$	0.000 000 91(6)	−0.000 000 206(24)$_{1/2}$	0.000 000 870(23)
		−0.000 000 206(24)$_{3/2}$	
$E^{(0)}_{\rm L,2}$	0.000 000 048 61(12)	0.000 000 053 57(12)	0.000 000 062 80(12)
$E^{(1)}_{\rm L,2}$	−0.000 000 131(24)	−0.000 000 122(24)	−0.000 000 167(24)
$C^{(0)}_{r^2_{\rm rms}}$	−0.666 646(5)	−1.045 611 0(9)	−0.870 791 5(3)
$C^{(1)}_{r^2_{\rm rms}}$	1.980 1(19)	2.136(15)	2.576 23(19)

where

$$\beta_0(n\,^2L)=\frac{2\beta(1s)+\beta(nL)/n^3}{2+\delta_{L,0}/n^3} \tag{18}$$

is the leading term in the $1/Z$ expansion, and

$$\sigma(n\,^2L)=-(A_1B_0-A_0B_1)/(2B_0^2) \tag{19}$$

accounts for the next-to-leading term. The one-electron Bethe logarithms $\beta(nL)$ are tabulated by Drake and Swainson [13]. The $1/Z$ expansion coefficients from Drake and Goldman [10] provide the new value $\sigma(3\,^2S)=-0.001\,38$, together with results of improved accuracy for the other states, as listed in Table II.

A parallel calculation can be applied to the mass polarization corrections to the Bethe logarithm, except that one uses μ/M instead of $1/Z$ as the expansion parameter. The two-electron data from Drake and Goldman [10] for $Z=3$ yield the coefficients $\Delta\beta_{\rm MP}$ listed in Table II. The contributions to the (positive) ^{7}Li–^{6}Li isotope shifts for the $3\,^2S$–$2\,^2S$ and $2\,^2P$–$2\,^2S$ transition frequencies are –0.018 and –0.004 MHz, respectively, which is too small to be significant at current levels of experimental accuracy.

The remaining two-electron QED shift is given by

$$E_{\rm L,2}=\alpha^3\left(\tfrac{14}{3}\ln\alpha+\tfrac{164}{15}-\alpha\pi\ln\alpha\right)\langle\delta(\mathbf{r}_{ij})\rangle-\tfrac{14}{3}\alpha^3Q, \tag{20}$$

where $Q=1/(4\pi)\langle r_{ij}^{-3}(\epsilon)\rangle$ is defined analogously to Eq. (2). The above includes the $\alpha^4\ln\alpha$ term discussed in Ref. [14], but not the terms of pure order α^4 recently derived for the ^{1}S states of helium by Yelkhovsky [15]. The total contribution for the latter turns out to be quite small for the ground state [16], and can probably be neglected at this stage relative to other uncertainties. The μ/M corrections to the expectation values $\langle\delta(\mathbf{r}_{ij})\rangle$ and Q generate contributions to the ^{7}Li–^{6}Li isotope shifts of about 0.01 MHz, as listed in the tables.

III. RESULTS

The previous section provides values for the δE_{Q_1} term that should be added to the results in paper I for the isotope shifts of lithium, together with an estimate of the Bethe logarithm screening parameter σ for the $3\,^2S$ state. The latter allows an interesting new comparison with experiment for the total transition frequencies, as well as the isotope shifts.

Table III summarizes the various contributions to the transition frequencies, and to the total ionization energy of the $2\,^2S$ state, expressed as coefficients of the parameters μ/M and $r^2_{\rm rms}$, where $r_{\rm rms}$ is the rms nuclear charge radius. The mass-independent coefficients are now added to our previous tabulation in Table IV of paper I, along with updated values for the QED terms. The nonrelativistic energy coefficients and other matrix elements are as given in Tables II and III of paper I (with the notation $\lambda=-\mu/M$).

