Hyperfine splitting in $^{6,7}Li^+$

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We present a detailed derivation of the QED effects of order $\alpha^7\, m$ to the hyperfine structure (hfs) of the ^3S states of helium-like ions and perform numerical calculations for $^6Li^+$ and $^7Li^+$. By comparing the theoretical point-nucleus results with the measured hfs of Li^+, we determine the nuclear-structure contribution parameterized in terms of the effective Zemach radius. Using the experimental hfs results for Li^+, we obtain accurate predictions for the hfs of $^6Li^{2+}$ and $^7Li^{2+}$, for which no experimental data is available so far. By examining the normalized differences of the hfs of Li^+ and Li and of the corresponding isotope-shift differences, we test the consistency of the hfs measurements in $^{6,7}Li^+$ and $^{6,7}Li$.

I. INTRODUCTION

The hyperfine structure (hfs) of atomic levels with vanishing orbital angular momentum arises from the interaction between the nuclear spin and the intrinsic angular momentum (spin) of the electrons within an atom. The energy level of an atomic S state can be conveniently represented as a sum of the centroid energy level $E_{\rm cent}$, the magnetic dipole hyperfine structure E_{M1} and the electric quadrupole hyperfine structure E_{E2},

$$\begin{aligned} E &= E_{\rm cent} + E_{M1} + E_{E2} \\ &\equiv E_{\rm cent} + A\,\langle \vec I\cdot\vec S\rangle + B\,\langle (I^iI^j)^{(2)}(S^iS^j)^{(2)}\rangle\,, \end{aligned} \tag{1}$$

where A and B are the so-called hyperfine constants, $\vec S$ is the total spin of electrons, $\vec I$ is the nuclear spin operator, $(a^ia^j)^{(2)}$ denotes the irreducible second-rank tensor, and the summation over repeated indices is implicit. The matrix elements are given by

$$\langle \vec I\cdot\vec S\rangle = \big[F(F+1) - I(I+1) - S(S+1)\big]/2\,, \tag{2}$$

and

$$\begin{aligned} \langle (I^iI^j)^{(2)}(S^iS^j)^{(2)}\rangle &= \langle \vec I\cdot\vec S\rangle^2 + \langle \vec I\cdot\vec S\rangle/2 \\ &\quad - I(I+1)S(S+1)/3\,. \end{aligned} \tag{3}$$

We note that the electric quadrupole structure is present only for the electron states with the total momentum $J = S > 1/2$; in particular, it vanishes for the ground state of atomic Li and Li^{2+}.

In the present work we are interested in the magnetic dipole hfs. In order to obtain experimental results for the A constant from the measured spectra, one needs to eliminate the quadrupole structure by combining several hfs transitions. Using the most accurate experimental results summarized in Table I, we get for the Li^+ ion

$$A_{\rm exp}(^6Li^+) = \frac{1}{6}\,\nu_{0-1} + \frac{5}{12}\,\nu_{1-2}\,, \tag{4}$$

$$A_{\rm exp}(^7Li^+) = \frac{1}{6}\,\nu_{1/2-3/2} + \frac{3}{10}\,\nu_{3/2-5/2}\,, \tag{5}$$

TABLE I: Experimental hfs intervals in Li^+ and Li, in MHz.

System	Interval	Experiment	Ref.
$^6Li^+$	$2^3S_1^{0-1}$	3001.783(12)	[1]
$^6Li^+$	$2^3S_1^{1-2}$	6003.619(11)	[1]
$^7Li^+$	$2^3S_1^{1/2-3/2}$	11 890.088(65)	[2]
$^7Li^+$	$2^3S_1^{3/2-5/2}$	19 817.696(42)	[2]
^6Li	$2^2S_{1/2}^{1/2-3/2}$	228.205 259 0(30)	[3]
^7Li	$2^2S_{1/2}^{1-2}$	803.504 086 6(10)	[3]

where $\nu_{F-F'}$ are the measured $F-F'$ transition energies. For atomic Li, the quadrupole structure is absent, so we have just

$$A_{\rm exp}(^6Li) = \frac{2}{3}\,\nu_{1/2-3/2}\,, \tag{6}$$

$$A_{\rm exp}(^7Li) = \frac{1}{2}\,\nu_{1-2}\,. \tag{7}$$

II. HFS THEORY OF LIGHT HYDROGEN-LIKE IONS

We start with summarizing the existing theory for the magnetic dipole hfs of S states of hydrogen-like atoms. To the leading order in the fine-structure constant α, it is given by

$$E_F = \frac{4}{3}(Z\alpha)^4\,\frac{m_{\rm r}^3}{m\,M}\,g\,\langle \vec I\cdot\vec S\rangle\,, \tag{8}$$

where $m_{\rm r} = mM/(m+M)$ is the reduced mass, m and M are the mass of the electron and nucleus, respectively, Z is the nuclear charge number, and the nuclear g-factor is defined as

$$\vec\mu = \frac{Z\,e}{2\,M}\,g\,\vec I\,, \tag{9}$$

where $\vec{\mu}$ is the nuclear magnetic moment operator. The leading-order hfs contribution in Eq. (8) is also known as the Fermi energy.

The complete hyperfine structure of S states in hydrogenic systems is represented as an expansion in terms of α,

$$E_{M1} = E_F\,(1+\delta)\,, \tag{10}$$

where

$$\delta = \kappa + \delta^{(2)} + \delta^{(3)} + \delta^{(4)} + \delta^{(2)}_{\rm rec.rel} + \delta_{\rm struct}\,. \tag{11}$$

Here, κ is the magnetic moment anomaly of a free electron, $\kappa = \alpha/(2\pi) + O(\alpha^2)$, $\delta^{(i)}$ are QED corrections of order $\alpha^i E_F$, $\delta^{(2)}_{\rm rec.rel}$ is the relativistic recoil correction of order $\alpha^2\,E_F$, and $\delta_{\rm struct}$ is the nuclear structure correction.

The results for the QED corrections for an S state and a point and infinitely heavy nucleus are given by [4, 5]

$$\delta^{(2)} = \frac{3}{2}\,(Z\,\alpha)^2 + \alpha\,(Z\,\alpha)\Big(\ln 2 - \frac{5}{2}\Big)\,, \tag{12}$$

$$\begin{aligned}\delta^{(3)} &= \frac{\alpha\,(Z\,\alpha)^2}{\pi}\Big[-\frac{8}{3}\ln(Z\,\alpha)\Big(\ln(Z\,\alpha) - \ln 4 + \frac{281}{480}\Big)\\ &\quad + 17.122\,338\,751\,3 - \frac{8}{15}\,\ln 2 + \frac{34}{225}\Big]\\ &\quad + \frac{\alpha^2\,(Z\,\alpha)}{\pi}\,0.770\,99(2)\,,\end{aligned} \tag{13}$$

$$\begin{aligned}\delta^{(4)} &= \frac{17}{8}\,(Z\,\alpha)^4 + \alpha\,(Z\,\alpha)^3\,\Big[\Big(\frac{547}{48} - 5\,\ln 2\Big)\,\ln(Z\,\alpha)\\ &\quad + G^{(4)}_{\rm SE}(Z\alpha) + \frac{13}{24}\,\ln 2 + \frac{539}{288}\Big]\\ &\quad - \frac{\alpha^2\,(Z\,\alpha)^2}{\pi^2}\,\Big[\frac{4}{3}\,\ln^2(Z\,\alpha) + 1.278\,\ln(Z\,\alpha) + 10.0 \pm 2.5\Big]\\ &\quad \pm \frac{\alpha^3\,(Z\,\alpha)}{\pi^2}\,.\end{aligned} \tag{14}$$

Here, $G^{(4)}_{\rm SE}(Z\alpha)$ is the one-loop self-energy correction which needs to be calculated numerically. For Li, we use the result from Ref. [6] of $G^{(4+)}_{\rm SE}(3\alpha) = -4.587\,5(1)$ which includes higher orders in $Z\,\alpha$ for $Z = 3$. Furthermore, the last term in $\delta^{(4)}$ represents the estimate of the unknown three-loop binding QED correction.

The relativistic recoil correction was derived in Ref. [7]. It has a finite point-nucleus limit and is given by

$$\begin{aligned}\delta^{(2)}_{\rm rec.rel} &= (Z\,\alpha)^2\,\frac{m_{\rm r}^2}{m\,M}\,\Big\{-\Big[-6 + \frac{7}{2}g + \frac{14}{g}\Big]\,\frac{\ln(Z\,\alpha)}{4}\\ &\quad - \Big[-2 + \frac{11}{2}g + \frac{46}{g}\Big]\,\frac{\ln 2}{4} + \frac{1}{36}\Big[-51 + \frac{31}{2}g + \frac{300}{g}\Big]\Big\}\,.\end{aligned} \tag{15}$$

The last term in Eq. (11) is the nuclear-structure contribution $\delta_{\rm struct}$. Its dominant part is the elastic contribution of order $\alpha\,E_F$, which is parameterized in terms of the Zemach radius r_Z,

$$\delta^{(1)}_{\rm struct}({\rm elastic}) = -\,2\,Z\,\alpha\,m_{\rm r}\,r_Z\,, \tag{16}$$

where

$$r_Z = \int d^3r_1 \int d^3r_2\,\rho_E(\vec{r}_1)\,\rho_M(\vec{r}_2)\,|\vec{r}_1 - \vec{r}_2|\,, \tag{17}$$

and ρ_E and ρ_M are the Fourier transforms of the electric and magnetic form factors of the nucleus normalized to unity.

There are many further contributions to $\delta_{\rm struct}$, both of the elastic and the inelastic kind. So far there is no established theory for calculating the inelastic nuclear effects in hfs for a compound nucleus. For this reason, we parameterize the *whole* nuclear structure contribution in terms of the *effective* Zemach radius $\tilde{r}_Z$, which is, by definition,

$$\delta_{\rm struct} \equiv -2\,Z\,\alpha\,m_{\rm r}\,\tilde{r}_Z\,. \tag{18}$$

It should be noted that the definition of the nuclear structure contribution (and, therefore, the effective Zemach radius) is not unique. In particular, in our previous study of He^+ [8] we separated out from $\delta_{\rm struct}$ the nuclear recoil correction $\delta^{(1)}_{\rm rec}$ and the elastic higher-order nuclear contribution $\delta^{(2)}_{\rm nuc}$. Moreover, many previous studies (among them, Refs. [1, 9]) disregarded all higher-order nuclear contributions, thus making no difference between the elastic Zemach radius r_Z and the effective Zemach radius $\tilde{r}_Z$. In the present work, we define the nuclear structure contribution by Eq. (11), where we separated out only those corrections that have a well-defined point-nucleus limit.

