Higher-Order QED Corrections to the Hyperfine Splitting in ³He

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We present a calculation of the hyperfine splitting of the 2^3S state in the ³He atom with inclusion of all QED effects up to $\alpha^3 E_F$, where E_F is the Fermi splitting. Using the experimental value of the $1S$ hyperfine splitting in ³He⁺, we eliminate uncertainties from the nuclear structure and obtain the theoretical prediction for ³He of $\nu_{\rm hfs} = -6\,739\,701\,181(41)$ Hz, which is in perfect agreement with the experimental value $-6\,739\,701\,177(16)$ Hz [S. D. Rosner and F. M. Pipkin, Phys. Rev. A **1**, 571 (1970)]. This result constitutes a 40-fold improvement in precision as compared to the previous value and is the most accurate theoretical prediction ever obtained for a nonhydrogenic system.

Introduction.—Interaction of the magnetic moment of the nucleus with that of the electron leads to the splitting of atomic energy levels known as the hyperfine splitting (hfs). The hfs of atoms can be measured with outstanding accuracy, e.g., the ground-state hfs of hydrogen is experimentally known up to 12 digits [1–3]. This makes hfs an excellent candidate for high-precision tests of the quantum electrodynamics (QED) of bound states [4] and for searches of physics beyond the standard model [5].

An impediment to performing such tests is that theoretical hfs predictions are severely limited by nuclear effects, which are manifested already at the 10^{-4} level and cannot be accurately calculated at present. This impediment can be circumvented [3,6,7] by making use of the fact that the hfs of different atomic states is strongly correlated, being largely proportional to the electron charge density at the nucleus. Therefore, one can employ an experimental hfs value measured for one state in order to obtain an improved theoretical prediction for another state. This idea has been realized for hydrogen [7,8], where theory was able to predict the hfs of excited nS states with a sub-Hertz accuracy with help of the experimental $1S$ hfs value, in agreement with the recent measurement of $2S$ hfs [9] which also achieved sub-Hertz accuracy.

The same idea has been recently applied to the HD⁺ molecule. Specifically, the nuclear-structure effects have been eliminated by using experimental hfs values of H and D atoms. The spin-averaged transitions measured by several groups [10–12] agreed very well with theoretical predictions [13] and provided the most accurate determination of the electron mass. However, the hfs from one of these measurements [11] deviated by 9σ from the theoretical predictions [14]. This disagreement is very intriguing, because HD⁺ is a molecule with only one electron and can be calculated almost as precisely as hydrogen atom.

Another system whose hfs can be accurately measured and predicted theoretically is the helium atom. Up to now, its theoretical calculations were hampered by severe difficulties in QED treatment of the electron-electron correlations, which limited the theoretical accuracy on the level of about 1 kHz [15,16]. In this Letter, we demonstrate that the rigorous QED treatment of hfs of few-electron atoms is possible up to the order of $\alpha^3 E_F$, where α is the fine-structure constant and E_F is the Fermi splitting. We perform numerical calculations for the 2^3S state of ³He and use the experimental He⁺ hfs value to eliminate nuclear uncertainties. Our calculation increases the theoretical accuracy by more than an order of magnitude. The updated theoretical result has an accuracy of 41 Hz and is in excellent agreement with the experimental value [17]. This constitutes the strongest test of QED hfs theory in few-body systems, which is of particular importance now in view of the discrepancy observed in HD⁺ [11].

Hyperfine splitting.—The QED theory of hfs in the S state starts with the leading contribution given by the so-called Fermi splitting E_F,

$$E_F \equiv \langle V_F \rangle = \frac{4\pi Z\alpha}{3mM} g\langle \vec{I} \cdot [\vec{s}_1\delta^3(r_1) + \vec{s}_2\delta^3(r_2)]\rangle, \quad (1)$$

where $\vec{I}$ and M are the nuclear spin and mass, respectively, $\vec{s}_i$ and m are the spin and the mass of the electrons, respectively, Z is the nuclear charge number, α is the fine-structure constant, and the natural nuclear g factor is defined from the nuclear magnetic moment $\vec{\mu}$ by $\vec{\mu} = Ze/(2M)g\vec{I}$. The leading QED correction to the Fermi splitting is obtained by multiplying E_F by the magnetic moment anomaly of the free electron $\kappa = (g_e - 2)/2$. Rigorous theory of the hfs of light atomic systems is

constructed within the nonrelativistic quantum electrodynamics (NRQED) in the form of an expansion in the fine-structure constant. We represent it as follows

$$E_{\text{hfs}} = E_F(1 + \kappa) + E^{(6)} + E^{(7)} + E^{(8)} + E_{\text{nuc}} + E_{\text{rec}}. \quad (2)$$