Collecting together the various terms in Table III, the total isotope-dependent transition energies are (in units of $2R_\infty$)

TABLE IV. Comparison between theory and experiment for the ^{7}Li transition frequencies and ionization potential. Units are cm^{-1}.

Transition	Theory	Experiment	Difference
$2\,^2P_{1/2}-2\,^2S_{1/2}$	14 903.6477(39)	14 903.648 130(14)[a]	−0.0004(39)
$2\,^2P_{3/2}$–$2\,^2S_{1/2}$	14 903.9830(39)	14 903.983 648(14)[a]	−0.0005(39)
$3\,^2S_{1/2}$–$2\,^2S_{1/2}$	27 206.0924(39)	27 206.0952(10)[b]	−0.0028(39)
$2\,^2S_{1/2}$ I.P.	43 487.1520(40)	43 487.150(5)[c]	0.0020(64)

[a] Sansonetti *et al.* [23].
[b] Radziemski *et al.* [26].
[c] Moore [27].

$$f_{3\,^2S-2\,^2S}=0.123\,970\,539(18)-0.133\,766\,3(6)(\mu/M)+0.123\,648\,10(29)\,(\mu/M)^2-0.666\,646(5)r_{\mathrm{rms}}^2+1.980\,1(19)r_{\mathrm{rms}}^2(\mu/M), \tag{21}$$

$$f_{2\,^2P_{1/2}-2\,^2S}=0.067\,915\,636(18)-0.122\,991\,7(8)(\mu/M)-0.003\,95(14)\,(\mu/M)^2-1.045\,611\,0(9)r_{\mathrm{rms}}^2+2.136(15)r_{\mathrm{rms}}^2(\mu/M), \tag{22}$$

$$f_{2\,^2P_{3/2}-2\,^2S}=0.067\,917\,164(18)-0.122\,996\,3(8)(\mu/M)-0.003\,95(14)(\mu/M)^2-1.045\,611\,0(9)r_{\mathrm{rms}}^2+2.136(15)r_{\mathrm{rms}}^2(\mu/M), \tag{23}$$

$$f_{2\,^2S}=0.198\,158\,546(18)-0.211\,013\,8(5)(\mu/M)+0.235\,286\,29(17)(\mu/M)^2-0.870\,791\,5(3)r_{\mathrm{rms}}^2+2.576\,23(19)r_{\mathrm{rms}}^2(\mu/M), \tag{24}$$

in place of Eqs. (37)–(39) of paper I.

A. Total transition frequencies

The transition frequencies and ionization potential resulting from these equations are compared with experiment in Table IV for the isotope ^{7}Li. All results are well within the estimated uncertainties with the exception of the $3\,^2S_{1/2}$–$2\,^2S_{1/2}$ transition, where the difference is $-0.0028(20)$ cm^{-1}. By far the largest source of theoretical uncertainty is the Bethe logarithm screening constants $\sigma(2\,^2S)=-0.008\,42$ and $\sigma(3\,^2S)=-0.001\,38$ (see Table II). The corresponding contribution to the transition frequency is $\Delta E_\sigma=0.0250(15)$ cm^{-1}. If the discrepancy is attributed to $\sigma(2\,^2S)$, then an adjusted value of $\sigma(2\,^2S)=-0.009\,31$ would bring theory and experiment into exact agreement. However, this would spoil the agreement with the higher precision measurements for the $2\,^2P_J$–$2\,^2S_{1/2}$ transitions, and it would increase the discrepancy for the $2\,^2S_{1/2}$ ionization potential to 0.0048(50) cm^{-1}. The reason for the $3\,^2S_{1/2}-2\,^2S_{1/2}$ discrepancy is therefore not clear. On balance, it is reasonable to say that the comparison with experiment verifies the calculated σ screening constants at the ±10% level or better, and that the calculated ionization potential of 43 487.1520(40) cm^{-1} is probably as accurate as the experimental determination.

