Lithium transition energies and isotope shifts: QED recoil corrections

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A QED recoil correction of order $(\mu/M)\alpha^5 mc^2$ 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 $^7Li$ 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 $^7Li-^6Li$ 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.

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 $(\mu/M)\alpha^5 mc^2$ contains a new term of the form (in atomic units a.u.)

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

(1)

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

$$Q_1 = (1/4\pi) \lim_{\epsilon \to 0} \int \int (r_i^{-3} (\epsilon + 4\pi (\gamma_{eu} + \ln \epsilon) \delta(r_i))).$$

(2)

In the above, $\gamma_{eu}$ is Euler’s constant, $\epsilon$ 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 $\Delta E_{Q_1}$ corresponds to a well-known term in the one-electron Lamb shift, and so it is only the difference between the exact $\Delta E_{Q_1}$ 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 $\Delta E_{Q_1}$ term.

In paper I, we calculated isotope shifts for the $2^2P_{1/2}-2^2S_{1/2}$ and $3^2S_{1/2}-2^2S_{1/2}$ transition energies in lithium, including nonrelativistic and relativistic terms of orders $O(\mu/M)$, $O(\mu^2/M^2)$, and $O(\alpha^2 \mu/M)$ a.u., and the lowest-order finite nuclear size correction. The QED recoil corrections of order $O(\alpha^5 \mu/M)$ 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 $2^2P_{1/2}$ 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

$$E = \sum_i \frac{\epsilon_i r_i^2}{2} + \frac{\sum_{ij}^N a_{ij} e^{-r_{ij}}}{r_{ij}} - \frac{\sum_{ij}^N a_{ij} e^{-r_{ij}}}{r_{ij}} \epsilon_i \epsilon_j,$$

(3)

where $r_{ij}$ is the distance between the two electrons $i$ and $j$ in the system, $\epsilon_i$ is the energy of the $i$th electron, and $a_{ij}$ is the $i$th Galilean transformation of the $j$th electron. The only correction to this variational energy is the relativistic correction due to the Bethe logarithm, written in atomic units a.u.

$$\Delta E_R = \frac{1}{3} \sum_i \frac{m^2}{2M} \int \int \frac{1}{r_i^3} (\epsilon + 4\pi (\gamma_{eu} + \ln \epsilon) \delta(r_i)).$$

(4)

The purpose of this correction is to account for the finite nuclear size by including the screening of the nuclear charge inside the electron’s radius. The QED recoil correction is given by

$$\Delta E_R = \frac{1}{3} \sum_i \frac{m^2}{2M} \int \int \frac{1}{r_i^3} (\epsilon + 4\pi (\gamma_{eu} + \ln \epsilon) \delta(r_i))^2,$$

(5)

which is the correction to the Bethe logarithm due to the finite nuclear size. The correction to the Bethe logarithm is

$$\Delta E_R = \frac{1}{3} \sum_i \frac{m^2}{2M} \int \int \frac{1}{r_i^3} (\epsilon + 4\pi (\gamma_{eu} + \ln \epsilon) \delta(r_i))^2,$$

(6)

which is the correction to the Bethe logarithm due to the finite nuclear size. The correction to the Bethe logarithm is

$$\Delta E_R = \frac{1}{3} \sum_i \frac{m^2}{2M} \int \int \frac{1}{r_i^3} (\epsilon + 4\pi (\gamma_{eu} + \ln \epsilon) \delta(r_i))^2,$$

(7)

which is the correction to the Bethe logarithm due to the finite nuclear size. The correction to the Bethe logarithm is

$$\Delta E_R = \frac{1}{3} \sum_i \frac{m^2}{2M} \int \int \frac{1}{r_i^3} (\epsilon + 4\pi (\gamma_{eu} + \ln \epsilon) \delta(r_i))^2,$$