Here, $E^{(n)}$ are the QED effects of order $m\alpha^n$ for the point-like and infinitely-heavy nucleus, E_{nuc} represents the nuclear structure effects, and E_{rec} is nuclear recoil correction. The nuclear effects E_{nuc} cannot be calculated accurately at present, so we extract them from the experimental hfs value in He$^+$. Calculations of the leading hfs term (i.e., E_F) are well established at present [18]. QED effects of order $\alpha^2 E_F$ (i.e., $E^{(6)}$) were calculated in Refs. [15,16]. Here we calculate the QED effects of order $\alpha^3 E_F$ (i.e., $E^{(7)}$) and the dominant part of the recoil correction of order $\alpha^2 (m/M) E_F$ (i.e., E_{rec}), which leads to a drastic improvement of theoretical accuracy.

QED effects of order $\alpha^3 E_F$.—The derivation described in the Appendix provides the complete expression for the $m\alpha^7$ QED correction which does not contain any divergences and can be used for numerical evaluation. The final result is separated into the low-energy (E_L), the first-order matrix-elements (E_{fo}) and the second-order matrix-elements (E_{sec}) parts. The first-order and second-order contributions are further split into the self-energy (se) and vacuum-polarization (vp) parts. We thus write, in atomic units and with the prefactor $m\alpha^7$ pulled out, $E^{(7)} \equiv m\alpha^7 \mathcal{E}^{(7)}$,

$$\mathcal{E}_{\text{hfs}}^{(7)} = \mathcal{E}_L + \mathcal{E}_{\text{fo}}(\text{se}) + \mathcal{E}_{\text{sec}}(\text{se}) + \mathcal{E}_{\text{fo}}(\text{vp}) + \mathcal{E}_{\text{sec}}(\text{vp}). \quad (3)$$

TABLE I. First-order matrix elements for the $2^3 S$ state, numerical results are from Ref. [19].

Operator	$\langle Q_i \rangle$
$Q_1 = 4\pi\delta^3(r_1)$	16.592 071
$Q_3 = 4\pi\delta^3(r_1)/r_2$	4.648 724
$Q_4 = 4\pi\delta^3(r_1)p_2^2$	2.095 714
$Q_9 = 1/r^3$	0.038 861
$Q_{11} = 1/r_1^2$	4.170 446
$Q_{12} = 1/(r_1 r_2)$	0.560 730
$Q_{13} = 1/(r_1 r)$	0.322 696
$Q_{14} = 1/(r_1 r_2 r)$	0.186 586
$Q_{15} = 1/(r_1^2 r_2)$	1.242 704
$Q_{16} = 1/(r_1^2 r)$	1.164 599
$Q_{17} = 1/(r_1 r^2)$	0.112 360
$Q_{18} = (\vec{r}_1 \cdot \vec{r})/(r_1^3 r^3)$	0.011 331
$Q_{24} = p_1^i(r^i r^j + \delta^{ij} r^2)/(r_1 r^3)p_2^j$	0.002 750
$Q_{28} = p_1^2/r_1 p_2^2$	1.597 727
$Q_{51} = 4\pi\vec{p}_1\delta^3(r_1)\vec{p}_1$	0.009 993
$Q_{53} = 1/r_1$	1.154 664
$Q_{56} = 1/r_1^3$	−23.022 535
$Q_{57} = 1/r_1^4$	25.511 837
$Q_{59} = 1/(r_1 r^3)$	0.051 914

The low-energy Bethe-logarithm-type correction $\mathcal{E}_L$ is defined by Eq. (A3). The first-order contributions $\mathcal{E}_{\text{fo}}$ can be conveniently expressed in terms of expectation values of Q_i operators, which were encountered in our previous investigation of the Lamb shift [19] and are defined in Table I. The result for the self-energy is