B. Fine structure splitting

Since the σ uncertainty cancels for the $2\,^2P_{3/2}$–$2\,^2P_{1/2}$ fine structure splitting, the calculated value is more accurate than the total energies. The result 0.335 273(100) cm^{-1} agrees with our previous value quoted as 0.335 273 13(39) cm^{-1} [17]. However, the much lower uncertainty of the latter value does not include contributions from uncalculated terms of order $(Z\alpha)^2$ relative to the lowest order Breit terms, such as the Douglas and Kroll terms and second-order Breit contributions. These terms are known to be important for the case of helium fine structure [18] at the level of ±0.0001 cm^{-1}, and a complete evaluation of these and other known higher-order corrections will be necessary

TABLE V. Comparison between theory and experiment for the fine structure splittings and ^{7}Li–^{6}Li splitting isotope shift (SIS). Units are MHz.

Reference	^{7}Li $2\,^2P_{3/2}$–$2\,^2P_{1/2}$	^{6}Li $2\,^2P_{3/2}$–$2\,^2P_{1/2}$	SIS
Present work	10 051.24(2) ± 3[a]	10 050.85(2) ± 3[a]	0.393(6)
Brog *et al.* [21]	10 053.24(22)	10 052.76(22)	0.48(31)
Scherf *et al.* [22]	10 053.4(2)	10 051.62(20)	1.78(28)
Walls *et al.* [19]	10 052.37(11)	10 053.044(91)	−0.67(14)
Orth *et al.* [20]	10 053.184(58)		
Recommended value	10 053.2(1)	10 052.8(1)	

[a] Result from paper I with additional uncertainty of ±3 MHz due to mass-independent higher-order terms not yet calculated.

TABLE VI. Contributions to the ^{7}Li–^{6}Li isotope shifts for the $1s^22p\,^2P_J$–$1s^22s\,^2S$ transitions and comparison with experiment. Units are MHz.

Contribution	$2\,^2P_{1/2}$–$2\,^2S$	$2\,^2P_{3/2}$–$2\,^2S$
	Theory	
μ/M	10 533.501 92(60)[a]	10 533.501 92(60)[a]
$(\mu/M)^2$	0.057 3(20)	0.057 3(20)
$\alpha^2\,\mu/M$	−1.399(68)	−1.006(68)
$\alpha^3\,\mu/M$, anom.	−0.000 175 3(84)	0.000 087 5(84)
$\alpha^3\,\mu/M$, 1-e	0.018(2)	0.018(2)
$\alpha^3\,\mu/M$, 2-e	0.010 5(20)	0.010 5(20)
r^2_{rms}	1.94 ± 0.61	1.94 ± 0.61
$r^2_{\mathrm{rms}}\,\mu/M$	−0.000 73(11)	−0.000 73(11)
Total	10 534.13(7) ± 0.61[b]	10 534.52(7) ± 0.61[b]
	Experiment	
Walls *et al.* [19]	10 534.26(13)	
Sansonetti *et al.* [23]	10 532.9(6)	10 533.3(5)
Windholz *et al.* [24]	10 534.3(3)	10 539.9(1.2)
Scherf *et al.* [22]	10 533.13(15)	10 534.93(15)

[a] The additional uncertainty from the atomic mass determinations is ±0.008 MHz.

[b] Additional uncertainty due to the nuclear radii.

to further improve the accuracy. All one can say at present is that theory is consistent with both the recent measurement by Walls *et al.* [19] of 0.335 3110(37) cm^{-1}, and with the earlier measurement by Orth *et al.* [20] of 0.335 3381(19) cm^{-1}, although they do not agree with each other. Other less accurate measurements are tabulated by Walls *et al.* The discrepancies are further discussed in the following section and a resolution suggested.