(8)

which is the correction to the Bethe logarithm due to the finite nuclear size. The correction to the Bethe logarithm is

$$\Delta E_R = \frac{1}{3} \sum_i \frac{m^2}{2M} \int \int \frac{1}{r_i^3} (\epsilon + 4\pi (\gamma_{eu} + \ln \epsilon) \delta(r_i))^2.$$
TABLE I. Values of physical constants used.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_\infty )</td>
<td>( 109,737.315,685,49(83) ) cm(^{-1} )</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>1/137.035 999 76(50)</td>
</tr>
<tr>
<td>( \mu/M(\text{Li}) )</td>
<td>9.121 676 23(76) \times 10^{-5}</td>
</tr>
<tr>
<td>( \mu/M(\text{Li}) )</td>
<td>7.820 202 24(56) \times 10^{-5}</td>
</tr>
<tr>
<td>( R_{\text{cm}}(\text{Li}) )</td>
<td>2.55(4) fm</td>
</tr>
<tr>
<td>( R_{\text{cm}}(\text{Li}) )</td>
<td>2.39(3) fm</td>
</tr>
</tbody>
</table>

\[
E_{\text{tot}} = E_{\text{NR}} + E_{\text{el}} + E_{\text{anom}} + E_{\text{QED}},
\]

where \( E_{\text{NR}} \) is the nonrelativistic energy, \( E_{\text{el}} \) is the \( O(\alpha^2) \) a.u. relativistic correction from matrix elements of the Breit interaction, \( E_{\text{anom}} \) is the anomalous magnetic moment correction of \( O(\alpha^2) \) a.u. for states with angular momentum \( L > 0 \), and \( E_{\text{QED}} \) represents the sum of other QED corrections of \( O(\alpha^2) \) a.u. and higher. Each term has an expansion in powers of \( \mu/M \), where \( \mu/M \) 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 \( (1/M)\sum_{ij}p_i \cdot p_j \) in the nonrelativistic Hamiltonian, which can be treated either as a perturbation, or included explicitly in the Hamiltonian.

All terms up to \( E_{\text{QED}} \) 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 \( E_{\text{QED}} \) 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

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

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

\[
\langle \delta(\mathbf{r}) \rangle = \langle \delta(\mathbf{r}) \rangle^{(0)} + (\mu/M)\langle \delta(\mathbf{r}) \rangle^{(1)} + \cdots
\]

the QED shift for a \( 1s^2nL^2 \) state of lithium then has the form

\[
E_{\text{QED}} = E_{L,1} + E_{M,1} + E_{R,1} + E_{L,2}
\]

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

\[
E_{L,1} = \frac{4Z\alpha^3}{3} \left[ \frac{\ln(Z\alpha)}{3} - \beta(n^2L) + \frac{19}{30} \right] L,1
\]

\[
+ (3\pi\alpha Z)0.765 405 577 + \frac{\alpha}{\pi}[0.404 17]
\]

\[
- (3\alpha Z/4)21.556 85 + (Z\alpha)^2 \left[ -\frac{3}{4} \ln^2(Z\alpha)^{-2} \right] \]

\[
+ C_60(n^2L)\ln(Z\alpha)^{-2}
\]

\[
+ C_{60}(n^2L) \right],
\]

the mass scaling and mass polarization corrections are

\[
E_{M,1} = \frac{\mu(\delta(\mathbf{r}))^{(1)}}{M(\delta(\mathbf{r}))^{(0)}} E_{L,1}
\]

\[
+ \frac{4Z\alpha^3\mu(\delta(\mathbf{r}))^{(0)}}{3M} \left[ 1 - \Delta \beta_{\text{mp}}(n^2L) \right],
\]

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

\[
E_{R,1} = \frac{4Z^2\alpha^3\mu(\delta(\mathbf{r}))^{(0)}}{3M} \left[ \frac{1}{4} \ln(Z\alpha)^{-2} - 2\beta(n^2L) - \frac{1}{12} \right]
\]

\[
- \frac{7}{4} a(n^2L) - \frac{3}{4}(\pi\alpha)1.364 49 + \frac{3}{4}\pi\alpha D_{50}(n^2L)
\]

\[
+ \frac{1}{2} \alpha^2 Z \ln(Z\alpha)^{-2} \right].
\]

These equations involve contributions to the hydrogenic Lamb shift obtained by many authors, as summarized by Eides et al. [7]. The quantity \( \beta(n^2L) = \ln(k_0/Z^2\alpha_c) \) is the three-electron Bethe logarithm, and the two terms \( 1 - \Delta \beta_{\text{mp}}(n^2L) \) 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 \( C_{60}(n^2L), C_{60}(n^2L), \) and \( D_{50}(n^2L) \) are all estimated from the generic formula