$$
\begin{aligned}
\mathcal{E}_{\text{fo}}(\text{se}) = \frac{g\,m}{2\pi M}\langle \vec{I}\cdot\vec{S}\rangle \Bigg\{ &\frac{1}{9}\left(\frac{71}{3} + 32\ln\frac{\alpha^{-2}}{2}\right)Z^2 Q_1 Q_{53} + \left(\frac{143}{108} + \frac{8}{9}\ln\frac{\alpha^{-2}}{2}\right)Z^2 Q_{57} \\
&- \frac{1}{3}\left(\frac{85}{6} + 16\ln\frac{\alpha^{-2}}{2}\right)\frac{Z^2}{2}Q_3 - \frac{56}{9}ZQ_9 Q_{53} + \frac{56}{9}ZQ_{59} - \frac{13}{12}ZQ_{18} + \frac{4Z}{3}E^{(4)}Q_{53} \\
&+ \frac{2Z}{3}\left(-2E_0 Q_{13} + Q_{17} + E_0^2 Q_{53} + 2ZE_0 Q_{11} + 2ZE_0 Q_{12} - 2ZQ_{14} - 2ZQ_{16} + 3Z^2 Q_{15} + Z^2 Q_{56}\right) \\
&- \frac{Z}{3}Q_{28} + \frac{2Z}{3}Q_{24} + \frac{Z}{36}\left(\frac{77}{6} + 16\ln\frac{\alpha^{-2}}{2}\right)Q_{51} - \frac{Z}{36}\left(\frac{95}{3} + 32\ln\frac{\alpha^{-2}}{2}\right)\left(E_0 Q_1 - Q_3 - \frac{1}{2}Q_4\right) \\
&+ \left[-\frac{7}{6} - \frac{44\pi^2}{27} - \frac{10}{3}\zeta(3) + \frac{896}{27}\ln 2 + \frac{16}{9}\ln^2 2 - \frac{938}{27}\ln\alpha - \frac{64}{9}\ln^2\alpha + \frac{256}{9}\ln 2\ln\alpha\right]\frac{Z^3}{4}Q_1 \Bigg\}. \quad (4)
\end{aligned}
$$

The second-order self-energy contribution is given by

$$\mathcal{E}_{\text{sec}}(\text{se}) = \frac{g\,m}{2\pi M}\langle\vec{I}\cdot\vec{S}\rangle\left\{\frac{2}{9}\left[\left(\frac{5}{6} + \ln\frac{\alpha^{-2}}{2}\right)S_1 - 7S_2 + \frac{3}{2}S_3\right] + \frac{Z}{3}\left(\frac{Z}{2}S_4 - S_5\right) - \frac{Z}{8}S_6\right\}, \quad (5)$$

where the second-order matrix elements S_i are defined in Table II. For the vacuum polarization we obtain the following results

TABLE II. Second-order corrections for the 2^3S state.

Term	Value
$S_1 = \langle V_R[1/(E_0 - H_0)']V_R\rangle$	$-2634.595\,12$
$S_2 = \langle V_R[1/(E_0 - H_0)'](1/r^3)\rangle$	$0.371\,13$
$S_3 = \langle V_R[1/(E_0 - H_0)']H_R\rangle$	$202.676\,07$
$S_4 = \langle [(\vec{r}_1/r_1^3) \times \vec{p}_1 + (\vec{r}_2/r_2^3) \times \vec{p}_2][1/(E_0 - H_0)'][(\vec{r}_1/r_1^3) \times \vec{p}_1 + (\vec{r}_2/r_2^3) \times \vec{p}_2]\rangle$	$-0.004\,69$
$S_5 = \langle [(\vec{r}_1/r_1^3) \times \vec{p}_1 + (\vec{r}_2/r_2^3) \times \vec{p}_2][1/(E_0 - H_0)'](\vec{r}/r^3) \times (\vec{p}_1 - \vec{p}_2)\rangle$	$-0.007\,07$
$S_6 = \langle [(\delta^{ij}/r_1^3) - (3r_1^i r_1^j/r_1^5) + (\delta^{ij}/r_2^3) - (3r_2^i r_2^j/r_2^5)][1/(E_0 - H_0)'][(\delta^{ij}/r^3) - 3(r^i r^j/r^5)]\rangle$	$-0.011\,28$

$$\mathcal{E}_{\rm fo}({\rm vp}) = -\frac{g\,m}{45\pi M}\langle \vec{I}\cdot\vec{S}\rangle\left[16Z^2 Q_1 Q_{53} + 2ZQ_{51}\right.$$
$$+ 4Z(1 - 3Z)Q_3 - 4ZE_0 Q_1 + 2ZQ_4$$
$$\left.+ 4Z^2 Q_{57} + Z^3\left(\frac{236}{15} + 8\ln\alpha\right)Q_1\right], \quad (6)$$

and

$$\mathcal{E}_{\rm sec}({\rm vp}) = -\frac{g\,m}{45\pi M}\langle \vec{I}\cdot\vec{S}\rangle S_1. \quad (7)$$

The numerical calculations of the $m\alpha^7$ corrections are carried out with the basis set of exponential functions $e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r}$ introduced by Korobov [20], where $r = |\vec{r}_1 - \vec{r}_2|$. The method of calculations follows the one developed in our previous investigations and described in Ref. [21]. The calculation of the low-energy Bethe-logarithm-type contribution follows our previous work [22]. Numerical results for the individual $m\alpha^7$ corrections to the hfs of the 2^3S state in ^{3}He are presented in Table III.