III. HFS THEORY OF LIGHT FEW-ELECTRON ATOMS

For the S states, the leading-order magnetic dipole hyperfine structure is given by

$$E_F \equiv \langle V_F\rangle = \frac{4\,\pi\,Z\alpha}{3\,m\,M}\,g\,\Big\langle \vec{I}\cdot\sum_a \vec{s}_a\,\delta^3(r_a)\Big\rangle\,. \tag{19}$$

The matrix element in the above expression is assumed to be calculated for a finite nuclear mass and thus implicitly contains the reduced mass prefactor. For a hydrogen-like atom, Eq. (19) reduces to Eq. (8). It is often convenient to separate out the dependence on the total angular momentum by introducing the hyperfine constant A_F which does not depend on the hyperfine state,

$$E_F = A_F\,\langle \vec{I}\cdot\vec{S}\rangle\,. \tag{20}$$

The complete magnetic dipole hyperfine structure is expressed analogously to Eq. (10)

$$E_{M1} = E_F(1+\delta)\,, \tag{21}$$

where

$$\delta = \kappa + \delta^{(2)} + \delta^{(3)} + \delta^{(4)} + \delta^{(2)}_{\rm rec} + \delta_{\rm struct}\,. \qquad (22)$$

Calculations of the leading-order magnetic dipole hfs in helium and helium-like atoms are presently well established [10]. The leading QED correction of order $\alpha^2 E_F$, $\delta^{(2)}$, was derived and calculated for helium in our previous investigations [11, 12]. For the Li^+ and Be^{2+} ions, similar calculations were carried out in Refs. [1, 9, 13]. The higher-order QED correction $\delta^{(3)}$ has been unknown until recently. The first calculation was reported by us for helium atom in Ref. [14]. In the next section, we present the detailed derivation of formulas and perform numerical calculations of $\delta^{(3)}$ for Li^+. The higher-order QED correction $\delta^{(4)}$ is approximated by the hydrogen-like value in Eq. (14). While it is a relatively small correction, its uncertainty will define the overall uncertainty of our theoretical predictions for the point-nucleus hfs.

The complete relativistic recoil correction $\delta^{(2)}_{\rm rec}$ for few-electron systems is presently unknown. In this work we approximate it by a sum of the relativistic recoil correction for the corresponding hydrogenic ion and the mixing contribution $\delta^{(2)}_{\rm rec.mix}$,

$$\delta^{(2)}_{\rm rec} = \delta^{(2)}_{\rm rec.rel}({\rm Li}^{2+}) + \delta^{(2)}_{\rm rec.mix}\,. \qquad (23)$$

The mixing correction $\delta^{(2)}_{\rm rec.mix}$ is a second-order (in the magnetic moment) contribution due to mixing with closely-lying excited states. This correction is specific for the helium-like ions, where the reference 2^3S state and the first excited 2^1S state are separated by a small energy interval. Namely, for the 2^3S reference state, the following mixing contribution is present

$$\begin{aligned}
&\frac{\langle 2^3S|V_F|2^1S\rangle\,\langle 2^1S|V_F|2^3S\rangle}{E(2^3S)-E(2^1S)}\\
&= I^i\,I^j\,\frac{\langle 2^3S|V_F^i|2^1S\rangle\,\langle 2^1S|V_F^j|2^3S\rangle}{E(2^3S)-E(2^1S)}\\
&\sim \frac{i}{2}\,\epsilon^{ijk}\,I^k\,\frac{\langle 2^3S|V_F^i|2^1S\rangle\,\langle 2^1S|V_F^j|2^3S\rangle}{E(2^3S)-E(2^1S)}\\
&= A_F\,\vec{I}\cdot\vec{S}\,\delta^{(2)}_{\rm rec.mix}\,, \qquad (24)
\end{aligned}$$

where we retained only the contribution to the magnetic dipole hfs. Despite being second order in the electron-nucleus mass ratio, this correction is significant because of the small energy difference in the denominator. We note that a similar correction contributes to the electric quadrupole structure and is present even when the quadrupole moment of the nucleus is zero.

The nuclear-structure contribution $\delta_{\rm struct}$ cannot be calculated at present. Instead, we will extract it from the experimental value of hfs in Li^+. It is important that with high accuracy, the nuclear structure contribution expressed in terms of $\delta_{\rm struct}$ is the same for Li^{2+}, Li^+, and Li. This fact will allow us to predict the hyperfine structure of Li^{2+} and to cross-check the experimental results for Li^+ against those for Li.

IV. QED CORRECTION OF ORDER $\alpha^3 E_F$

We now turn to the derivation of the QED contribution of the order of $m\alpha^7$ ($\equiv \alpha^3 E_F$) to the magnetic dipole hyperfine structure of triplet S states in few-electron atoms. The $m\alpha^7$ contribution to E_{M1} consists of the photon-exchange terms (no radiative loops), the one-loop self-energy, the one-loop vacuum polarization, and the two-loop QED effects. It can be represented in terms of the first- and second-order matrix elements as

$$\begin{aligned}
E^{(7)} \equiv E_F\,\delta^{(3)} &= E_L + 2\left\langle H^{(4)}_{\rm hfs}\frac{1}{(E_0-H_0)'}\,H^{(5)}\right\rangle\\
&+ 2\left\langle H^{(5)}_{\rm hfs}\frac{1}{(E_0-H_0)'}\,H^{(4)}\right\rangle + \langle H^{(7)}_{\rm hfs}\rangle + E_{\rm 2loop}\,, \qquad (25)
\end{aligned}$$

where E_L is the low-energy Bethe-logarithm-type contribution; $H^{(4)}_{\rm hfs}$, $H^{(5)}_{\rm hfs}$, and $H^{(7)}_{\rm hfs}$ are the effective hfs Hamiltonians of order $m\alpha^4$, $m\alpha^5$, and $m\alpha^7$, respectively; $H^{(4)}$ is the Breit Hamiltonian, $H^{(5)}$ is the effective QED Hamiltonian of order $m\alpha^5$, and H_0 and E_0 are the nonrelativistic Hamiltonian and its reference-state eigenvalue. The lowest-order hfs Hamiltonian $H^{(4)}_{\rm hfs}$ is given by Eqs. (5)-(11) of Ref. [12], where one should put the electron anomalous magnetic moment (amm) to zero. The next-order hfs Hamiltonian $H^{(5)}_{\rm hfs}$ is the amm correction to $H^{(4)}_{\rm hfs}$ and is immediately obtained from Eqs. (5)-(11) of Ref. [12]. The Breit-Pauli Hamiltonian is well known and given, e.g., by Eq. (7) of Ref. [15]. The effective QED Hamiltonian of order $m\alpha^5$ is

$$\begin{aligned}
H^{(5)} = &\left(\frac{5}{6} - \frac{1}{5} + \ln\frac{\alpha^{-2}}{2\lambda}\right)\frac{4\,\alpha^2 Z}{3\,m^2}\left[\delta^3(r_1)+\delta^3(r_2)\right]\\
&- \frac{7\,\alpha^2}{3\,\pi\,m^2}\,\frac{1}{r^3} + H^{(5)}_{\rm fs}\,, \qquad (26)
\end{aligned}$$

where $r = |\vec{r}_1 - \vec{r}_2|$, λ is the low-energy cutoff of photon momenta, and $H^{(5)}_{\rm fs}$ is the amm correction to the spin-dependent Breit-Pauli Hamiltonian, given by Eq. (14) of Ref. [15]. $E_{\rm 2loop}$ is the two-loop contribution which has the same form as in hydrogen-like atoms, see the last term in Eq. (13), and is given by

$$E_{\rm 2loop} = E_F\,\frac{\alpha^2\,(Z\,\alpha)}{\pi}\,0.770\,99(2)\,. \qquad (27)$$

The derivation of the low-energy contribution E_L and the first-order $m\alpha^7$ effective Hamiltonian $H^{(7)}_{\rm hfs}$ is presented below.

A. Low-energy contribution E_L

In this section, it will be convenient to use the atomic units, and pull out the overall prefactor α^7. Also, in the rest of the paper we will set the electron mass to unity, $m = 1$, unless specified otherwise.

In the low-energy region the momentum of the virtual photon k is of the order $k \approx \alpha^2$. The corresponding low-energy hfs contribution comes from the perturbation of the Bethe logarithm by the Fermi contact interaction operator

$$\mathcal{V}_F = \frac{g}{M}\frac{2\,\pi\,Z}{3}\,\vec{I}\cdot\vec{S}\left[\delta^3(r_1)+\delta^3(r_2)\right]. \tag{28}$$

The low-energy contribution E_L is

$$E_L \;= \frac{2}{3\,\pi}\int_0^\lambda dk\,k P_L(k)\,, \tag{29}$$

where

$$P_L(k) = 2\left\langle \mathcal{V}_F \frac{1}{(E_0-H_0)'}\,\vec{P}\,\frac{1}{E_0-H_0-k}\,\vec{P}\right\rangle + \left\langle \vec{P}\,\frac{1}{E_0-H_0-k}\left[\mathcal{V}_F-\langle\mathcal{V}_F\rangle\right]\frac{1}{E_0-H_0-k}\,\vec{P}\right\rangle, \tag{30}$$

and $\vec{P}=\vec{p}_1+\vec{p}_2$ is the total momentum operator. The large-k expansion of $P_L(k)$ is

$$kP_L(k) \;= A+\frac{B}{\sqrt{k}}+\frac{C\,\ln k}{k}+\frac{D}{k}+\dots\,, \tag{31}$$

where A, B, C, and D are the asymptotic constants summarized in Appendix A. The λ-dependent part of E_L is separated as

$$E_L = E'_L + \frac{2}{3\,\pi}\left(\frac{C}{2}\ln^2\lambda + D\,\ln\lambda\right), \tag{32}$$

where the finite λ-independent part is expressed as

$$E'_L = \frac{2}{3\,\pi}\left\{\int_0^K kdk\,P_L(k)+\int_K^\infty dk\left[kP_L(k) - A - \frac{B}{\sqrt{k}} - \frac{C\ln k}{k} - \frac{D}{k}\right] - \left[A\,K+2\,B\,\sqrt{K}+\frac{C}{2}\ln^2 K + D\,\ln K\right]\right\}, \tag{33}$$

where $K \geq 1$ is a free parameter.