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

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.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$1s^22s^2S$</th>
<th>$1s^23s^2S$</th>
<th>$1s^22p^2P_J$</th>
<th>$1s^21^1S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\delta r_i)^{(0)}$</td>
<td>13.842 609 64(5)</td>
<td>13.736 509 69(9)</td>
<td>13.676 195 49(13)</td>
<td>13.704 018 869</td>
</tr>
<tr>
<td>$(\delta r_i)^{(1)}$</td>
<td>-42.012 42(3)</td>
<td>-41.679 3(3)</td>
<td>-41.672 5(24)</td>
<td>-41.602 401</td>
</tr>
<tr>
<td>$Q^{(0)}$</td>
<td>0.544 329 8(3)</td>
<td>0.536 175 2(5)</td>
<td>0.532 281 4(5)</td>
<td>0.533 722 537</td>
</tr>
<tr>
<td>$Q^{(1)}$</td>
<td>-1.550 974 9(4)</td>
<td>-1.530 15(4)</td>
<td>-1.530 11(10)</td>
<td>-1.523 97</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.021 778 21(21)</td>
<td>0.015 799 79(9)</td>
<td>0.022 998 9(9)</td>
<td>0.014 232 18</td>
</tr>
<tr>
<td>$C_{\alpha}$</td>
<td>0.065(5)</td>
<td>0.084(6)</td>
<td>0.079(5)</td>
<td>0.088 55</td>
</tr>
<tr>
<td>$Q^{(0)}$</td>
<td>-24.534 8(2)</td>
<td>-24.345 6(2)</td>
<td>-24.232 66(3)</td>
<td>-24.287 724 58</td>
</tr>
<tr>
<td>$\beta_0$</td>
<td>2.973 989 8</td>
<td>2.980 192 8</td>
<td>2.982 252 5</td>
<td>2.984 128 556</td>
</tr>
<tr>
<td>$\Delta \beta_{MP}$</td>
<td>-0.008 42</td>
<td>-0.001 38</td>
<td>-0.001 61</td>
<td>0.002 255 $^a$</td>
</tr>
<tr>
<td>$C_{60}$</td>
<td>0.110 4</td>
<td>0.101 3</td>
<td>0.109 4</td>
<td>0.109 6</td>
</tr>
<tr>
<td>$D_{S0}$</td>
<td>3.987 1</td>
<td>3.970 8</td>
<td>3.964 7</td>
<td>3.964 5</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>2.973 989 8</td>
<td>2.980 192 8</td>
<td>2.982 252 5</td>
<td>2.984 128 556</td>
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<td>-0.008 42</td>
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<td>-0.001 61</td>
<td>0.002 255 $^a$</td>
</tr>
</tbody>
</table>

$^a$Reproduces the exact $\beta(1s^21^1S)=2.982 624 555(4)$ for Li$^+$ [10].

$$
\bar{a}(nL) = -2 \left[ \frac{2}{n^2} + \sum_{q=1}^{n-1} q^{-1} + 1 - \frac{1}{2n} \right] \delta_{L,0} \\
+ \frac{1 - \delta_{L,0}}{L(L+1)(2L+1)}. 
$$

(11)

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

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

(12)

[the extra $2\ln(Z)\delta_{L,0}$ term comes from the Z-scaling of $\ln e$ 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 $a_{\alpha}(n^2L)$ term for lithium can be written in the form

$$
a_{\alpha}(n^2L) = \frac{2Q_1}{(\delta r_i)^{(0)}} + 2\ln Z - 3.
$$

(13)

With this substitution, Eq. (9) for $E_{R,1}$ agrees with Eq. (15) of Pachucki and Sapirstain [6] for their $E_{R,2}$. It is therefore only the difference

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

(14)

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

Since $r_i^{-3}(e)$ is logarithmically divergent, it is necessary to extract the terms proportional to $\gamma_{e^+}\ln e$ analytically and to cancel the corresponding term in the definition of $Q_1$. A procedure has been developed [9] to evaluate $r_i^{-3}(e)$, as well as $r_i^{-3}(e)$ (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 $a_{\alpha}(2^2S) = -4.3476$. 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 frequencies, 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 1/2Z 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 $A=A_0+A_1Z^{-1}+\cdots$ for the three-electron case are determined by the corresponding two-particle coefficients by the equations

$$
A_0(1s^2nL^2L) = \frac{1}{2}[A_0(1s^22S) + \frac{1}{2}A_0(1snL^1L)] \\
+ \frac{1}{2}A_0(1snL^3L)],
$$