Hyperfine mixing correction.—For the 2^3S_1 state the nuclear recoil effects are dominated by the second-order hyperfine correction induced by the Fermi contact interaction V_F, specifically, by the 2^3S_1-2^1S_0 mixing contribution. The Fermi interaction mixes states with different values of the total momentum J and the 2^3S_1-2^1S_0 mixing

TABLE III. $m\alpha^7$ corrections to the hfs of the 2^3S state. $\mathcal{E}$ are in units of $\alpha^3 E_F$ and $\delta^3 = \mathcal{E}^{(7)}\alpha^3$.

Term	Value
$\mathcal{E}_L$	$22.05\,873(88)$
$\mathcal{E}_{\rm fo}({\rm se})$	$8.31\,316$
$\mathcal{E}_{\rm sec}({\rm se})$	$-83.11\,218$
$\mathcal{E}_{\rm fo}({\rm vp})$	$0.88\,943$
$\mathcal{E}_{\rm sec}({\rm vp})$	$1.68\,478$
$\mathcal{E}^{(7)}({\rm He})$	$-50.16\,609$
$\mathcal{E}^{(7)}({\rm He}^+)$	$-50.64\,036(88)$
$\mathcal{E}^{(7)}({\rm He\text{-}He}^+)$	$0.47\,428(88)$
$\delta^{(3)}({\rm He\text{-}He}^+)$	$0.1843(3) \times 10^{-6}$

is strongly enhanced because of the small energy difference of these states [15]. The leading mixing contribution is of order $\alpha^2(m/M)E_F$ and given by

$$E_{\rm mix}^{(6)} = \frac{\langle 2^3S|V_F|2^1S\rangle^2}{E_0(2^3S) - E_0(2^1S)}, \quad (8)$$

which leads to a surprisingly large result, $E_{\rm mix}^{(6)} = -8.9921 \times 10^{-6}E_F$. The numerical value of $E_{\rm mix}^{(6)}$ is so large that we have to consider higher-order corrections to it, which are small but not negligible at our level of interest. First, we consider the recoil correction to Eq. (8). Using the matrix element with full mass dependence

$$4\pi\langle 2^3S_1|[\delta^3(r_1) - \delta^3(r_2)]|2^1S_0\rangle_M = \left(\frac{\mu}{m}\right)^3 29.135\,080, \quad (9)$$

[with $\mu = mM/(m + M)$] and including the recoil correction in the energy denominator, we obtain $\delta E_{\rm mix,rec} = 0.0032 \times 10^{-6}E_F$ for the nuclear mass correction beyond that in E_F. Second, we take into account the corrections due to the anomalous magnetic moment and the nuclear effects to the operator and the relativistic correction to the energies,

$$\delta E_{\rm mix,rad} = E_{\rm mix}^{(6)}\left[\left(1 + \kappa + \frac{E_{\rm nuc}}{E_F}\right)^2 - 1 - \frac{\delta E_{\rm rel}}{\delta E}\right], \quad (10)$$

where $\delta E_{\rm rel}/\delta E$ is the relative contribution of the relativistic correction to the 2^3S-2^1S energy difference. This yields $\delta E_{\rm mix,rad} = -0.0152 \times 10^{-6}E_F$. Finally, we consider the correction due to the mixing with higher excited states. The summation over the complete spectrum in the second-order contribution will lead to the infinite result, which indicates that it is not a complete recoil correction. Following Ref. [15], we here consider the normalized difference of this correction between helium atom and helium ion,

TABLE IV. Contributions to the 2^3S_1 hfs of ^{3}He.

Term	$\times 10^{-6}$	[Hz]	D_{21} [kHz]
$\delta^{(2)}$(He-He$^+$)	3.012 0	$-20\,279.$	$-1\,152.44$
$\delta^{(2+)}_{\rm rec}$(He-He$^+$)	$-8.993\,7\,(21)$	$60\,552.(14)$	-0.80
$\delta^{(3)}$(He-He$^+$)	$0.184\,3(3)$	$-1\,241.(2)$	-36.03
$\delta^{(4)}$(He-He$^+$)	$0.005\,8\,(58)$	$-39.(39)$	-1.14
δ(He-He$^+$)	$-5.791\,6\,(62)$	$38\,993.(41)$	
$1 + \delta$(He$^+$) [23]		$-6\,739\,740\,174.$	
$\nu_{\rm hfs,theo}$(He)		$-6\,739\,701\,181.(41)$	
$\nu_{\rm hfs,exp}$(He) [17]		$-6\,739\,701\,177.(16)$	

$$\delta E_{\rm mix,exc} = \left\langle V_F \frac{1}{(E-H)'} V_F \right\rangle \Bigg|_{\rm He} - \frac{3}{4} \frac{\langle \pi[\delta^3(r_1) + \delta^3(r_2)] \rangle}{8}$$
$$\times \left\langle V_F \frac{1}{(E-H)'} V_F \right\rangle \Bigg|_{\rm He^+}, \tag{11}$$

which is finite and yields a numerical contribution of $\delta E_{\rm mix,exc} = 0.0103 \times 10^{-6} E_F$. Finally, the total recoil correction is given by the sum $\Delta E_{\rm rec} = E^{(6)}_{\rm mix} + \delta E_{\rm mix,rec} + \delta E_{\rm mix,rad} + \delta E_{\rm mix,exc}$, with the numerical result presented in Table IV.