In order to remove the dominant Z- and state-dependence from E'_L, it is convenient to define the δ-function-perturbed Bethe logarithm β_δ as

$$E'_L = \beta_\delta \frac{Z^2}{4\pi}\langle\mathcal{V}_F\rangle - \frac{2}{3\pi}\left(\frac{C}{2}\ln^2 Z^2 + D\ln Z^2\right). \tag{34}$$

Defined in such a way, β_δ depends very weakly on Z and its numerical values for few-electron atoms are very close to the hydrogenic values.

B. $m\alpha^7$ Hamiltonian $H^{(7)}_{\rm hfs}$

The effective $m\alpha^7$ Hamiltonian $H^{(7)}_{\rm hfs}$ can be represented as

$$H^{(7)}_{\rm hfs} = H^{(7)}_{{\rm hfs},A} + H^{(7)}_{{\rm hfs},B} + \dots\,, \tag{35}$$

where $\dots$ denotes terms that are proportional to the electron-nucleus Dirac δ function, $\delta^3(r_a)$. At the first stage of the derivation we will routinely drop such terms; the corresponding contribution will be restored later by matching the high-Z limit of the obtained formulas to the known hydrogenic result, see Sec. IV C. More specifically, we will omit terms proportional to $Z^3\,\delta^3(r_a)$; all other terms proportional to $\delta^3(r_a)$ will be preserved throughout the derivation.

The first part of $H^{(7)}_{\rm hfs}$ comes from the spin-dependent terms in the generalized Breit-Pauli Hamiltonian $H_{\rm BP}$ that are proportional to the electron amm κ. Specifically,

$$\delta H_{\rm BP} = \sum_a \kappa\left\{\frac{Z\alpha}{2}\,\vec{\sigma}_a\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{\pi}_a + \frac{e}{8}\left\{\vec{\pi}_a\cdot\vec{B}_a\,,\,\vec{\pi}_a\cdot\vec{\sigma}_a\right\} + \frac{e}{16}\left[\pi_a^i\,,\,[\pi_a^i\,,\,\vec{\sigma}_a\cdot\vec{B}_a]\right]\right\} + \sum_{a\neq b}\frac{\alpha\,\kappa}{2\,r_{ab}^3}\vec{\sigma}_a\cdot\vec{r}_{ab}\times(\vec{\pi}_b-\vec{\pi}_a)\,, \tag{36}$$

where $\vec{\pi}=\vec{p}-e\,\vec{A}$ and

$$e\,\vec{A}(\vec{r}) = \frac{e}{4\pi}\vec{\mu}\times\frac{\vec{r}}{r^3} = -Z\alpha\,\frac{g}{2\,M}\vec{I}\times\frac{\vec{r}}{r^3}\,, \tag{37}$$

$$e\,B^i(\vec{r}) = (\nabla\times\vec{A})^i = -Z\alpha\,\frac{g}{2\,M}\frac{8\pi}{3}\delta^3(r)\,I^i + Z\alpha\,\frac{g}{2\,M}\frac{1}{r^3}\left(\delta^{ij}-3\frac{r^i r^j}{r^2}\right)I^j\,. \tag{38}$$

Performing calculations as described in Appendix B we obtain

$$H^{(7)}_{{\rm hfs},A} = \frac{g\,Z\alpha\,\kappa}{4\,M}\,\vec{I}\cdot\vec{S}\left\{\frac{2Z\alpha}{3\,r_1^4} - \frac{1}{6}\left(\frac{8\pi}{3}\,p_1^i\,\delta^3(r_1)\,p_1^i - p_1^i\,\frac{1}{r_1^5}\left(r_1^2\,\delta^{ij}-3\,r_1^i r_1^j\right)p_1^j\right) + \frac{\pi}{3}\,\Delta\,\delta^3(r_1) - \frac{4}{3}\alpha\,\frac{\vec{r}\cdot\vec{r}_1}{r^3\,r_1^3}\right)\Bigg\} + (1\leftrightarrow 2)\,. \tag{39}$$

Some operators in the above expression are singular at the origin and thus are not well-defined, but this ambiguity will be eliminated by matching with the known hydrogenic result.

The second part of $H^{(7)}_{\rm hfs}$ is a middle-energy contribution that can be expressed in terms of slopes of form factors and the one-loop vacuum polarization. The derivation described in Appendix B yields

$$H^{(7)}_{{\rm hfs},B} = \frac{2\pi}{3}\,\frac{g\,Z\alpha}{M}\,\vec{I}\cdot\vec{S}\left[F_1'(0)+F_2'(0)-\frac{\alpha}{15\,\pi}\right] \times\Delta\,\delta^3(r_1)+(1\leftrightarrow 2)\,, \tag{40}$$

where the slopes of form factors are given by

$$F_1'(0)+F_2'(0) = \frac{\alpha}{\pi}\left[\frac{17}{72}+\frac{1}{3}\ln\frac{\alpha^{-2}}{2\lambda}\right]. \tag{41}$$

TABLE II: Expectation values of operators Q_i for the 2^3S state of Li^+, in atomic units. Singular operators Q_{56} and Q_{57} are defined according to Ref. [18].

Q_1	$4\pi\delta^3(r_1)$	57.350354
Q_3	$4\pi\delta^3(r_1)/r_2$	27.981057
Q_4	$4\pi\delta^3(r_1)\,p_2^2$	22.668097
Q_9	$1/r^3$	0.195563
Q_{11}	$1/r_1^2$	9.601760
Q_{12}	$1/(r_1r_2)$	1.472668
Q_{13}	$1/(r_1r)$	0.860969
Q_{14}	$1/(r_1r_2r)$	0.837624
Q_{15}	$1/(r_1^2r_2)$	5.002281
Q_{16}	$1/(r_1^2r)$	4.660766
Q_{17}	$1/(r_1r^2)$	0.514395
Q_{18}	$(\vec{r}_1\cdot\vec{r})/(r_1^3r^3)$	0.083179
Q_{24}	$p_1^i\,(r^ir^j+\delta^{ij}r^2)/(r_1r^3)\,p_2^j$	0.019568
Q_{28}	$p_1^2/r_1\,p_2^2$	17.346919
Q_{51}	$4\pi\,\vec{p}_1\,\delta^3(r_1)\,\vec{p}_1$	0.051166
Q_{53}	$1/r_1$	1.780585
Q_{56}	$1/r_1^3$	−102.905512
Q_{57}	$1/r_1^4$	271.277651
Q_{59}	$1/(r_1r^3)$	0.405548

C. Regularization of divergencies and restoration of the $\delta^3(r_a)$ part

From now on we will use atomic units and pull out the overall α^7 prefactor. The second-order matrix elements in Eq. (25) contain divergences coming from the summation over the intermediate states. They arise when operators on the left and on the right of the resolvent $1/(E_0-H_0)'$ are sufficiently singular, so that their first-order matrix elements are finite but the second-order matrix elements diverge. Specifically, there are two such "problematic" operators in our case, the electron-nucleus Dirac δ function and the spin-independent part of the Breit Hamiltonian $H^{(4)}_{\rm nfs}$, given by Eq. (6) of Ref. [16]. The divergences become more tractable if one moves them to first-order matrix elements. This can be accomplished [17] by representing the problematic singular operators as an anticommutator with the Schrödinger Hamiltonian H_0 plus some more regular operator. Specifically, for the Dirac δ function, we use the following identity

$$4\pi Z\left[\delta^3(r_1)+\delta^3(r_2)\right] = \{H_0-E_0,Q\}+V_R\,, \qquad (42)$$

$$Q = 2\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right), \qquad (43)$$

where V_R is the regularized operator defined by its action on an eigenfunction ϕ of Hamiltonian H_0 on the right as

$$V_R|\phi\rangle = -2\left(\frac{Z\vec{r}_1}{r_1^3}\cdot\vec{\nabla}_1+\frac{Z\vec{r}_2}{r_2^3}\cdot\vec{\nabla}_2\right)|\phi\rangle\,. \qquad (44)$$

For the spin-independent part of the Breit Hamiltonian we use a similar identity

$$H^{(4)}_{\rm nfs} = \{H_0-E_0,\tilde{Q}\}+H_R\,, \qquad (45)$$

$$\tilde{Q} = -\frac{1}{4}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right), \qquad (46)$$

where H_R is defined by its action on the eigenfunction of H_0 on the right as

$$H_R|\phi\rangle = \left[\frac{1}{4}p_1^2p_2^2-\frac{1}{2}(E_0-V)^2-\frac{1}{2}\,p_1^i\left(\frac{\delta^{ij}}{r}+\frac{r^ir^j}{r^3}\right)p_2^j - \frac{Z}{4}\frac{\vec{r}_1\cdot\vec{\nabla}_1}{r_1^3}-\frac{Z}{4}\frac{\vec{r}_2\cdot\vec{\nabla}_2}{r_2^3}+\frac{\vec{r}}{2r^3}\cdot(\vec{\nabla}_1-\vec{\nabla}_2)\right]|\phi\rangle\,, \qquad (47)$$

where $V=-Z/r_1-Z/r_2+1/r$. By applying these identities as described in Appendix C, we express the second-order contributions in Eq. (25) as

$$2\left\langle H^{(4)}_{\rm hfs}\,\frac{1}{(E_0-H_0)'}\,H^{(5)}\right\rangle + 2\left\langle H^{(5)}_{\rm hfs}\frac{1}{(E_0-H_0)'}\,H^{(4)}\right\rangle = E_{\rm sec}({\rm se})+E_{\rm sec}({\rm vp})+E_{{\rm fo},A}\,, \qquad (48)$$

where $E_{\rm sec}({\rm se})$ and $E_{\rm sec}({\rm vp})$ are the finite second-order contributions given by Eqs. (E2) and (E7) that correspond to the self-energy and vacuum polarization, respectively, with regularized operators Q_R and H_R, and $E_{{\rm fo},A}$ is an additional first-order contribution. As previously, in our derivation we dropped terms proportional to the electron-nucleus Dirac δ function in the first-order matrix elements, which will be restored later.

