Second-order hyperfine correction to H, D, and ^{3}He energy levels

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The complete second-order hyperfine-interaction correction is calculated for centroid energy levels of H, D, and ^{3}He atoms. For ^{3}He, the corrections of -2.075 kHz and -0.305 kHz beyond the leading hyperfine-mixing contribution are obtained for the 2^1S and 2^3S states, respectively. These results shift the nuclear charge radii difference derived from the ^{3}He$-^4$He isotope shift and largely resolve the previously reported disagreement between the muonic and electronic helium determinations [van der Werf *et al.*, arXiv:2306.02333 (2023); Schuhmann *et al.*, arXiv:2305.11679 (2023)].

I. INTRODUCTION

The nuclear magnetic moment causes a shift of atomic energy levels, depending on the total angular momentum $\vec{F} = \vec{I} + \vec{J}$, where $\vec{I}$ is the nuclear spin and $\vec{J}$ represents the electron angular momentum [1]. This effect is known as hyperfine splitting (HFS). In hydrogen-like atoms, it is relatively small compared to the fine structure, which arises from the electron's spin-orbit coupling.

Due to its small magnitude, hyperfine interaction is typically treated using first-order perturbation theory. The second-order HFS correction has rarely been addressed in the literature, and when it has, it is often treated incorrectly, primarily due to the presence of crossed diagrams [2] and the fact that it diverges in the point-nucleus limit. A proper analysis of the second-order HFS correction has been conducted only for hydrogen and muonic hydrogen (μH) atoms so far, in the context of the two-photon exchange contribution [3, 4]. This was required because the hydrogen HFS has been measured precisely [5] and accurate measurements of HFS in light muonic atoms are underway [6–9].

The second-order HFS corrections modify not only the HFS but also the centroid energies. The corresponding correction has usually been neglected due to its small size, with the leading order in hydrogenic systems starting at $(Z\alpha)^6 m^3/M^2$, where M is the nuclear mass, m is the electron mass, Z is the nuclear charge number, and α is the fine-structure constant. This correction forms part of a complete quadratic recoil correction, which has recently been derived in Ref. [10].

In helium-like atoms, the hyperfine interaction causes mixing between triplet and singlet states, which results in significant corrections. For instance, the HFS of the helium 2^3S state is impacted by it by as much as 60 kHz [11, 12], exceeding even the relativistic correction [12]. Similarly, the 2^3S-2^1S mixing contributes a substantial correction to the ^{3}He$-^4$He isotope shift, around 80 kHz [13].

In light of the discrepancy in the nuclear charge radii difference between ^{3}He and ^{4}He, as determined by electronic versus muonic measurements [14–16], examining all possible corrections to the ^{3}He$-^4$He isotope shift has become critically important. Recently, Qi and collaborators [17] found that the mixing with $n > 2$ excited states yields an additional correction to the helium isotope shift of about 1.37 kHz, which partially explains this discrepancy. In this work, we calculate the complete second-order HFS correction, finding an even larger correction of 1.77 kHz. Combined with an improved value of the field shift contribution, this result brings the electronic and muonic determinations of the nuclear charge radii difference [14, 15] into a $1.3\,\sigma$ agreement.

II. HYDROGENIC ATOM

Let us begin by considering the HFS interaction in hydrogenic systems. The Dirac Hamiltonian in the external electromagnetic field is (in natural units $\hbar = c = 1$)

$$\begin{aligned} H_{\rm EM} &= \vec{\alpha}\cdot(\vec{p} - e\,\vec{A}_{\rm hfs}) + \beta\, m + e\, A^0 \\ &= H_{\rm D} + V_{\rm hfs}, \end{aligned} \tag{1}$$

where e is the electron charge, A_0 is the Coulomb field from the nucleus

$$V \equiv e\, A^0 = -\frac{Z\,\alpha}{r}\,, \tag{2}$$

and $\vec{A}_{\rm hfs}$ is the vector potential from the nuclear magnetic moment $\vec{\mu}$

$$\vec{A}_{\rm hfs} = \frac{1}{4\,\pi}\,\vec{\mu}\times\frac{\vec{r}}{r^3}\,. \tag{3}$$