Results and discussion.—For the final analysis it is convenient to represent all corrections to hfs as multiplicative factors to E_F,

$$E_{\rm hfs} = E_F(1 + \delta), \tag{12}$$

where

$$\delta = \kappa + \delta^{(2)} + \delta^{(3)} + \delta^{(4)} + \delta_{\rm nuc} + \delta_{\rm rec}, \tag{13}$$

which is equivalent to Eq. (2) with $\delta^{(k)} = E^{(k+4)}/E_F$. The main advantage of this representation is that the δ coefficients are strongly correlated with those in He$^+$. In order to exploit this correlation, we split δ in Eq. (12) into two parts,

$$\delta({\rm He}) = \delta({\rm He^+}) + \delta({\rm He\text{-}He^+}), \tag{14}$$

where δ(He$^+$) will be extracted from the experiment on He$^+$ and δ(He-He$^+$) is calculated theoretically.

The individual theoretical contributions to δ(He-He$^+$) are presented in Table IV. The leading term, $\delta^{(2)}$, is of order $\alpha^2 E_F$. It was calculated first by one of the authors in Ref. [15] and later improved in Ref. [16]. The next-order QED correction of order $\alpha^3 E_F$, $\delta^{(3)}$, and the recoil contribution, $\delta_{\rm rec}$, are calculated as described above.

In order to estimate the higher-order QED contribution $\delta^{(4)}$(He-He$^+$), for which no direct calculations exist so far, we use results obtained in Ref. [7] for the normalized

difference of the hfs intervals in He$^+$, $D_{21} = 8E_{\rm hfs}(2S) - E_{\rm hfs}(1S)$. Specifically, we assume the ratio $\delta^{(4)}/\delta^{(3)}$ for the He-He$^+$ difference to be the same as the corresponding ratio for D_{21}, with a 100% uncertainty. Similarly, we obtain the uncertainty of $\delta_{\rm rec}$ by examining the ratio of $\delta^{(2+)}_{\rm rec}/\delta^{(2)}$ for D_{21} and assuming the same ratio holds for He-He$^+$ difference, thus obtaining the estimate of the omitted nonmixing hfs recoil contributions.

Adding the contribution δ(He$^+$) inferred from the experimental result of the $1S$ hfs in ^{3}He$^+$ from Ref. [23], we obtain the theoretical prediction for the He(2^3S_1) hfs with an accuracy of 41 Hz, see Table IV, in perfect agreement with the experimental result of Ref. [17].

Conclusion.—In this Letter, we have demonstrated that advanced QED calculations are now capable of predicting the hfs of helium with precision of several tens of Hz by using the experimental hfs value for the corresponding hydrogen-like ion. We derived formulas and performed numerical calculations for the 2^3S state in ^{3}He. This improved the theoretical accuracy by a factor of 40 as compared to previous calculations. The present theoretical precision of ^{3}He(2^3S_1) hfs is 41 Hz, which makes it the most accurate theoretical prediction ever achieved for nonhydrogenic systems.

The excellent agreement of theory and experiment for the helium hfs contrasts sharply with the 9σ discrepancy observed for the HD$^+$ [11,14]. The disagreement is very surprising, taking into account the fact that the same theoretical approach is used in both systems. If the discrepancy is confirmed in forthcoming studies, this would be a signal of some unknown physics.

Our calculations can also be extended to helium- and lithiumlike ions, in particular, to Li$^+$, for which accurate experimental results are available [24,25]. The developed method can be used for extending the advanced tests of QED to more complicated systems or, alternatively, for determining the effective Zemach radii $\tilde{r}_Z$ of light nuclei. The later direction is of particular interest in view of the confirmed anomalies for the Zemach radii in ^{6}Li and ^{7}Li [25,26] and a significant discrepancy for hfs in μD [27].