(15)

$$
A_1(1s^2nL^2L) = [A_1(1s^22S) + \frac{1}{2}A_1(1snL^1L) \\
+ \frac{1}{2}A_1(1snL^3L)],
$$

(16)

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

$$
\beta(n^2L) = \beta_0(n^2L) + \ln([Z-\sigma(n^2L)]^2),
$$

(17)
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 1/2 expansion, and

$$\sigma(n^2L) = -(A_1 B_1 + A_0 B_1)/(2 B_0^2) \tag{19}$$

accounts for the next-to-leading term. The one-electron Bethe logarithms $\beta(nL)$ are tabulated by Drake and Swainson [13]. The 1/2 expansion coefficients from Drake and Goldman [10] provide the new value $\sigma(3^2S) = -0.00138$, 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 $\mu/M$ instead of 1/2 as the expansion parameter. The two-electron data from Drake and Goldman [10] for $Z = 3$ yield the coefficients $\Delta\beta_{MP}$ 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

$$E_{\text{L,2}} = \alpha^3 \left( \frac{14}{3} \ln \alpha + \frac{16\pi}{31} - \alpha \pi \ln \alpha \right) \langle \delta(r_{ij}) \rangle - \frac{4}{3} \alpha^3 Q, \tag{20}$$

where $Q = 1/(4 \pi) \langle r_{ij}^{-3} \rangle$ is defined analogously to Eq. (2). The above includes the $\alpha^2 \ln \alpha$ term discussed in Ref. [14], but not the terms of pure order $\alpha^4$ recently derived for the $1S$ 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 $\mu/M$ corrections to the expectation values $\langle \delta(r_{ij}) \rangle$ 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 $\delta E_{Q,1}$ 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 $\sigma$ 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 $\mu/M$ and $r_{\text{rms}}^2$, where $r_{\text{rms}}$ 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$^{-1}$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Theory</th>
<th>Experiment</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2P_{1/2} - ^2S_{1/2}$</td>
<td>14.903.647(39)</td>
<td>14.903.648 130(14)$^a$</td>
<td>$-0.0004(39)$</td>
</tr>
<tr>
<td>$^2P_{3/2} - ^2S_{1/2}$</td>
<td>14.903.983(39)</td>
<td>14.903.983 648(14)$^a$</td>
<td>$-0.0005(39)$</td>
</tr>
<tr>
<td>$^3S_{1/2} - ^2S_{1/2}$</td>
<td>27.206.0924(39)</td>
<td>27.206.0952(10)$^b$</td>
<td>$-0.0028(39)$</td>
</tr>
<tr>
<td>$^2S_{1/2}$ I.P.</td>
<td>43.487.1520(40)</td>
<td>43.487.150(5)$^c$</td>
<td>0.0020(64)</td>
</tr>
</tbody>
</table>

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

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

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

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 $^3S_{1/2} - ^2S_{1/2}$ transition, where the difference is $-0.0028(20)$ cm$^{-1}$. By far the largest source of theoretical uncertainty is the Bethe logarithm screening constants $\sigma(2^2S)= -0.00842$ and $\sigma(3^2S)= -0.00138$ (see Table II). The corresponding contribution to the transition frequency is $\Delta E_p = 0.0250(15)$ cm$^{-1}$. If the discrepancy is attributed to $\sigma(2^2S)$, then an adjusted value of $\sigma(2^2S)$ = $-0.00931$ 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 $\sigma$ screening constants at the $\pm 10\%$ level or better, and that the calculated ionization potential of $43.487.1520(40)$ cm$^{-1}$ is probably as accurate as the experimental determination.