The corresponding hyperfine interaction for a point nucleus is

$$\begin{aligned} V_{\rm hfs} &= -e\,\vec{\alpha}\cdot\vec{A}_{\rm hfs} \\ &= \frac{e}{4\,\pi}\,\vec{\mu}\cdot\vec{\alpha}\times\frac{\vec{r}}{r^3}\,. \end{aligned} \tag{4}$$

The second-order hyperfine correction to energy is uv divergent for a point nucleus. Therefore, we cannot ignore the charge and magnetic moment nuclear form factors, but for simplicity we assume that they are equal to each other, thus

$$\rho_E(r) = \rho_M(r) = \rho(r)\,, \tag{5}$$

and neglect the higher order nuclear electromagnetic moments. Thus, potentials take the general form

$$V = -Z\,\alpha\left[\frac{1}{r}\right]_{\rm fs} \equiv -\frac{Z\alpha}{r}\,F_C(r)\,, \tag{6}$$

$$V_{\rm hfs} = \frac{e}{4\,\pi}\,\vec\mu\cdot\vec\alpha\times\left[\frac{\vec r}{r^3}\right]_{\rm fs} \equiv \frac{e}{4\,\pi}\,\vec\mu\cdot\frac{\vec\alpha\times\vec r}{r^3}\,F_{\rm hfs}(r)\,, \tag{7}$$

and $F_C(r) = F_{\rm hfs}(r) = 1$ for the point nucleus.

The second-order hyperfine correction to energy in the hydrogenic system is

$$E_{\rm hfs2} = \langle\phi|V_{\rm hfs}\,\frac{1}{(E_D-H_D)'}\,V_{\rm hfs}|\phi\rangle\,. \tag{8}$$

The product of the nuclear magnetic moments in the above is to be replaced by $\mu^a\,\mu^b \to \delta^{ab}\,\vec\mu^{\,2}/3$, because here we are interested in corrections to energy levels but not to the hyperfine structure. Using the spectral representation of the Green function, we express Eq. (8) as

$$\begin{aligned}E_{\rm hfs2} = {}& \frac{1}{3}\,(Z\alpha)^2\,m^3\,\left(\frac{g}{2M}\right)^2\,I(I+1)\sum_{n,\kappa_n,\mu_n}{}'\,\frac{1}{\varepsilon_a-\varepsilon_n}\\ &\times\langle n_a\kappa_a\mu_a|F_{\rm hfs}(r)\,\frac{(\vec\alpha\times\vec r)_i}{r^3}|n\kappa_n\mu_n\rangle\\ &\times\langle n\kappa_n\mu_n|F_{\rm hfs}(r)\,\frac{(\vec\alpha\times\vec r)_i}{r^3}|n_a\kappa_a\mu_a\rangle\,,\end{aligned} \tag{9}$$

where we introduced the nuclear g-factor g as

$$\vec\mu = \frac{q}{2\,M}\,g\,\vec I, \tag{10}$$

where $q = Z\,|e|$. Performing the angular-momentum algebra in Eq. (9), we obtain, for the $1s$ reference state ($\kappa_a = -1$),

$$E_{\rm hfs2} = \frac{2}{3}\,(Z\alpha)^2\,m^3\,\left(\frac{g}{2M}\right)^2\,I(I+1)\,\mathcal{E}\,, \tag{11}$$

where $\mathcal{E}$ is

$$\begin{aligned}\mathcal{E} = {}& \sum_{\kappa_n=-1,2} a_{\kappa_n}\sum_n{}'\,\frac{1}{\varepsilon_a-\varepsilon_n}\\ &\times\left\{\int_0^\infty x^2dx\,\frac{F_{\rm hfs}(x)}{x^2}\,[g_a(x)\,f_n(x)+f_a(x)\,g_n(x)]\right\}^2.\end{aligned} \tag{12}$$