Appendix: Appendix on derivation of the $\alpha^3 E_F$ effects.—The QED effects to hfs of the order $m\alpha^7 (= \alpha^3 E_F)$ can be represented as

$$E^{(7)} = E_L + 2\left\langle H^{(4)}_{\rm hfs} \frac{1}{(E_0 - H_0)'} H^{(5)} \right\rangle$$
$$+ 2\left\langle H^{(5)}_{\rm hfs} \frac{1}{(E_0 - H_0)'} H^{(4)} \right\rangle + \langle H^{(7)}_{\rm hfs} \rangle. \tag{A1}$$

Here, E_L is the Bethe-logarithm-type low-energy contribution, H_0 and E_0 denote the nonrelativistic Hamiltonian and its reference-state eigenvalue, respectively, $H^{(4)}$ is the Breit-Pauli Hamiltonian of order $m\alpha^4$, $H^{(5)}$ is the effective QED Hamiltonian of order $m\alpha^5$, and $H_{\text{hfs}}^{(4)}$ and $H_{\text{hfs}}^{(5)}$ are effective hfs Hamiltonians of order $m\alpha^4$ and $m\alpha^5$, respectively. The Breit-Pauli Hamiltonian $H^{(4)}$ is well known and given, e.g., by Eq. (7) of Ref. [28]. The effective hfs Hamiltonian of order α^4, $H_{\text{hfs}}^{(4)}$, is responsible for the leading-order hfs splitting. It can be obtained from Eqs. (5)–(11) of Ref. [16] by setting the electron magnetic anomaly to zero. The next-order effective hfs Hamiltonian $H_{\text{hfs}}^{(5)}$ is obtained from the same equations by picking up the linear part in the electron magnetic anomaly. The QED Hamiltonian $H^{(5)}$ is expressed as

$$H^{(5)} = \left(\frac{5}{6} - \frac{1}{5} + \ln\frac{\alpha^{-2}}{2\lambda}\right)\frac{4\alpha^2 Z}{3m^2}\left[\delta^3(r_1) + \delta^3(r_2)\right]$$
$$- \frac{7\alpha^2}{3\pi m^2}\frac{1}{r^3} + H_{\text{fs}}^{(5)}, \qquad (A2)$$

where $H_{\text{fs}}^{(5)}$ is the spin-dependent part of $H^{(5)}$ and is given by Eq. (14) of Ref. [28], and λ is the low-energy photon-momenta cutoff. The dependence on the cutoff cancels out when all terms in Eq. (A1) are considered together, which is explicitly demonstrated in the detailed derivation [29]. Therefore, for simplicity, we will set $\lambda = 1$ in the following formulas.

The low-energy Bethe-logarithm-type contribution E_L comes from the virtual photon momenta of the order $k \approx m\alpha^2$. It can be represented (in atomic units, with the $m\alpha^7$ prefactor pulled out) as

$$\mathcal{E}_L = -\frac{2}{3\pi}\delta_{V_F}\langle\vec{P}(H_0 - E_0)\ln(H_0 - E_0)\vec{P}\rangle, \qquad (A3)$$

where $\delta_{V_F}\langle S\rangle$ denotes the first-order perturbation of the matrix element $\langle S\rangle$ by the Fermi contact interaction V_F defined by Eq. (1) and $\vec{P} = \vec{p}_1 + \vec{p}_2$ is the electron momentum operator. The low-energy contribution E_L is very similar to the Bethe-logarithm-type contribution E_{L1} encountered in our previous study of the $m\alpha^7$ effects in the Lamb shift [22]. In fact, all necessary formulas for E_L can be obtained by repeating the derivation of Ref. [22] for the perturbation V_F instead of the spin-independent Breit Hamiltonian. We thus refer the reader to our previous work for detailed description of the evaluation of the low-energy contribution.

The second-order matrix elements in Eq. (A1) are problematic because of divergences originating 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 nearly 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 $H_{\text{nfs}}^{(4)}$ given by Eq. (6) of Ref. [30]. In order to make the divergences more tractable, we transfer them to first-order matrix elements. This can be accomplished [31] by representing the problematic operators as an anticommutator with the Schrödinger Hamiltonian H_0 plus some more regular operator. Specifically,

$$4\pi Z\left[\delta^3(r_1) + \delta^3(r_2)\right] = 2\left\{H_0 - E_0, \frac{Z}{r_1} + \frac{Z}{r_2}\right\} + V_R, \quad (A4)$$

$$H_{\text{nfs}}^{(4)} = -\frac{1}{4}\left\{H_0 - E_0, \frac{Z}{r_1} + \frac{Z}{r_2}\right\} + H_R. \qquad (A5)$$