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 $\sigma(2^2S)= -0.00842$ and $\sigma(3^2S)= -0.00138$ (see Table II). The corresponding contribution to the transition frequency is $\Delta E_p = 0.0250(15)$ cm$^{-1}$. If the discrepancy is attributed to $\sigma(2^2S)$, then an adjusted value of $\sigma(2^2S)$ = $-0.00931$ 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 $\sigma$ screening constants at the $\pm 10\%$ 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 $\sigma$ 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 0.335 273 139(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 $\pm 0.0001$ 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.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$^7$Li $^2^2P_{3/2} - ^2^2P_{1/2}$</th>
<th>$^6$Li $^2^2P_{3/2} - ^2^2P_{1/2}$</th>
<th>SIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>10.051.24(2) ± 3$^a$</td>
<td>10.050.85(2) ± 3$^a$</td>
<td>0.393(6)</td>
</tr>
<tr>
<td>Brog et al. [21]</td>
<td>10.053.24(22)</td>
<td>10.053.76(22)</td>
<td>0.48(31)</td>
</tr>
<tr>
<td>Scherfl et al. [22]</td>
<td>10.053.4(2)</td>
<td>10.051.62(20)</td>
<td>1.78(28)</td>
</tr>
<tr>
<td>Walls et al. [19]</td>
<td>10.052.37(11)</td>
<td>10.053.04(91)</td>
<td>-0.67(14)</td>
</tr>
<tr>
<td>Orth et al. [20]</td>
<td>10.053.184(58)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended value</td>
<td>10.053.2(1)</td>
<td>10.052.8(1)</td>
<td></td>
</tr>
</tbody>
</table>

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

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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 \(0.335\, 3110(37)\, \text{cm}^{-1}\), and with the earlier measurement by Orth et al. [20] of \(0.335\, 3381(19)\, \text{cm}^{-1}\), 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 \(E^{(1)}_{\text{rel}}\) term of \(O(\alpha^2 \mu/M)\) a.u. The calculated value is \(0.393(6)\, \text{MHz}\) for the \(^7\text{Li}–^6\text{Li}\) isotope shift (i.e., the fine structure splitting should be larger in \(^7\text{Li}\) than in \(^6\text{Li}\) by \(0.393(6)\, \text{MHz}\). 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 \(^7\text{Li}\) provides further evidence that the correct experimental value for the fine structure splitting is \(10\, 053.2(1)\, \text{MHz}\) for \(^7\text{Li}\) and \(10\, 052.8(1)\, \text{MHz}\) for \(^6\text{Li}\).

The calculated \(^7\text{Li}–^6\text{Li}\) isotope shifts for the \(1s^2\, 2p^2\, P_{J=2}–1s^2\, 2s^2\, S_{1/2}\) and \(1s^2\, 3s^2\, S–1s^2\, 2s^2\, S\) 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 \(2\, P_{3/2}–2\, S_{1/2}\) and \(2\, P_{1/2}–2\, S_{1/2}\) isotope shifts) consistent with the theoretical value \(0.393(6)\, \text{MHz}\). However, both isotope shifts are lower than theory by \(1.2(3)\, \text{MHz}\). 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 \(2\, P_{1/2}–2\, S_{1/2}\) 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 VI. Contributions to the \(^7\text{Li}–^6\text{Li}\) isotope shifts for the \(1s^2\, 2p^2\, P_{J=2}–1s^2\, 2s^2\, S\) transitions and comparison with experiment. Units are MHz. |
|---------------------------------|----------------|----------------|
| Contribution                    | \(2\, P_{3/2}–2\, S_{1/2}\) | \(2\, P_{1/2}–2\, S_{1/2}\) |
| \(\mu/M\)                      | \(10\, 533.501\, 92(60)^a\) | \(10\, 533.501\, 92(60)^a\) |
| \((\mu/M)^2\)                   | \(0.057\, 3(20)\)                      | \(0.057\, 3(20)\)                      |
| \(\alpha^2\, \mu/M\)            | \((-1.399(68)\)                      | \((-1.006(68)\)                      |
| \(\alpha^3\, \mu/M\), 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       | \(0.010\, 5(20)\)                  | \(0.010\, 5(20)\)                  |
| \(r_{\text{rms}}\)              | \(1.94\, \pm\, 0.61\)              | \(1.94\, \pm\, 0.61\)              |
| Total                           | \(10\, 534.13(7)\, \pm\, 0.61^b\) | \(10\, 535.52(7)\, \pm\, 0.61^b\) |