Here, $a_{-1} = 2/3$, $a_2 = 1/3$, and $g_a(x)$ and $f_a(x)$ are the upper and the lower radial components of the Dirac wave function of the reference state. For the dipole parametrization with $r_M = r_C$, the magnetic and electric distribution functions are

$$\begin{aligned}F_{\rm hfs}(x) &= 1 - e^{-\lambda x}\Big[1+\lambda x+\frac{1}{2}(\lambda x)^2\Big]\,,\\ F_C(x) &= 1-\Big(1+\frac{\lambda x}{2}\Big)\,e^{-\lambda x}\,,\end{aligned} \tag{13}$$

with $\lambda = 2\sqrt{3}/r_C$. We evaluate numerically Eq. (12) for the dipole nuclear model by representing the summation over the spectrum as a sum over the pseudostates in the basis of B-splines [18, 19]. A series of calculations were performed for a fixed nuclear charge Z but for different nuclear radii r_C. The obtained results were fitted to the form

$$\mathcal{E}(r_C) = (Z\alpha)^4\,\big[a\ln r_C + b + c\,r_C + \ldots\big]\,, \tag{14}$$

which yielded the following result for the leading logarithmic coefficient,

$$a = 5.00\,(1)\,, \tag{15}$$

in agreement with the result of analytical calculations in Eq. (74). Next, we performed numerical calculations of $\mathcal{E}$ for different values of Z with a fixed value of r_C and fitted the results to the form

$$\mathcal{E}(Z\alpha) = (Z\alpha)^4\,\big[5\ln(Z\alpha\,m\,r_C) + B + Z\alpha\,C + \ldots\big]\,. \tag{16}$$

We obtained the nonlogarithmic coefficient B as

$$B = 2.700\,(2)\,, \tag{17}$$

again in agreement with the analytical result in Eq. (74). The numerical results for the leading $Z\alpha$-expansion coefficients serve as a valuable test of the correctness of the analytical derivation for few-electron atoms.

III. NRQED APPROACH FOR A FEW ELECTRON SYSTEMS

For light few-electron systems, the best computational approach is that based on nonrelativistic quantum electrodynamics (NRQED), because we can account accurately for relativistic effects and electron correlations on the same footing. In fact, the derivation is similar to that of the internuclear spin-spin interaction in molecules by Ramsey [20], with the difference that here we have the same nucleus and thus have to include the hard electron-nucleus interaction, which is highly singular. Therefore, we will use the dimension regularization for the derivation of NRQED operators, see Appendix A for details. Because we know that the shift is proportional to $\vec I^{\,2}$, we can assume initially that $I = 1/2$ and later after cancellation of $1/\varepsilon$ terms, replace it by an arbitrary I. Therefore, in $d = 3-2\,\varepsilon$ dimensions the vector potential takes the form

$$A^i_{\rm hfs}(\vec q) = -\,i\,Z\,e\,\frac{g}{4\,M}\,\sigma^{ij}_N\,\frac{q^j}{q^2}\,\tilde\rho(q^2)\,, \tag{18}$$

where $\tilde\rho$ is a Fourier transform of ρ in Eq. (5) and σ^{ij}_N is d-dimensional spin operator for the nucleus defined in Eq. (A1). In the coordinate representation it is

$$A^i_{\rm hfs}(\vec r) = -\,i\,Z\,e\,\frac{g}{4\,M}\,\sigma^{ij}_N\int\frac{d^dq}{(2\,\pi)^d}\,e^{i\,\vec q\cdot\vec r}\,\frac{q^j}{q^2}\,\tilde\rho(q^2)$$

$$= \frac{Z\,e}{4\,\pi}\,\frac{g}{4\,M}\,\sigma_N^{ij}\left[\frac{r^j}{r^3}\right]_{\mathrm{fs},\varepsilon}. \tag{19}$$

In $d = 3$ dimensions, $\sigma^{ij} = \epsilon^{ijk}\,\sigma^k$ and for a point nucleus $A^i_{\mathrm{hfs}}(\vec{r})$ becomes

$$\vec{A}_{\mathrm{hfs}}(\vec{r}) = -\frac{Z\,e}{4\,\pi}\,\frac{g}{2\,M}\,\vec{I}\times\frac{\vec{r}}{r^3} = \frac{1}{4\,\pi}\,\vec{\mu}\times\frac{\vec{r}}{r^3}\,, \tag{20}$$

as it should.