A similar regularization of the Fermi contact interaction was carried out in the calculation of the low-energy part E_L, for the integrand $P_L(k)$ in Eq. (30). The integrand $P_L(k)$ does not contain any divergences, so the regularization is not obligatory but it greatly improves the convergence of numerical basis-set calculations. For the first term in the right-hand-side of Eq. (30) we used the representation (42), whereas for the second term we employed a more general identity

$$4\pi Z\left[\delta^3(r_1)+\delta^3(r_2)\right] = \left\{H_0-E_0,Q\right\}+\widetilde{V}_R\,, \qquad (49)$$

where

$$\widetilde{V}_R = 4\,(E_0-V)\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right) - 2\,\vec{p}_1\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\vec{p}_1-2\,\vec{p}_2\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\vec{p}_2\,, \qquad (50)$$

and Q is defined in Eq. (43). It might be noted that the dependence on E_0 in the above equations cancels out, so that they represent a general operator identity.

Now we turn to restoring the contribution proportional to the electron-nucleus Dirac δ function. This is accomplished by evaluating the large-Z limit of the derived $m\alpha^7$ contributions. In the $Z\to\infty$ limit, all effects of the electron-electron interaction vanish (since they are suppressed by a factor of $1/Z$ as compared to the electron-nucleus interaction) and the result should agree with the $m\alpha^7$ correction derived for the hydrogen-like ions. This matching gives us the coefficient at the electron-nucleus

TABLE III: Second-order matrix elements for the 2^3S state of Li^+, in atomic units. "Symmetry" denotes the symmetry of the intermediate states.

		Symmetry	Value
S_1	$\left\langle V_R \, \frac{1}{(E_0-H_0)'} \, V_R \right\rangle$	${}^3S$	−30611.3035
S_2	$\left\langle V_R \, \frac{1}{(E_0-H_0)'} \, \frac{1}{r^3} \right\rangle$	${}^3S$	4.33362
S_3	$\left\langle V_R \, \frac{1}{(E_0-H_0)'} \, H_R \right\rangle$	${}^3S$	2399.03334
S_4	$\left\langle \left(\frac{\vec r_1}{r_1^3} \times \vec p_1 + \frac{\vec r_2}{r_2^3} \times \vec p_2 \right) \frac{1}{(E_0-H_0)'} \left(\frac{\vec r_1}{r_1^3} \times \vec p_1 + \frac{\vec r_2}{r_2^3} \times \vec p_2 \right) \right\rangle$	${}^3P^e$	−0.01580
S_5	$\left\langle \left(\frac{\vec r_1}{r_1^3} \times \vec p_1 + \frac{\vec r_2}{r_2^3} \times \vec p_2 \right) \frac{1}{(E_0-H_0)'} \left(\frac{\vec r}{r^3} \times (\vec p_1 - \vec p_2) \right) \right\rangle$	${}^3P^e$	−0.03892
S_6	$\left\langle \left(\frac{\delta^{ij}}{r_1^3} - \frac{3 r_1^i r_1^j}{r_1^5} + \frac{\delta^{ij}}{r_2^3} - \frac{3 r_2^i r_2^j}{r_2^5} \right) \frac{1}{(E_0-H_0)'} \left(\frac{\delta^{ij}}{r^3} - 3 \, \frac{r^i r^j}{r^5} \right) \right\rangle$	${}^3D^e$	−0.07872

Dirac δ function. The evaluation of the large-Z limit of our formulas and the matching with the hydrogenic results is described in Appendix D. As a result, we obtain an additional first-order contribution proportional to the electron-nucleus Dirac δ function,

$$E_{\rm fo,B} = \eta \, \langle \vec I \cdot \vec S \rangle \, Z^3 \pi \langle \big[\delta^3(r_1) + \delta^3(r_2) \big] \rangle \,, \tag{51}$$

with the coefficient η given by

$$\eta = \frac{g}{4\,\pi\,M} \bigg[-\frac{5351}{1350} - \frac{44\pi^2}{27} - \frac{10}{3}\zeta(3) + \frac{896}{27}\ln 2 + \frac{16}{9}\ln^2 2 - \frac{4882}{135}\ln\alpha - \frac{64}{9}\ln^2\alpha + \frac{256}{9}\ln 2 \ln\alpha \bigg] , \tag{52}$$

where we dropped the λ-dependent terms.

Finally we obtain the total first-order contribution as

$$\langle H^{(7)}_{\rm hfs,A} \rangle + \langle H^{(7)}_{\rm hfs,B} \rangle + E_{\rm fo,A} + E_{\rm fo,B} = E_{\rm fo}({\rm se}) + E_{\rm fo}({\rm vp}) \,, \tag{53}$$

where $E_{\rm fo}({\rm se})$ and $E_{\rm fo}({\rm vp})$ are given by Eqs. (E3) and (E8), respectively.

So far the individual $m\alpha^7$ contributions depend on the logarithm of the low-energy cutoff of photon momenta, $\ln\lambda$. Naturally, the complete $m\alpha^7$ correction should not depend on λ. The cancellation of the λ-dependent terms is demonstrated in Appendix E; this constituted an important cross-check of the derivation. After the cancellation is proven, we set $\lambda \to 1$ in all formulas.

D. Final formulas

We now collect all the contributions and obtain the complete result for the $m\alpha^7$ hfs correction for the ${}^3S$ states of helium-like ions. It is convenient to separate out the vacuum-polarization contribution and write the final result as

$$E^{(7)} = \langle \vec I \cdot \vec S \rangle \, A^{(7)} \,, \tag{54}$$

where

$$A^{(7)} = A_L + A_{\rm fo}({\rm se}) + A_{\rm sec}({\rm se}) + A_{\rm fo}({\rm vp}) + A_{\rm sec}({\rm vp}) + A_{\rm 2loop}. \tag{55}$$

Here, the first three terms come from the one-loop self-energy, the fourth and fith terms are the one-loop vacuum-polarization contribution, and the last term is two-loop correction. The low-energy self-energy contribution $E'_L = \langle \vec I \cdot \vec S \rangle \, A_L$ is given by Eq. (33). The first-order self-energy contribution $A_{\rm fo}$ is conveniently expressed in terms of Q_i operators which were encountered in our previous investigation of the $m\alpha^7$ effects to the Lamb shift [18] and are defined in Table II. The result is

$$\begin{aligned} A_{\rm fo}({\rm se}) = \frac{g}{2\,\pi\,M} \bigg\{ & \frac{1}{9} \left(\frac{71}{3} + 32 \ln \frac{\alpha^{-2}}{2} \right) Z^2 \, Q_1 \, Q_{53} + \left(\frac{143}{108} + \frac{8}{9} \ln \frac{\alpha^{-2}}{2} \right) Z^2 \, Q_{57} \\ & - \frac{1}{3} \left(\frac{85}{6} + 16 \ln \frac{\alpha^{-2}}{2} \right) \frac{Z^2}{2} \, Q_3 - \frac{56}{9} \, Z \, Q_9 \, Q_{53} + \frac{56}{9} \, Z \, Q_{59} - \frac{13}{12} \, Z \, Q_{18} + \frac{4Z}{3} \, E^{(4)} \, Q_{53} \\ & + \frac{2Z}{3} \Big(-2E_0 Q_{13} + Q_{17} + E_0^2 Q_{53} + 2Z E_0 Q_{11} + 2Z E_0 Q_{12} - 2Z Q_{14} - 2Z Q_{16} + 3Z^2 Q_{15} + Z^2 Q_{56} \Big) \\ & - \frac{Z}{3} \, Q_{28} + \frac{2Z}{3} \, Q_{24} + \frac{Z}{36} \left(\frac{77}{6} + 16 \ln \frac{\alpha^{-2}}{2} \right) Q_{51} - \frac{Z}{36} \left(\frac{95}{3} + 32 \ln \frac{\alpha^{-2}}{2} \right) \Big(E_0 \, Q_1 - Q_3 - \frac{1}{2} \, Q_4 \Big) \end{aligned}$$

$$+\left[-\frac{7}{6}-\frac{44\pi^2}{27}-\frac{10}{3}\zeta(3)+\frac{896}{27}\ln 2+\frac{16}{9}\ln^2 2-\frac{938}{27}\ln\alpha-\frac{64}{9}\ln^2\alpha+\frac{256}{9}\ln 2\ln\alpha\right]\frac{Z^3}{4}\,Q_1\Bigg\}. \quad (56)$$

The second-order self-energy contribution is

$$A_{\rm sec}({\rm se})=\frac{g}{2\,\pi\,M}\left\{\frac{2}{9}\left[\left(\frac{5}{6}+\ln\frac{\alpha^{-2}}{2}\right)S_1-7\,S_2+\frac{3}{2}\,S_3\right]+\frac{Z}{3}\left(\frac{Z}{2}\,S_4-S_5\right)-\frac{Z}{8}\,S_6\right\}, \quad (57)$$

TABLE IV: Individual $m\alpha^7$ corrections to the magnetic dipole hfs of the 2^3S state in Li^+. Units are $\alpha^3\,A_F$.

Term	Value
A_L	45.0968 (22)
$A_{\rm fo}({\rm se})$	50.8070
$A_{\rm sec}({\rm se})$	−186.2134
$A_{\rm fo}({\rm vp})$	1.3752
$A_{\rm sec}({\rm vp})$	3.7756
$A_{\rm 2loop}$	0.7362
$A^{(7)}$	−84.4226 (22)

where the second-order matrix elements S_i are defined in Table III. The vacuum-polarization contribution is given by

$$A_{\rm fo}({\rm vp})=-\frac{g}{45\,\pi\,M}\Bigg[16Z^2\,Q_1\,Q_{53}+2Z\,Q_{51}+4Z^2Q_{57}+4Z(1-3Z)\,Q_3-4Z\left(E_0\,Q_1-\frac{1}{2}Q_4\right)+Z^3\left(\frac{236}{15}+8\ln\alpha\right)Q_1\Bigg], \quad (58)$$

and

$$A_{\rm sec}({\rm vp})=-\frac{g}{45\,\pi\,M}S_1\,. \quad (59)$$

The two-loop QED contribution $E_{\rm 2loop}=\langle\vec{I}\cdot\vec{S}\rangle\,A_{\rm 2loop}$ is given by Eq. (27).