| TABLE VII. Contributions to the \(^7\text{Li}–^6\text{Li}\) isotope shift for the \(1s^2\, 3s^2\, S–1s^2\, 2s^2\, S\) transition. Units are MHz. |
|---------------------------------|----------------|----------------|
| Contribution                    | \(3\, 2\, S–2\, 2\, S\) |
| \(\mu/M\)                      | \(11\, 454.668\, 801(29)^a\) |
| \((\mu/M)^2\)                   | \((-1.793\, 864\, 0(41)\)          |
| \(\alpha^2\, \mu/M\)            | \(0.190(55)\)                      |
| \(\alpha^3\, \mu/M\), 1-e       | \((-0.078(5)\)                      |
| \(\alpha^3\, \mu/M\), 2-e       | \(0.011\, 2(20)\)                  |
| \(r_{\text{rms}}\)              | \(1.24\, \pm\, 0.39\)              |
| \(r_{\text{rms}}\, \mu/M\)      | \((-0.000\, 677(98)\)              |
| Total                           | \(11\, 454.24(5)\, \pm\, 0.39^b\) |

| Contribution                    | \(11\, 434(20)\) |
|---------------------------------|----------------|----------------|

\(a^a\)The additional uncertainty from the atomic mass determinations is ±0.008 MHz.

\(b\)Additional uncertainty due to the nuclear radii.
independent and is given by $C$ listed in Table VIII. The constant $C$ where

$$E_{\text{ms}}(^4\text{Li}) = E_{\text{ms}}(^6\text{Li}) + \frac{E_{\text{meas}} - E_0^A}{C},$$

(25)

where $E_{\text{meas}}$ is the measured isotope shift for $^4\text{Li}$ relative to $^6\text{Li}$, 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 $2^2P_{1/2} - 2^2S_{1/2}$ 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 $R_{\text{ms}}(^7\text{Li}) - R_{\text{ms}}(^6\text{Li}) = -0.84 \pm 0.06$ fm$^2$, in comparison with the value $-0.79 \pm 0.25$ fm$^2$ from nuclear scattering measurements (see Ref. [25] and Table II). The spectroscopic value is thus more accurate by a factor of 4.

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>$E_0^A(2^2P_{1/2} - 2^2S)$</th>
<th>$E_0^A(2^2P_{3/2} - 2^2S)$</th>
<th>$E_0^A(3^2S - 2^2S)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^7\text{Li}$</td>
<td>10 532.19(7)</td>
<td>10 532.58(7)</td>
<td>11 453.00(6)</td>
</tr>
<tr>
<td>$^8\text{Li}$</td>
<td>18 472.86(12)</td>
<td>18 473.55(12)</td>
<td>20 088.10(10)</td>
</tr>
<tr>
<td>$^9\text{Li}$</td>
<td>24 631.11(16)</td>
<td>24 632.03(16)</td>
<td>26 785.01(13)</td>
</tr>
<tr>
<td>$^{10}\text{Li}$</td>
<td>29 575.46(20)</td>
<td>29 576.56(20)</td>
<td>32 161.92(17)</td>
</tr>
<tr>
<td>$^{11}\text{Li}$</td>
<td>33 615.19(24)</td>
<td>33 616.45(24)</td>
<td>36 555.11(21)</td>
</tr>
</tbody>
</table>

nuclear radius for an arbitrary isotope $^4\text{Li}$ relative to, say, $^6\text{Li}$ from an equation of the form

The primary result of this paper is an accurate value for the $\Delta E_{Q_1}$ 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 Sapirstein [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 $\text{Li}^+$ 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 $E_{\text{rel}}^{(1)}$ 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 $2^2P_{1/2} - 2^2S_{1/2}$ SIS 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.

### ACKNOWLEDGMENTS

Research support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. Z.C.Y. was also supported by the University of New Brunswick.

[8] G.W.F. Drake and W.C. Martin, Can. J. Phys. 76, 679 (1998); “Fully screened” means that for $L \geq 1$, one-electron matrix elements are evaluated in a hydrogenic approximation for the outer electron with an effective nuclear charge of $Z–2$ for
lithium. In paper I, an unscreened approximation was used for the coefficient $a(T^2P)$ in Eq. (9), and that accounts for $0.097$ MHz of the total $0.18$ MHz change in the isotope shift for the $2^2P_J–2^2S_{1/2}$ transitions in Table VI relative to those in Table VI of paper I.