C. Isotope shifts

For the isotope shifts, all the mass-independent uncertainties cancel, resulting in calculated isotope shifts that are much more accurate than the individual transition frequencies. Beginning first with the fine structure isotope shift (SIS), this comes almost entirely from just the $E^{(1)}_{\mathrm{rel}}$ term of $O(\alpha^2\mu/M)$ a.u. The calculated value is 0.393(6) MHz for the ^{7}Li–^{6}Li isotope shift (i.e., the fine structure splitting should be larger in ^{7}Li than in ^{6}Li by 0.393(6) MHz). This provides a sensitive consistency check for experimental data, free of theoretical uncertainties. As shown in Table V, only the level-crossing measurement of Brog *et al.* [21] is consistent with the theoretical SIS. The measurements of Scherf *et al.* [22] and Walls *et al.* [19] differ sharply from the theoretical value and in opposite directions. In both cases, one can state with considerable confidence that the fine structure splitting must be incorrect for at least one of the two isotopes. The agreement between the Brog *et al.* measurement and the single optical double resonance measurement by Orth *et al.* [20] for ^{7}Li provides further evidence that the correct experimental value for the fine structure splitting is 10 053.2(1) MHz for ^{7}Li and 10 052.8(1) MHz for ^{6}Li.

TABLE VII. Contributions to the ^{7}Li–^{6}Li isotope shift for the $1s^23s\,^2S$–$1s^22s\,^2S$ transition. Units are MHz.

Contribution	$3\,^2S$–$2\,^2S$
μ/M	11 454.668 801(29)[a]
$(\mu/M)^2$	−1.793 864 0(41)
$\alpha^2\,\mu/M$	0.190(55)
$\alpha^3\,\mu/M$, 1-e	−0.078(5)
$\alpha^3\,\mu/M$, 2-e	0.011 2(20)
r^2_{rms}	1.24 ± 0.39
$r^2_{\mathrm{rms}}\,\mu/M$	−0.000 677(98)
Total	11 454.24(5) ± 0.39[b]
King [28]	11 446.1
Vadla *et al.* (experiment) [29]	11 434(20)

[a] The additional uncertainty from the atomic mass determinations is ±0.008 MHz.

[b] Additional uncertainty due to the nuclear radii.

The calculated ^{7}Li–^{6}Li isotope shifts for the $1s^22p\,^2\mathrm{P}_J$–$1s^22s\,^2S$ and $1s^23s\,^2S$–$1s^22s\,^2S$ transitions are compared with experiment in Tables VI and VII. As discussed in paper I, the measurements of Sansonetti *et al.* [23], Windholz and Umfer [24], and Scherf *et al.* [22] are inconsistent with each other and with theory. Only in the case of the Sansonetti *et al.* measurement is the SIS (derived from the difference in the $2\,^2P_{3/2}$–$2\,^2S_{1/2}$ and $2\,^2P_{1/2}$–$2\,^2S_{1/2}$ isotope shifts) consistent with the theoretical value 0.393(6) MHz. However, both isotope shifts are lower than theory by 1.2(3) MHz. The difference is twice the additional ±0.61 MHz uncertainty due to the nuclear radii. The recent measurement by Walls *et al.* [19] therefore plays a particularly important role in confirming theory for the $2\,^2P_{1/2}$–$2\,^2S_{1/2}$ isotope shift (see Table VI).

D. Determination of nuclear radii

As discussed in paper I, the principal motivation for a detailed understanding of the isotope shift is to determine the

TABLE VIII. Values of E_0^A to determine $R_{\rm rms}^2$ from the measured isotope shift in various transitions. Units are MHz.