The leading second-order hyperfine-interaction correction is of the order $m\,\alpha^6\,(m/M)^2$. We represent it as a sum of three terms

$$E_{\mathrm{hfs2}} = E_{\mathrm{sec}} + E_{\mathrm{diam}} + E_{\mathrm{high}}\,, \tag{21}$$

which we calculate in the following three sections. Similarly to the first-order HFS correction, which is proportional to the Fermi coefficient E_F, the second-order HFS correction is proportional to the second-order Fermi coefficient E_{F2},

$$E_{F2} = \alpha^6\,m\left(\frac{Z\,g\,m}{2\,M}\right)^2 I(I+1)\,. \tag{22}$$

IV. E_{sec}

E_{sec} is a second-order correction of the form

$$E_{\mathrm{sec}} = \left\langle H_{\mathrm{hfs}}\,\frac{1}{E-H}\,H_{\mathrm{hfs}}\right\rangle, \tag{23}$$

where H is the nonrelativistic Hamiltonian

$$H = \frac{p_1^2}{2\,m} + \frac{p_2^2}{2\,m} + \left[\frac{\alpha}{r_{12}} - \frac{Z\,\alpha}{r_1} - \frac{Z\,\alpha}{r_2}\right]_\varepsilon, \tag{24}$$

and H_{hfs} is the leading hyperfine interaction. It is obtained from the nonrelativistic expansion of V_{hfs} for a point nucleus

$$V_{\mathrm{hfs}} = -\frac{Z\,\alpha\,g}{4\,M}\,\alpha^i\,\sigma_N^{ij}\left[\frac{r^j}{r^3}\right]_\varepsilon, \tag{25}$$

namely

$$H_{\mathrm{hfs}} = -\frac{Z\,\alpha\,g}{4\,M}\,\sigma_N^{ij}\left\{\sigma^i\left[\frac{r^j}{r^3}\right]_\varepsilon,\,\frac{\sigma^k\,p^k}{2\,m}\right\}, \tag{26}$$

where $\{A\,,\,B\} = A\,B + B\,A$. In d-dimensions

$$\begin{aligned}\sigma^i\,\sigma^k &= \frac{1}{2}\,\{\sigma^i\,,\,\sigma^k\} + \frac{1}{2}\,[\sigma^i\,,\,\sigma^k]\\ &= \delta^{ik} + i\,\sigma^{ik}\,,\end{aligned} \tag{27}$$

thus

$$\begin{aligned}H_{\mathrm{hfs}} = &-\frac{Z\,\alpha\,g}{4\,m\,M}\,\sigma_N^{ij}\left(\sigma^{ik}\,\frac{i}{2}\left[\frac{r^j}{r^3}\,,\,p^k\right]_\varepsilon + \left[\frac{r^j}{r^3}\right]_\varepsilon p^i\right)\\ &= H_{\mathrm{hfsA}} + H_{\mathrm{hfsB}} + H_{\mathrm{hfsC}}\,,\end{aligned} \tag{28}$$

where after summing over all electrons

$$H_{\mathrm{hfsA}} = \sum_a \frac{Z\,\alpha\,g}{2\,m\,M}\,\sigma_N^{ij}\,\sigma_a^{ij}\,\frac{\pi}{d}\,\delta^d(r_a)\,, \tag{29}$$

$$H_{\mathrm{hfsB}} = \sum_a \frac{Z\,\alpha\,g}{8\,m\,M}\,\sigma_N^{ij}\,\sigma_a^{ik}\left[\frac{\delta^{jk}}{r_a^3} - 3\,\frac{r_a^j\,r_a^k}{r_a^5}\right]_\varepsilon, \tag{30}$$

$$H_{\mathrm{hfsC}} \overset{d=3}{=} \sum_a \frac{Z\,\alpha\,g}{2\,m\,M}\,\vec{I}\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{p}_a\,. \tag{31}$$