V. RESULTS

A. Li^+ hfs

Our numerical calculations of the $m\alpha^7$ corrections were carried out with the basis set of exponential functions $e^{-\alpha_i\,r_1-\beta_i\,r_2-\gamma_i\,r}$ introduced by Korobov [19]. The method of calculations follows the one developed in our previous investigations and reviewed in Ref. [20]. The most difficult numerical part is the computation of the Bethe-logarithm contribution E_L. This contribution is very similar to the low-energy $m\alpha^7$ contributions for the Lamb shift; so we refer the reader to our previous work [21] for details of the numerical approach. Expressed in terms of β_δ, our numerical results for the low-energy $m\alpha^7$ contribution are

$$\beta_\delta(2^3S,Z=2)=70.5314\,(28)\,, \quad (60)$$

$$\beta_\delta(2^3S,Z=3)=70.0036\,(34)\,, \quad (61)$$

which can be compared with the hydrogenic limit [22]

$$\beta_\delta(1s2s,Z=\infty)=68.834\,482\,. \quad (62)$$

Numerical results for the individual $m\alpha^7$ corrections to the hfs of the 2^3S state of Li^+ are presented in Table IV.

We now collect all available theoretical contributions to the magnetic dipole hfs in $^6Li^+$ and $^7Li^+$. Accurate values of the nuclear magnetic moments were obtained in Ref. [23],

$$\frac{\mu}{\mu_N}=\begin{cases}0.822\,044\,63\,(37) & \text{for } {}^6{\rm Li}\,,\\ 3.256\,416\,19\,(55) & \text{for } {}^7{\rm Li}\,,\end{cases} \quad (63)$$

and, therefore,

$$g({}^6{\rm Li})=1.635\,878\,84(74)\,,$$
$$g({}^7{\rm Li})=5.039\,258\,37(85)\,. \quad (64)$$

The nuclear masses

$$M({}^6{\rm Li})=6.013\,477\,3618(15)\,{\rm u},$$
$$M({}^7{\rm Li})=7.014\,357\,9087(45)\,{\rm u}, \quad (65)$$

were obtained from the atomic masses from Ref. [24] by subtracting the electron rest masses and the binding energies. Values of other physical constants were taken from Ref. [5].

Table V presents results for individual theoretical contributions to the magnetic dipole hfs of the 2^3S_1 state in $^6Li^+$ and $^7Li^+$. The numerical results are expressed in terms of δ defined by Eq. (22). The theoretical uncertainty is defined by the QED contribution of order $m\alpha^8$, for which no direct calculations exist so far; it was estimated by using the corresponding hydrogenic result listed in Sec. II. The entry $\delta_{\rm theo}$ is the total theoretical prediction without the nuclear-structure contribution. The difference $\delta_{\rm exp}-\delta_{\rm theo}$ then determines the nuclear-structure contribution $\delta_{\rm struct}$.

B. Effective Zemach radius

The nuclear structure contribution $\delta_{\rm struct}$ is parameterized in terms of the effective Zemach radius $\tilde{r}_Z$ according

TABLE V: Contributions to the magnetic dipole hfs of the 2^3S_1 state in $^6Li^+$ and $^7Li^+$ and the determination of the nuclear structure contribution $\delta_{\rm struct}$.

Term	$^6Li^+$	$^7Li^+$
κ	0.001 159 7	0.001 159 7
$\delta^{(2)}$	0.000 443 5	0.000 443 5
$\delta^{(3)}$	−0.000 032 8	−0.000 032 8
$\delta^{(4)}$	−0.000 002 1(5)	−0.000 002 1(5)
$\delta^{(2)}_{\rm rec.mix}$	0.000 002 4	0.000 006 2
$\delta^{(2)}_{\rm rec.rel}$	0.000 000 3	0.000 000 4
$\delta_{\rm theo}$	0.001 570 9(5)	0.001 574 9(5)
$\delta_{\rm theo}$ [9]	0.001 576(2)	0.001 580(2)
A_F[GHz]	2.997 908 1(14)	7.917 508 1(13)
$A_{\rm exp}$[GHz] [1, 2]	3.001 805 1(7)	7.926 990 1(23)
$\delta_{\rm exp} = A_{\rm exp}/A_F - 1$	0.001 299 9(24)	0.001 197 6(29)
$\delta_{\rm struct} = \delta_{\rm exp} - \delta_{\rm theo}$	−0.000 271 0(24)	−0.000 377 3(30)

TABLE VI: Results for the effective Zemach radius $\tilde{r}_Z$ of ^{6}Li and ^{7}Li, in fermi.

System	Reference	^{6}Li	^{7}Li
Li^+	This work	2.39 (2)	3.33 (3)
Li^+	Sun *et al.* [1]	2.44 (2)	
Li^+	Qi *et al.* [9]	2.40 (16)	3.33 (7)
Li^+	Qi *et al.* [9]	2.47 (8)	3.38 (3)
Li	Puchalski *et al.* [25]†	2.29 (4)	3.23 (4)

† recalculated for the nuclear momenta given by Eq. (63).

to Eq. (18). Numerical results for $\tilde{r}_Z$ of ^{6,7}Li are listed in Table VI. This table also compares the present values of $\tilde{r}_Z$ with previous determinations. The result from Puchalski *et al.* [25] was recalculated by including $\delta_{\rm rec.rel}$ and by using the updated magnetic moments of ^{6,7}Li, given by Eq. (63). We confirm the surprising result, first pointed out in Ref. [25], that the effective Zemach radius of ^{6}Li is smaller than for ^{7}Li, in spite of the fact that the nuclear charge radius of ^{6}Li is larger than for ^{7}Li. The probable explanation is a large contribution of inelastic effects. Previously, significant inelastic contributions were found in hfs of D [26] and μD [27].

C. Li^{2+} hfs

Theory of the magnetic dipole hfs of hydrogenlike atoms is summarized by Eqs. (10)-(14). This theory alone is not capable of predicting the hfs energy splittings since the nuclear structure contribution $\delta_{\rm struct}$ cannot be accurately calculated from the first principles at present. We can circumvent this problem by using the nuclear structure contribution extracted from the Li^+ hfs measurements in order to predict the Li^{2+} hfs. An equivalent way is to calculate the difference of the normalized hfs values in Li^{2+} and Li^+ and use the experimental result for the Li^+ hfs to predict the hfs in Li^{2+}. Such a determination is presented in Table VII. The table lists theoretical values for $\delta^{(2)}$, $\delta^{(2)}_{\rm rec.mix}$, and $\delta^{(3)}$ for the Li^{2+}-Li^+ difference. The sum of the theoretical contributions and the experimental value $\delta_{\rm exp}(Li^+)$ gives the prediction for $\delta(Li^{2+})$. It is remarkable that the uncertainty of our prediction for the Li^{2+} hfs comes exclusively from the uncertainty of the experimental Li^+ hfs value.

TABLE VII: Hfs splitting in Li^{2+}.

Term	^{6}Li	^{7}Li
$\delta^{(2)}(Li^{2+}\text{-}Li^+)$	−0.000 013 3	−0.000 013 3
$\delta^{(2)}_{\rm rec.mix}(Li^{2+}\text{-}Li^+)$	−0.000 002 4	−0.000 006 2
$\delta^{(3)}(Li^{2+}\text{-}Li^+)$	−0.000 000 5	−0.000 000 5
$\delta_{\rm exp}(Li^+)$ [1, 2]	0.001 299 9 (24)	0.001 197 6 (29)
$\delta(Li^{2+})$	0.001 283 8 (24)	0.001 177 6 (29)
$E_F(Li^{2+})$ [GHz]	8.468 319(4)	29.819 898(5)
$E_{\rm hfs}(Li^{2+})$ [GHz]	8.479 190 (21)	29.855 013 (86)

TABLE VIII: Li−Li^+ hfs difference.

Term	^{6}Li	^{7}Li
$\delta^{(2)}(Li\text{-}Li^+)$	0.000 204 8	0.000 204 8
$\delta^{(2)}_{\rm rec.mix}(Li\text{-}Li^+)$	−0.000 002 4	−0.000 006 2
$\delta^{(3)}(Li\text{-}Li^+)$	−0.000 000 5 (47)	−0.000 000 5 (47)
$\delta(Li\text{-}Li^+)_{\rm theo}$	0.000 201 9 (47)	0.000 198 0 (47)
$\delta(Li\text{-}Li^+)_{\rm exp}$ [1–3]	0.000 212 9 (24)	0.000 209 5 (29)

D. Li−Li^+ hfs difference

Our present calculation of hfs in Li^+ allows us to check the consistency between the theoretical and experimental results for hfs in Li and Li^+. Only few theoretical contributions to $\delta(Li\text{-}Li^+)$ are nonvanishing, namely, the relativistic and QED terms $\delta^{(2)}$ and $\delta^{(3)}$, and the hyperfine mixing contribution $\delta^{(2)}_{\rm rec.mix}$ (absent in the case of Li atom). The results are presented in Table VIII, where we used the Li result for $\delta^{(2)}$ from Ref. [25]. The dominant theoretical uncertainty comes from the estimation of the $\delta^{(3)}$ correction for Li, which we assumed to be the same as in Li^{2+}. We observe a $2\,\sigma$ tension between the theoretical and experimental hfs results, which might result from a larger than expected $\delta^{(3)}$ correction in atomic Li. This supposition can be verified by a direct calculation of this QED correction in atomic Li.

TABLE IX: ^{6}Li-^{7}Li isotope shift of atomic ground-state hfs.