The regularized operators V_R and H_R are acting on the eigenfunction of H_0 as

$$V_R|\phi\rangle = -2Z\left(\frac{\vec{r}_1}{r_1^3}\cdot\vec{\nabla}_1 + \frac{\vec{r}_2}{r_2^3}\cdot\vec{\nabla}_2\right)|\phi\rangle, \qquad (A6)$$

and

$$H_R|\phi\rangle = \left[\frac{1}{4}p_1^2 p_2^2 - \frac{1}{2}(E_0 - V)^2 - \frac{1}{2}p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_2^j\right.$$
$$\left. - \frac{Z}{4}\frac{\vec{r}_1\cdot\vec{\nabla}_1}{r_1^3} - \frac{Z}{4}\frac{\vec{r}_2\cdot\vec{\nabla}_2}{r_2^3} + \frac{1}{2}\frac{\vec{r}}{r^3}\cdot(\vec{\nabla}_1 - \vec{\nabla}_2)\right]|\phi\rangle, \tag{A7}$$

with $V = -Z/r_1 - Z/r_2 + 1/r$. The second-order contribution is thus transformed into

$$2\left\langle H_{\text{hfs}}^{(4)}\frac{1}{(E_0 - H_0)'}H^{(5)}\right\rangle + 2\left\langle H_{\text{hfs}}^{(5)}\frac{1}{(E_0 - H_0)'}H^{(4)}\right\rangle$$
$$= m\alpha^7\left[\mathcal{E}_{\text{sec}}(\text{se}) + \mathcal{E}_{\text{sec}}(\text{vp}) + \mathcal{E}_{\text{fo},A}\right], \qquad (A8)$$

where $\mathcal{E}_{\text{sec}}(\text{se})$ and $\mathcal{E}_{\text{sec}}(\text{vp})$ are regularized second-order corrections given by Eqs. (5) and (7), and $\mathcal{E}_{\text{fo},A}$ is the first-order contribution given by

$$\mathcal{E}_{\text{fo},A} = \langle \vec{I} \cdot \vec{S} \rangle \frac{g\, m}{3\pi M} \left\{ \frac{1}{3} \left[\left(\frac{5}{6} - \frac{1}{5} + \ln \frac{\alpha^{-2}}{2} \right) \left(\langle 16\pi Z [\delta^3(r_1) + \delta^3(r_2)] \rangle \left\langle \frac{Z}{r_1} + \frac{Z}{r_2} \right\rangle - \langle 16\pi Z [\delta^3(r_1) + \delta^3(r_2)] \right. \right. \right.$$

$$\left. \times \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \right\rangle + 2 \left\langle \frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4} \right\rangle \bigg) - 14 \left\langle \frac{1}{r^3} \right\rangle \left\langle \frac{Z}{r_1} + \frac{Z}{r_2} \right\rangle + 14 \left\langle \frac{1}{r^3} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \right\rangle \bigg]$$

$$+ \frac{1}{2} \left[\frac{1}{4} \left\langle \frac{Z^2}{r_1^4} + \frac{Z^2}{r_2^4} - 2 \left(\frac{Z\vec{r}_1}{r_1^3} - \frac{Z\vec{r}_2}{r_2^3} \right) \cdot \frac{\vec{r}}{r^3} \right\rangle + \left\langle \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) (E_0 - V)^2 \right\rangle - \frac{1}{2} \left\langle p_1^2 \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) p_2^2 \right\rangle \right.$$

$$\left. \left. + 2 E^{(4)} \left\langle \frac{Z}{r_1} + \frac{Z}{r_2} \right\rangle + \left\langle p_1^i \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p_2^j \right\rangle - \langle \pi Z [\delta^3(r_1) + \delta^3(r_2)] \rangle \left\langle \frac{Z}{r_1} + \frac{Z}{r_2} \right\rangle \right] \right\}, \tag{A9}$$

where $m\alpha^4 E^{(4)}$ is the relativistic correction to the energy centroid. The singularities are now moved into the first-order terms in Eq. (A9). Divergences in singular operators Z^2/r_a^4 and Z^3/r_a^3 are handled according to Ref. [19].

$H_{\text{hfs}}^{(7)}$ is an effective Hamiltonian of order $m\alpha^7$. It comes from the one-loop self-energy and the one-loop vacuum polarization only, because no photon-exchange terms contribute at this order. It is represented as

$$H_{\text{hfs}}^{(7)} = H_{\text{hfs},A}^{(7)} + H_{\text{hfs},B}^{(7)} + \cdots, \tag{A10}$$

where … denotes terms that are proportional to the electron-nucleus Dirac δ function, $\propto Z^3 \delta^3(r_a)$. At the current stage of the derivation we 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. $H_{\text{hfs},A}^{(7)}$ is induced by the spin-dependent terms in the generalized Breit-Pauli Hamiltonian H_{BP} (see Eqs. (15)–(17) of Ref. [32]) that are proportional to the magnetic moment anomaly,

$$H_{\text{hfs},A}^{(7)} = \kappa \sum_a \left[\frac{Z\alpha}{2m^2} \vec{\sigma}_a \cdot \frac{\vec{r}_a}{r_a^3} \times [-e\vec{A}_a] \right.$$