The corresponding second-order contributions

$$E_{\mathrm{sec}} = E_{\mathrm{secA}} + E_{\mathrm{secB}} + E_{\mathrm{secC}} \tag{32}$$

are angular averaged [see Eqs. (A2) and (A3) in Appendix A] and expressed in atomic units.

We proceed first with the calculation of E_{secA},

$$\begin{aligned}E_{\mathrm{secA}} &= \left\langle H_{\mathrm{hfsA}}\,\frac{1}{(E-H)'}\,H_{\mathrm{hfsA}}\right\rangle\\ &= \frac{E_{F2}}{d^3\,(d-1)}\sum_{a,b}\\ &\times\left\langle\sigma_a^{ij}\,4\,\pi\,\delta^d(r_a)\,\frac{1}{(E-H)'}\,\sigma_b^{ij}\,4\,\pi\,\delta^d(r_b)\right\rangle,\end{aligned} \tag{33}$$

where atomic units are used for the matrix elements, and E_{F2} is assumed to be the d-dimensional generalization of Eq. (22) with $I(I+1) \to \langle\vec{I}^{\,2}\rangle_\varepsilon$. The expression in Eq. (33) is singular and needs to be transformed to the regular form by pulling out the $1/\varepsilon$ singularity from the second-order matrix elements. This is achieved by the use of the identity

$$H_a|\phi\rangle \equiv \{H - E\,,\,Q_a\}|\phi\rangle + V_a|\phi\rangle\,, \tag{34}$$

where ϕ is the reference state,

$$H_a = 4\,\pi\,\delta^d(r_a)\,, \tag{35}$$

$$Q_a = 2\left[\frac{1}{r_a}\right]_\varepsilon, \tag{36}$$

$$V_a = -2\left[\frac{\vec{r}_a}{r_a^3}\right]_\varepsilon\cdot\vec{\nabla}_a\,, \tag{37}$$

to obtain

$$\begin{aligned}\left\langle H_a\,\frac{1}{(E-H)'}\,H_b\right\rangle = &\left\langle V_a^+\,\frac{1}{(E-H)'}\,V_b\right\rangle + \langle H_a\rangle\,\langle Q_b\rangle\\ &+ \langle H_b\rangle\,\langle Q_a\rangle - \langle H_a\,Q_b\rangle - \langle H_b\,Q_a\rangle\\ &+ \langle Q_a\,(H-E)\,Q_b\rangle\,,\end{aligned} \tag{38}$$

where V_a^+ is a Hermitian conjugation of V_a. The resulting form of E_{secA} is

$$E_{\rm secA} = E_{F2}\,\frac{1}{d^3\,(d-1)}\,\sum_{a,b}\sigma_a^{ij}\,\sigma_b^{ij}\left[\left\langle V_a^{+}\,\frac{1}{(E-H)'}\,V_b\right\rangle + \langle 4\,\pi\,\delta^3(r_a)\rangle\left\langle\frac{2}{r_b}\right\rangle + \langle 4\,\pi\,\delta^3(r_b)\rangle\left\langle\frac{2}{r_a}\right\rangle \right.$$
$$\left. - \left\langle 4\,\pi\,\delta^d(r_a)\,2\left[\frac{1}{r_b}\right]_\varepsilon\right\rangle - \left\langle 4\,\pi\,\delta^d(r_b)\,2\left[\frac{1}{r_a}\right]_\varepsilon\right\rangle + 2\,\delta_{ab}\left\langle\left[\frac{\vec r_a}{r_a^3}\right]_\varepsilon\cdot\left[\frac{\vec r_b}{r_b^3}\right]_\varepsilon\right\rangle\right]. \tag{39}$$