Term	Value
$\delta(^6\text{Li-}^7\text{Li})_{\text{theo}}$	−0.000 000 1
$\delta(^6\text{Li-}^7\text{Li})_{\text{exp}}$ [3]	0.000 105 7(5)
$\delta_{\text{struc}}(^6\text{Li-}^7\text{Li})$	0.000 105 8(5)
$\delta_{\text{struc}}(^6\text{Li}^+\text{-}^7\text{Li}^+)$	0.000 106 3(38)

E. ^{6}Li-^{7}Li isotopic hfs difference

A further test of consistency of the measured hfs values can be obtained by examining the isotope shift of the normalized hfs values in Li and Li^+. On the theoretical side, all QED contributions vanish in the isotope-shift difference. The only noticeable correction is the nuclear recoil contribution, which is nevertheless tiny and amounts to $\delta^{(2)}_{\text{rec}}(^6\text{Li-}^7\text{Li}) = -1 \times 10^{-7}$. Therefore, the ^{6}Li-^{7}Li difference of the normalized experimental hfs values can be almost solely attributed to the nuclear structure effect. This means that the isotope-shift difference of the nuclear structure contributions can be extracted from the experimental hfs values of atomic Li almost without any theoretical input, see Table IX. The table presents the ^{6}Li-^{7}Li isotope shift of the nuclear-structure contribution δ_{struc} obtained from the experimental hfs values of atomic Li [3]. The result is compared with the corresponding value extracted from Li^+ (see Table V). We observe very good agreement of the isotope-shift differences of δ_{struc} obtained from atomic Li and Li^+, which indicates the consistency of the experimental results.

This consistency can be studied further by constructing the difference Δ from the normalized hfs isotope shifts as follows,

$$\Delta = [\delta(^6\text{Li}^+) - \delta(^7\text{Li}^+)] - [\delta(^6\text{Li}) - \delta(^7\text{Li})]\,. \qquad (66)$$

From the theoretical point of view, this difference comes mostly from $\delta^{(2)}_{\text{rec.mix}}$, is very small numerically and can be calculated very accurately. We obtain

$$\Delta_{\text{theo}} = -3.9 \times 10^{-6}\,, \qquad (67)$$

which can be compared to the experimental value

$$\Delta_{\text{exp}} = -3.4\,(3.8) \times 10^{-6}\,, \qquad (68)$$

obtained from the experimental results [1–3]. The conservative estimate of uncertainty for Δ_{exp} is obtained by adding quadratically the uncertainties of individual independent measurements, with the assumption that they are not correlated.

The above comparison constitutes a strict test of consistency of the four different measurements of hfs in $^{6,7}Li^+$ and ^{6,7}Li [1–3]. By contrast, if we use the recent value for the ^{6}Li hfs: 228.201 5(14) MHz from Ref. [28], then the experimental difference moves away from the theoretical prediction and becomes $\Delta_{\text{exp}} = 13.1\,(7.2) \times 10^{-6}$, which casts some doubts about the correctness of the uncertainty estimation in Ref. [28].

VI. CONCLUSION

We have performed calculations of the QED effects of order $m\alpha^7(=\alpha^3 E_F)$ to the magnetic dipole hyperfine structure in Li^+. This calculation greatly improves the theoretical value of hfs in Li^+ in the point-nucleus limit. By comparing the theoretical point-nucleus result with the experimental Li^+ hfs value, we determine the nuclear-structure contribution and parameterize it in terms of the effective Zemach radius. We confirm the surprising result, first pointed out in Ref. [25], that the effective Zemach radius of ^{6}Li is smaller than that of ^{7}Li, which is in contrast with the charge radius of ^{6}Li being larger than that of ^{7}Li. The probable explanation of this fact is large contributions of inelastic effects, for which no calculations exist up to now.

It is demonstrated that the nuclear-structure contribution, when normalized by the Fermi energy E_F, is nearly the same numerically in Li^{2+}, Li^+, and atomic Li. The charge-state dependent contributions to δ_{struct} are of order $O(Z\,\alpha)^2$ and very small numerically. Using this statement, we obtain accurate predictions for the hfs in $^6Li^{2+}$ and $^7Li^{2+}$, for which no experimental data is available so far. Examination of the normalized differences of the hfs values of Li^+ and Li and of the corresponding isotope-shift differences allowed us to demonstrate the consistency of four different measurements of hfs in $^{6,7}Li^+$ and ^{6,7}Li [1–3]. By contrast, the recent measurement of ^{6}Li hfs [28] leads to a 2σ tension in the consistency test.

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Appendix A: The asymptotic expansion coefficients of the Bethe-logarithm contribution

Here we present a summary of formulas derived for the coefficients in the asymptotic expansion of the integrand $P_L(k)$ of the low-energy contribution E_L given by Eq. (31). As in Sec. IV A, we work in atomic units and pull out the overall α^7 prefactor. The asymptotic coefficient A is

$$A = -2\left\langle \vec{P}^2\,\frac{1}{(E_0-H_0)'}\,\mathcal{V}_F\right\rangle \tag{A1}$$

where $\vec{P}=\vec{p}_1+\vec{p}_2$ and $\mathcal{V}_F$ is given by Eq. (28). For the numerical evaluation, we transform the second-order matrix element to a more regular form by using the identity (42). After simple calculation, we obtain

$$\begin{aligned} A = \frac{g}{3\,M}\,\langle\vec{I}\cdot\vec{S}\rangle\Big[&-\left\langle \vec{P}^2\,\frac{1}{(E_0-H_0)'}\,V_R\right\rangle \\ &+4\,\pi\,Z\,\langle\delta^3(r_1)+\delta^3(r_2)\rangle + 2\left\langle\vec{P}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\vec{P}\right\rangle \\ &+\langle\vec{P}^2\rangle\left(4E_0-\left\langle\frac{2}{r}\right\rangle\right)\Big]. \end{aligned} \tag{A2}$$

The coefficients B and C originate from the exchange of high-momenta photons. The corresponding formulas are derived by considering the forward scattering amplitude with two and three photon exchanges, correspondingly, perturbed by the Fermi contact interaction. The results are proportional to the expectation values of the local contact interaction and are given by

$$B = -\frac{8\sqrt{2}\,g\,Z^2}{3\,M}\,\langle\vec{I}\cdot\vec{S}\rangle\,\langle\pi\big(\delta^3(r_1)+\delta^3(r_2)\big)\rangle\,, \tag{A3}$$

$$C = -\frac{4\,g\,Z^3}{3\,M}\,\langle\vec{I}\cdot\vec{S}\rangle\,\langle\pi\big(\delta^3(r_1)+\delta^3(r_2)\big)\rangle\,. \tag{A4}$$

The calculation of the coefficient D is more complicated. It consists of the low- and high-energy parts which are calculated separately using the dimensional regularization, similarly to that for the Lamb shift [21]. The result is

$$\begin{aligned} D = \frac{g}{6\,M}\,\langle\vec{I}\cdot\vec{S}\rangle\Big[&\langle 16\pi\,Z^2\big(\delta^3(r_1)+\delta^3(r_2)\big)\rangle\left\langle\frac{1}{r_1}+\frac{1}{r_2}\right\rangle \\ &+2\left\langle\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\right\rangle+\left\langle V_R\,\frac{1}{(E_0-H_0)'}\,V_R\right\rangle \\ &+\left\langle\vec{p}_1\,4\pi\,Z\,\delta^3(r_1)\,\vec{p}_1-\left(E_0+\frac{(3Z-1)}{r_2}-\frac{p_2^2}{2}\right.\right. \\ &\left.\left.-6Z^2+5Z^2\ln 2\right)8\pi\,Z\,\delta^3(r_1)+(1\leftrightarrow 2)\right\rangle\Big]. \end{aligned} \tag{A5}$$

Appendix B: Derivation of $H^{(7)}_{\rm hfs}$

In this section we derive $H^{(7)}_{{\rm hfs},A}$ and $H^{(7)}_{{\rm hfs},B}$ in Eq. (35). The effective operator $H^{(7)}_{{\rm hfs},A}$ is given by Eq. (36) which can be rewritten as

$$\begin{aligned} H^{(7)}_{{\rm hfs},A} = \sum_a \kappa\Big[&\frac{Z\alpha}{2}\,\vec{\sigma}_a\cdot\frac{\vec{r}_a}{r_a^3}\times\big(-e\vec{A}_a\big) \\ &-\frac{e}{16}\,\vec{\sigma}_a\cdot\Delta\vec{B}_a+\frac{e}{4}\,(\vec{p}_a\cdot\vec{\sigma}_a)(\vec{B}_a\cdot\vec{p}_a)\Big] \end{aligned}$$

$$+\sum_{a,b;a\neq b}\kappa\,\frac{\alpha}{2r_{ab}^3}\,\vec{\sigma}_a\cdot\vec{r}_{ab}\times\left(e\vec{A}_a-e\vec{A}_b\right). \tag{B1}$$

The individual parts of this expression are calculated as follows,

$$\sum_a\frac{Z\alpha}{2}\,\vec{\sigma}_a\cdot\frac{\vec{r}_a}{r_a^3}\times\left[-e\vec{A}(\vec{r}_a)\right]=\frac{g\,(Z\alpha)^2}{3\,M}\sum_a\frac{\vec{s}_a\cdot\vec{I}}{r_a^4}\,, \tag{B2}$$

$$\sum_a\frac{e}{4}\,(\vec{p}_a\cdot\vec{\sigma}_a)(\vec{B}(\vec{r}_a)\cdot\vec{p}_a)=\frac{g\,Z\alpha}{12\,M}\sum_a\vec{s}_a\cdot\vec{I}\left[-\frac{8\pi}{3}\,p_a^i\,\delta^3(r_a)\,p_a^i+p_a^i\,\frac{1}{r_a^3}\left(\delta^{ij}-3\frac{r_a^i r_a^j}{r_a^2}\right)p_a^j\right], \tag{B3}$$

$$\sum_a-\frac{e}{16}\,\vec{\sigma}_a\cdot\,\Delta\vec{B}(\vec{r}_a)=\frac{g\,Z\alpha}{6\,M}\sum_a\vec{s}_a\cdot\vec{I}\,\Delta\,\pi\,\delta^3(r_a)\,, \tag{B4}$$

$$\sum_{a,b;a\neq b}\frac{\alpha}{2r_{ab}^3}\,\vec{\sigma}_a\cdot\vec{r}_{ab}\times\left(e\vec{A}(\vec{r}_a)-e\vec{A}(\vec{r}_b)\right)=-\frac{g\,Z\alpha^2}{3\,M}\sum_{a,b;a\neq b}\vec{s}_a\cdot\vec{I}\,\frac{\vec{r}_{ab}}{r_{ab}^3}\cdot\left(\frac{\vec{r}_a}{r_a^3}-\frac{\vec{r}_b}{r_b^3}\right). \tag{B5}$$

Deriving the above formulas we used $\langle S^iI^j\rangle=\langle\vec{I}\cdot\vec{S}\rangle\,\delta^{ij}/3$, which is valid for the triplet S states. After simple calculations we obtain the result for $H^{(7)}_{\rm hfs,A}$ as given by Eq. (39).