$$\left. - \frac{e}{16m^3} \vec{\sigma}_a \cdot \Delta \vec{B}_a + \frac{e}{4m^3} (\vec{p}_a \cdot \vec{\sigma}_a)(\vec{B}_a \cdot \vec{p}_a) \right]$$

$$+ \kappa \sum_{a \neq b} \frac{\alpha}{2m^2 r_{ab}^3} \vec{\sigma}_a \cdot \vec{r}_{ab} \times [e\vec{A}_a - e\vec{A}_b], \tag{A11}$$

where a and b indices refer to the electrons, $\vec{A}_a = \vec{A}(\vec{r}_a)$ and

$$e\vec{A}(\vec{r}) = \frac{e}{4\pi} \vec{\mu} \times \frac{\vec{r}}{r^3} = -Z\alpha \frac{g}{2M} \vec{I} \times \frac{\vec{r}}{r^3}. \tag{A12}$$

After the spin averaging $S^i I^j \rightarrow \delta^{ij} \vec{I} \cdot \vec{S}/3$ with $\vec{S} = \vec{s}_1 + \vec{s}_2$ being the total spin of electrons, it becomes

$$H_{\text{hfs},A}^{(7)} = \frac{g\kappa Z\alpha}{4m^2 M} \vec{I} \cdot \vec{S} \left\{ \frac{2Z\alpha}{3} \frac{1}{r_1^4} - \frac{4\pi}{9m} p_1^i \delta^3(r_1) p_1^i \right.$$

$$+ \frac{1}{6m} p_1^i \frac{1}{r_1^5} (r_1^2 \delta^{ij} - 3 r_1^i r_1^j) p_1^j + \frac{\pi}{3m} \Delta \delta^3(r_1)$$

$$\left. - \frac{4}{3} \alpha \frac{\vec{r} \cdot \vec{r}_1}{r^3 r_1^3} \right\} + (1 \leftrightarrow 2). \tag{A13}$$

Operator $\Delta\delta^3(r_a)$ is transformed into regular Q_i operators from Table I with the help of Eq. (61) of Ref. [33]. The second part of $H_{\text{hfs}}^{(7)}$ is obtained by expanding (in q^2) the form factors and the vacuum polarization multiplied by the Fermi contact interaction,

$$H_{\text{hfs},B}^{(7)} = \frac{gZ\alpha}{4m^3 M} \left[F_1'(0) + F_2'(0) - \frac{\alpha}{15\pi} \right] \frac{8\pi}{3} \vec{I} \cdot \vec{S} \Delta\delta^3(r_1)$$

$$+ (1 \leftrightarrow 2), \tag{A14}$$

where the form-factor slopes are given by

$$F_1'(0) + F_2'(0) = \frac{\alpha}{\pi} \left[\frac{17}{72} + \frac{1}{3} \ln \frac{\alpha^{-2}}{2} \right]. \tag{A15}$$

We now turn to restoring the missing contribution proportional to the electron-nucleus Dirac δ function. This is accomplished by evaluating the large-Z limit of the above formulas. In the $Z \rightarrow \infty$ 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 hydrogenlike ions. This matching gives us the coefficient at the electron-nucleus Dirac δ function. As a result, we obtain an additional first-order contribution, which reads

$$E_{\text{fo},B} = \frac{\alpha(Z\alpha)^3 g}{4\pi M} \langle \vec{I} \cdot \vec{S} \rangle \pi \langle [\delta^3(r_1) + \delta^3(r_2)] \rangle \left[-\frac{5351}{1350} - \frac{44\pi^2}{27} \right.$$

$$- \frac{10}{3} \zeta(3) + \frac{896}{27} \ln 2 + \frac{16}{9} \ln^2 2 - \frac{4882}{135} \ln \alpha$$

$$\left. - \frac{64}{9} \ln^2 \alpha + \frac{256}{9} \ln 2 \ln \alpha \right]. \tag{A16}$$

Finally we obtain the total first-order contribution as

$$\left\langle H_{\text{hfs},A}^{(7)} \right\rangle + \left\langle H_{\text{hfs},B}^{(7)} \right\rangle + E_{\text{fo},A} + E_{\text{fo},B}$$
$$= m\alpha^7 [\mathcal{E}_{\text{fo}}(\text{se}) + \mathcal{E}_{\text{fo}}(\text{vp})], \qquad (A17)$$

where $\mathcal{E}_{\text{fo}}(\text{se})$ and $\mathcal{E}_{\text{fo}}(\text{vp})$ are given by Eqs. (4) and (6), respectively. The details of the derivation will be published elsewhere [29].

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