Isotopes	$E_0^A(2\,^2\mathrm{P}_{1/2}–2\,^2S)$	$E_0^A(2\,^2\mathrm{P}_{3/2}–2\,^2S)$	$E_0^A(3\,^2S–2\,^2S)$
^{7}Li–^{6}Li	10 532.19(7)	10 532.58(7)	11 453.00(6)
^{8}Li–^{6}Li	18 472.86(12)	18 473.55(12)	20 088.10(10)
^{9}Li–^{6}Li	24 631.11(16)	24 632.03(16)	26 785.01(13)
^{10}Li–^{6}Li	29 575.46(20)	29 576.56(20)	32 161.92(17)
^{11}Li–^{6}Li	33 615.19(24)	33 616.45(24)	36 555.11(21)

nuclear radius for an arbitrary isotope ^{A}Li relative to, say, ^{6}Li from an equation of the form

$$R_{\rm rms}^2(\,^A{\rm Li})=R_{\rm rms}^2(\,^6{\rm Li})+\frac{E_{\rm meas}^A-E_0^A}{C}, \tag{25}$$

where $E_{\rm meas}^A$ is the measured isotope shift for ^{A}Li relative to ^{6}Li, and E_0^A contains all the calculated contributions to the isotope shift with the exception of the shift due to finite nuclear size. Slightly revised values for the quantity E_0^A are listed in Table VIII. The constant C is nearly isotope-independent and is given by $C=-2.4565$ MHz/fm^2 and $C=-1.5661$ MHz/fm^2 for the $2\,^2P_J–2\,^2S_{1/2}$ and the $3\,^2S_{1/2}–2\,^2S_{1/2}$ isotope shifts, respectively. For example, the isotope shift of 105 34.26(13) MHz for the $2\,^2P_{1/2}–2\,^2S_{1/2}$ transition from the measurement by Walls *et al.* [19] implies a difference in nuclear radii of $R_{\rm rms}^2(\,^7{\rm Li})-R_{\rm rms}(\,^6{\rm Li})=-0.84\pm0.06$ fm^2, in comparison with the value -0.79 ± 0.25 fm^2 from nuclear scattering measurements (see Ref. [25] and Table II). The spectroscopic value is thus more accurate by a factor of 4.

IV. DISCUSSION

The primary result of this paper is an accurate value for the ΔE_{Q_1} QED recoil contribution to the isotope shift, thereby removing the largest source of uncertainty in paper I. We have shown that the new term obtained by Pachucki [5] and calculated by Pachucki and Sapristein [6] was already included in our previous work in a one-electron approximation, and so the correction to our previous results is correspondingly reduced.

The next largest potential source of uncertainty from QED corrections arises from finite mass terms associated with the Bethe logarithm $\beta(n\,^2L)$ and the mass polarization correction to it. However, our estimates for this term based on the corresponding Bethe logarithms for Li$^+$ and the two-particle coefficients of fractional parentage are in close agreement with the measured total transition frequencies, indicating that the screening correction $\sigma(n\,^2L)$ is accurate to within 10%. This is sufficient to make the uncertainty in the isotope shifts negligibly small (<0.005 MHz). A full calculation of Bethe logarithms for lithium is in progress to verify the screening estimates. The largest source of uncertainty in fact comes from the accuracy of the Breit interaction matrix elements of $O(\alpha^2)$ a.u. and the mass polarization corrections to them (the term $E_{\rm rel}^{(1)}$ in Table III).

The comparison with experiment for the splitting isotope shift (SIS) reveals surprisingly large deviations that are much larger than the estimated experimental uncertainties. Since the theoretical value of 0.393(6) MHz is free of QED or nuclear size uncertainties, it provides a direct check on the consistency of experimental data for isotope shift measurements. Since the experimental data are not consistent with each other or with the theoretical SIS, improved measurements would be of considerable value in establishing that the isotope shifts are sufficiently well understood for the determination of nuclear radii. Only the recent measurement of Walls *et al.* [19] for the $2\,^2P_{1/2}–2\,^2S_{1/2}$ isotope shift is in good agreement with theory, but the SIS from this same measurement is not. However, the difference in the nuclear radii squared derived from this measurement is in excellent agreement with nuclear scattering data, and is more accurate by a factor of 4. This illustrates the potential power of isotope measurements in the determination of nuclear radii.

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