Turning to $H^{(7)}_{\rm hfs,B}$, we evaluate it as

$$\begin{aligned}H^{(7)}_{\rm hfs,B}&=\sum_a-\frac{e}{2}\left[F_1'(0)+F_2'(0)-\frac{\alpha}{15\,\pi}\right]\vec{\sigma}_a\cdot\Delta\,\vec{B}(\vec{r}_a)\\&=\sum_a\frac{g}{2\,M}\,Z\alpha\left[F_1'(0)+F_2'(0)-\frac{\alpha}{15\,\pi}\right]\frac{8\pi}{3}\,\vec{s}_a\cdot\vec{I}\\&\quad\times\Delta\,\delta^3(r_a)\big]\,,\end{aligned} \tag{B6}$$

where the index $a=1,2$ runs over the two electrons. Deriving the above formula, we again omitted terms vanishing for the triplet S states. We simplify the result by rewriting all terms as a sum of symmetric and antisymmetric in spin parts. For example,

$$\begin{aligned}\sum_a\vec{s}_a\cdot\vec{I}\,\delta^3(r_a)&=\frac{1}{2}\big(\vec{s}_1+\vec{s}_2\big)\cdot\vec{I}\,\big[\delta^3(r_1)+\delta^3(r_2)\big]\\&+\frac{1}{2}\big(\vec{s}_1-\vec{s}_2\big)\cdot\vec{I}\,\big[\delta^3(r_1)-\delta^3(r_2)\big]\,.\end{aligned} \tag{B7}$$

The expectation value of the antisymmetric part vanishes for the triplet S states and only the symmetric part contributes. Taking into account that the sum of the spins of both electrons is equal to the total spin $\vec{S}$, we can make the replacement $\vec{s}_a\to\vec{S}/2$ in all expressions.

Appendix C: Regularized form of the second-order contribution

Here we consider the singular part of the second-order contributions in Eq. (25), namely, terms containing the Dirac δ functions. With the help of Eqs. (42) and (45) the singular second-order contributions are transformed into a form suitable for numerical calculation, whereas all divergences are transferred to the first-order matrix elements. We thus write

$$2\left\langle H^{(4)}_{\rm hfs}\,\frac{1}{(E_0-H_0)'}\left(\kappa\,H^{(4)}_{\rm nfs}+H^{(5)}_{\rm nfs}\right)\right\rangle=E_{{\rm sec},A}+E_{{\rm fo},A}\,. \tag{C1}$$

After simple but tedious calculations we obtain

$$E_{{\rm sec},A}=\frac{\alpha\,g}{9\,\pi\,M}\,\langle\vec{I}\cdot\vec{S}\rangle\left\langle V_R\,\frac{1}{(E_0-H_0)'}\left[\alpha^2\left(\frac{5}{6}-\frac{1}{5}+\ln\frac{\alpha^{-2}}{2\lambda}\right)V_R-\frac{7\,\alpha^2}{r^3}+3\pi\,\kappa\,H_R\right]\right\rangle \tag{C2}$$

and

$$E_{{\rm fo},A}=\langle\vec{I}\cdot\vec{S}\rangle\,\frac{g}{M}\left\{\frac{\alpha^3}{9\,\pi}\left[\left(\frac{5}{6}-\frac{1}{5}+\ln\frac{\alpha^{-2}}{2\lambda}\right)\Big(\big\langle16\pi\,Z[\delta^3(r_1)+\delta^3(r_2)]\big\rangle\left\langle\frac{Z}{r_1}+\frac{Z}{r_2}\right\rangle-\Big\langle16\pi\,Z[\delta^3(r_1)+\delta^3(r_2)]\right.\right.\right.$$

$$\times\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\Big\rangle+2\Big\langle\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}\Big\rangle\Big)-14\Big\langle\frac{1}{r^3}\Big\rangle\Big\langle\frac{Z}{r_1}+\frac{Z}{r_2}\Big\rangle+14\Big\langle\frac{1}{r^3}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\Big\rangle\Big]$$
$$+\frac{\kappa\,\alpha}{3}\Big[\frac{\alpha}{4}\Big\langle\frac{Z^2}{r_1^4}+\frac{Z^2}{r_2^4}-2\Big(\frac{Z\vec{r}_1}{r_1^3}-\frac{Z\vec{r}_2}{r_2^3}\Big)\cdot\frac{\vec{r}}{r^3}\Big\rangle+\Big\langle\Big(\frac{Z}{r_1}+\frac{Z}{r_2}\Big)(E_0-V)^2\Big\rangle-\frac{1}{2}\Big\langle p_1^2\Big(\frac{Z}{r_1}+\frac{Z}{r_2}\Big)p_2^2\Big\rangle$$
$$+2\,E^{(4)}\Big\langle\frac{Z}{r_1}+\frac{Z}{r_2}\Big\rangle+\Big\langle p_1^i\Big(\frac{Z\alpha}{r_1}+\frac{Z\alpha}{r_2}\Big)\Big(\frac{\delta^{ij}}{r}+\frac{r^ir^j}{r^3}\Big)p_2^j\Big\rangle-\big\langle\pi\,Z\alpha\,\big[\delta^3(r_1)+\delta^3(r_2)\big]\big\rangle\Big\langle\frac{Z}{r_1}+\frac{Z}{r_2}\Big\rangle\Big]\Big\}, \quad \text{(C3)}$$

where $E^{(4)}$ is the relativistic correction of order $m\alpha^4$ to the centroid energy. The above formulas contain contributions from the self-energy and the vacuum polarization. The latter is induced by the vacuum-polarization correction to the Coulomb potential,

$$\delta V^{(1)} \;=\; -\frac{4\,\alpha^2}{15}Z\,\delta^3(r_1)+(1\leftrightarrow 2)\,, \quad \text{(C4)}$$

and is a part of $H^{(5)}$ Hamiltonian in Eq. (26).

Appendix D: Matching the hydrogenic limit

In this section we obtain the hydrogenic ($Z\to\infty$) limit of our formulas derived for the helium-like atom. We first consider the normalized difference of hfs energies, $\Delta E^{(7)}\equiv n^3\,E^{(7)}(nS)-E^{(7)}(1S)$, for which the obtained limit should agree with the known results derived for the hydrogen-like atoms. Next, we consider the $1S$ state, for which the limit of our formulas should differ from the hydrogen result by a term proportional to the electron-nucleus Dirac δ function. By matching these two results, we obtain the missing δ-function contribution.

We start with the self-energy part. To get the hydrogenic limit of our formulas, we make the replacement $\vec{S}\to 2\vec{s}_1$ and drop all the electron-electron terms containing r and terms containing variables of the second electron. For the normalized hfs difference, omitting the low-energy part E_L' and using known results for the expectation values of effective operators with hydrogenic wave functions, we obtain

$$\Delta E^{(7)}(\mathrm{se})=\frac{Z^6}{\pi}\frac{g}{2\,M}\langle\vec{s}_1\cdot\vec{I}\rangle\Big[\frac{71}{18}-\frac{79}{27n}-\frac{55}{54n^2}$$
$$+\frac{214}{27}\big(\gamma+\Psi(n)-\ln(n)\big)+\big(-\ln(\alpha)^{-2}+\ln 2\big)$$
$$\times\Big(-\frac{16}{3}+\frac{64}{9n}-\frac{16}{9n^2}-\frac{64}{9}\big[\gamma+\Psi(n)-\ln(n)\big]\Big)\Big]. \quad \text{(D1)}$$

This agrees with the result from Ref. [29] after the replacement $\ln(Z\alpha)^{-2}\to\ln(\alpha)^{-2}$, which is caused by the different choices of the photon cutoff in the low-energy part. For the $1S$ state, the hydrogenic limit of our formulas is

$$E^{(7)}(\mathrm{se},1S)=\frac{Z^6}{\pi}\frac{g}{2\,M}\langle\vec{s}_1\cdot\vec{I}\rangle\Big[-\frac{319}{18}+16\ln\Lambda$$
$$+\frac{646}{27}\ln 2+\frac{214}{27}\ln Z-\frac{64}{9}\big(\ln^2 2+\ln 2\ln\Lambda$$
$$+\ln Z\ln\Lambda+\ln 2\ln Z\big)\Big]+2Z^6\,\eta_{\rm se}\,\langle\vec{s}_1\cdot\vec{I}\rangle\,, \quad \text{(D2)}$$

where $\eta_{\rm se}$ parameterizes the missing δ-function self-energy contribution. The above result should agree with the hydrogenic $1S$ self-energy result given by the sum of F_M and F_H in Eqs. (A12) and (A13) of Ref. [8]. In these equations the intermediate cutoff ϵ is the same as cutoff $\Lambda=\alpha^2\lambda$ used in this work. Matching Eq. (D2) with the result from Ref. [8], we get the missing contribution

$$\eta_{\rm se}=\frac{g}{4\,\pi\,M}\Big[-\frac{7}{6}-\frac{44\pi^2}{27}-\frac{10}{3}\zeta(3)+\frac{896}{27}\ln 2$$
$$+\frac{16}{9}\ln^2 2-\frac{64}{3}\ln\Lambda+\frac{16}{9}\ln^2\Lambda+\frac{160}{9}\ln 2\ln\Lambda$$
$$+\ln(\alpha)\Big(\frac{214}{27}-\frac{64}{9}\ln\Lambda-\frac{64}{9}\ln 2\Big)\Big]. \quad \text{(D3)}$$

Adding the corresponding contribution from the second electron, then employing Eq. (B7) to rewrite their sum as a combination of the symmetric and antisymmetric parts, and dropping the antisymmetric part since it does not contribute for the ${}^3S$ state, we get the complete δ-function self-energy contribution for helium.

For the vacuum polarization we proceed in a similar fashion. For normalized difference of S-states, the hydrogenic limit of our formulas

$$\Delta E^{(7)}(\mathrm{vp})=\;-\frac{32\,Z^6\,g}{45\,\pi\,M}\,\langle\vec{s}_1\cdot\vec{I}\rangle\Big[\frac{3}{4}-\frac{1}{n}$$
$$+\frac{1}{4n^2}+\gamma+\Psi(n)-\ln(n)\Big], \quad \text{(D4)}$$

agrees with the result in Ref. [29]. For the $1S$ state, the hydrogenic limit of our formulas

$$E^{(7)}(\mathrm{vp},1S)=\frac{Z^6}{\pi}\frac{2g}{45\,M}\langle\vec{s}_1\cdot\vec{I}\rangle\big(36-16\ln 2-16\ln Z\big)$$
$$+2Z^6\,\eta_{\rm vp}\,\langle\vec{s}_1\cdot\vec{I}\rangle\,, \quad \text{(D5)}$$

is matched with the literature result [4], yielding the missing δ-function contribution

$$\eta_{\rm vp}=-\frac{g}{45\pi\,M}\Big[\frac{472}{15}+16\ln(\alpha)\Big]. \quad \text{(D6)}$$

It should be noted that for the vacuum polarization we checked this result by a direct derivation of the δ-function contribution by using the dimensional regularization.

The sum of the self-energy and vacuum-polarization δ-function contributions yields the term $E_{\mathrm{fo},B}$ given by Eqs. (51) and (52).

Appendix E: Cancellation of λ-dependent terms

In this section we obtain the final formulas for the $m\alpha^7$ correction and demonstrate the cancellation of terms depending the low-energy cutoff λ. We start with the self-energy contribution, which is represented as a sum of three terms,

$$E^{(7)}(\mathrm{se}) = E_L + E_{\mathrm{sec}}(\mathrm{se}) + E_{\mathrm{fo}}(\mathrm{se})\,. \tag{E1}$$

Here, E_L is the Bethe-logarithm low-energy contribution given by Eq. (32). The second-order self-energy contribution $E_{\mathrm{sec}}(\mathrm{se})$ is obtained in Appendix C as

$$\begin{aligned}
E_{\mathrm{sec}}(\mathrm{se}) = \frac{g}{2\,\pi\,M}\Bigg\{&\frac{2}{9}\,\langle\vec{I}\cdot\vec{S}\rangle\left\langle V_R\,\frac{1}{(E_0-H_0)'}\left[\left(\frac{5}{6}+\ln\frac{\alpha^{-2}}{2\lambda}\right)V_R-\frac{7}{r^3}+\frac{3}{2}H_R\right]\right\rangle\\
&+2Z\left\langle\left[\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1+\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right]\cdot\vec{I}\,\frac{1}{(E_0-H_0)'}\left[\frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1+\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)-\frac{1}{2}\,\frac{\vec{r}}{r^3}\times(\vec{p}_1-\vec{p}_2)\right]\cdot\vec{S}\right\rangle\\
&-\frac{3}{2}Z\left\langle S^iI^j\left[\frac{1}{r_1^3}\left(\delta^{ij}-3\frac{r_1^ir_1^j}{r_1^2}\right)+\frac{1}{r_2^3}\left(\delta^{ij}-3\frac{r_2^ir_2^j}{r_2^2}\right)\right]\frac{1}{(E_0-H_0)'}\,\frac{1}{4}\left(\frac{\vec{\sigma}_1\,\vec{\sigma}_2}{r^3}-3\,\frac{\vec{\sigma}_1\cdot\vec{r}\,\vec{\sigma}_2\cdot\vec{r}}{r^5}\right)\right\rangle\Bigg\}\,.
\end{aligned} \tag{E2}$$

The first-order self-energy contribution reads

$$\begin{aligned}
E_{\mathrm{fo}}(\mathrm{se}) = \frac{g}{4\,\pi\,M}\,\langle\vec{I}\cdot\vec{S}\rangle\Bigg[&\frac{2}{9}\left(\frac{71}{3}+32\ln\frac{\alpha^{-2}}{2\lambda}\right)\langle\pi\,Z\,\delta^3(r_1)\rangle\left\langle\frac{Z}{r_1}+\frac{Z}{r_2}\right\rangle+\left(\frac{143}{108}+\frac{8}{9}\ln\frac{\alpha^{-2}}{2\lambda}\right)\left\langle\frac{Z^2}{r_1^4}\right\rangle\\
&-\frac{2}{3}\left(\frac{85}{6}+16\ln\frac{\alpha^{-2}}{2\lambda}\right)\left\langle\pi\,Z^2\,\delta^3(r_1)\frac{1}{r_2}\right\rangle-\frac{56}{9}\left\langle\frac{1}{r^3}\right\rangle\left\langle\frac{Z}{r_1}\right\rangle\\
&+\frac{56}{9}\left\langle\frac{Z}{r^3\,r_1}\right\rangle-\frac{13}{12}\left\langle\frac{Z\,\vec{r}_1}{r_1^3}\cdot\frac{\vec{r}}{r^3}\right\rangle+\frac{4Z}{3}\,E^{(4)}\left\langle\frac{1}{r_1}\right\rangle+\frac{2Z}{3}\left\langle\frac{1}{r_1}(E_0-V)^2\right\rangle\\
&-\frac{Z}{3}\left\langle p_1^2\frac{1}{r_1}p_2^2\right\rangle+\frac{2Z}{3}\left\langle p_1^i\,\frac{1}{r_1}\left(\frac{\delta^{ij}}{r}+\frac{r^ir^j}{r^3}\right)p_2^j\right\rangle+\frac{Z}{9}\left(\frac{77}{6}+16\ln\frac{\alpha^{-2}}{2\lambda}\right)\langle p_1^k\,\pi\,\delta^3(r_1)\,p_1^k\rangle\\
&-\frac{\pi\,Z}{9}\left(\frac{95}{3}+32\ln\frac{\alpha^{-2}}{2\lambda}\right)\left\langle\left(E_0-\frac{1}{r_2}-\frac{p_2^2}{2}\right)\delta^3(r_1)\right\rangle\Bigg]+\langle\vec{I}\cdot\vec{S}\rangle\,\eta_{\mathrm{se}}\,Z^3\,\pi\,\langle\delta^3(r_1)\rangle+(1\leftrightarrow2)\,.
\end{aligned} \tag{E3}$$

For the simplification of the result we used the identity

$$\begin{aligned}
\left\langle p_1^i\,\frac{1}{r_1^3}\left(\delta^{ij}-3\frac{r_1^ir_1^j}{r_1^2}\right)p_1^j\right\rangle = \left\langle\frac{2}{3}\,p_1^k\,Z\,\pi\,\delta^3(r_1)\,p_1^k+\frac{Z^2}{r_1^4}\right.\\
\left.-\frac{Z\,\vec{r}_1}{r_1^3}\cdot\frac{\vec{r}}{r^3}-\left(E_0+\frac{Z-1}{r_2}-\frac{p_2^2}{2}\right)Z\,\pi\delta^3(r_1)\right\rangle\,.
\end{aligned} \tag{E4}$$

By algebraic calculations we checked that the dependence on the photon momentum cutoff λ is canceled in the sum of E_L, $E_{\mathrm{sec}}(\mathrm{se})$, and $E_{\mathrm{fo}}(\mathrm{se})$. After that, we can remove the λ dependence by setting $\lambda = 1$ in all formulas. In this way we obtain the final formulas given by Eqs. (56) and (57). The second-order contribution in Eq. (57) is obtained from Eq. (E2) after spin averaging with help of a formula

$$\langle S^iI^jQ_1^{ij}\,\sigma_1^a\sigma_2^b\,Q_2^{ab}\rangle = \frac{\langle\vec{I}\cdot\vec{S}\rangle}{3}\,\langle Q_1^{ij}Q_2^{ij}\rangle\,, \tag{E5}$$

in the second and the third line of Eq. (E2), correspondingly.

The final result for the vacuum-polarization contribution is a sum of the corresponding parts of the second-order contribution in Eq. (C1), the first-order contribution contained in $H^{(7)}_{\mathrm{hfs}}$ in Eq. (35), and the additional Dirac-δ-like part obtained in Appendix D. We thus get

$$E^{(7)}(\mathrm{vp}) = E_{\mathrm{sec}}(\mathrm{vp}) + E_{\mathrm{fo}}(\mathrm{vp})\,, \tag{E6}$$

$$E_{\mathrm{sec}}(\mathrm{vp}) = -\frac{g}{45\,\pi\,M}\,\langle\vec{I}\cdot\vec{S}\rangle\left\langle V_R\,\frac{1}{(E_0-H_0)'}\,V_R\right\rangle, \tag{E7}$$

$$\begin{aligned}
E_{\mathrm{fo}}(\mathrm{vp}) = -\frac{g}{45\,\pi\,M}\,\langle\vec{I}\cdot\vec{S}\rangle\Bigg\{&\langle16\pi\,Z\,\delta^3(r_1)\rangle\left\langle\frac{Z}{r_1}+\frac{Z}{r_2}\right\rangle\\
&+4\,\langle\vec{p}_1\,\pi\,Z\,\delta^3(r_1)\,\vec{p}_1\rangle+\left\langle8\pi\,(Z-3Z^2)\,\delta^3(r_1)\frac{1}{r_2}\right\rangle\\
&-8\left\langle\left(E_0-\frac{p_2^2}{2}\right)\pi\,Z\,\delta^3(r_1)\right\rangle+2\left\langle\frac{Z^2}{r_1^4}\right\rangle\\
&+\left(\frac{472}{15}+16\ln(\alpha)\right)\langle\pi\,Z^3\,\delta^3(r_1)\rangle+(1\leftrightarrow2)\Bigg\}\,.
\end{aligned} \tag{E8}$$