For the second-order tensor contribution $E_{\rm secB}$ we use Eq. (A3) to contract indices, and

$$E_{\rm secB} = \left\langle H_{\rm hfsB}\,\frac{1}{E-H}\,H_{\rm hfsB}\right\rangle = E_{F2}\,\frac{(d-2)}{2\,d^2\,(d-1)^2}\,\sum_{a,b}\left\langle\sigma_a^{kl}\left[\frac{\delta^{ij}}{r_a^3} - 3\,\frac{r_a^i\,r_a^j}{r_a^5}\right]_\varepsilon\frac{1}{E-H}\,\sigma_b^{kl}\left[\frac{\delta^{ij}}{r_b^3} - 3\,\frac{r_b^i\,r_b^j}{r_b^5}\right]_\varepsilon\right\rangle, \tag{40}$$

we use the following identity to pull out $1/\varepsilon$ singularity from the matrix elements:

$$H_a^{ij}|\phi\rangle \;\equiv \{H-E, Q_a^{ij}\}|\phi\rangle + V_a^{ij}|\phi\rangle\,, \tag{41}$$

where

$$H_a^{ij} = \left[\frac{\delta^{ij}}{r_a^3} - 3\frac{r_a^i r_a^j}{r_a^5}\right]_\varepsilon = \Big(-\nabla^i\,\nabla^j + \frac{\delta^{ij}}{d}\,\vec\nabla^{\,2}\Big)\,\mathcal{V}(r_a)\,, \tag{42}$$

$$Q_a^{ij} = 2\left[\frac{\delta^{ij}}{6\,r_a} - \frac{r_a^i\,r_a^j}{2\,r_a^3}\right]_\varepsilon = 2\,\Big(-\nabla^i\,\nabla^j + \frac{\delta^{ij}}{d}\,\vec\nabla^{\,2}\Big)\,\mathcal{V}^{(2)}(r_a)\,, \tag{43}$$

$$V_a^{ij}|\phi\rangle = \left[-\,\frac{\delta^{ij} r_a^k + 3\,\delta^{ik} r_a^j + 3\,\delta^{jk} r_a^i}{3\,r_a^3} + 3\frac{r_a^i r_a^j r_a^k}{r_a^5}\right]\nabla_a^k|\phi\rangle\,, \tag{44}$$

with $\mathcal{V}$ and $\mathcal{V}^{(2)}$ defined in Appendix A. We obtain

$$\left\langle H_a^{ij}\,\frac{1}{E-H}\,H_b^{ij}\right\rangle = \left\langle V_a^{+ij}\,\frac{1}{E-H}\,V_b^{ij}\right\rangle - \langle H_a^{ij}\,Q_b^{ij}\rangle - \langle H_b^{ij}\,Q_a^{ij}\rangle + \langle Q_a^{ij}\,(H-E)\,Q_b^{ij}\rangle\,. \tag{45}$$

The result for $E_{\rm secB}$ is then

$$E_{\rm secB} = E_{F2}\,\frac{(d-2)}{2\,d^2\,(d-1)^2}\,\sum_{a,b}\sigma_a^{st}\,\sigma_b^{st}\left[\left\langle V_a^{+ij}\,\frac{1}{E-H}\,V_b^{ij}\right\rangle - 2\left\langle\left[\frac{\delta^{ij}}{r_a^3} - 3\frac{r_a^i r_a^j}{r_a^5}\right]_\varepsilon\left[\frac{\delta^{ij}}{6\,r_b} - \frac{r_b^i\,r_b^j}{2\,r_b^3}\right]_\varepsilon\right\rangle\right.$$
$$\left. - 2\left\langle\left[\frac{\delta^{ij}}{r_b^3} - 3\frac{r_b^i r_b^j}{r_b^5}\right]_\varepsilon\left[\frac{\delta^{ij}}{6\,r_a} - \frac{r_a^i\,r_a^j}{2\,r_a^3}\right]_\varepsilon\right\rangle + 2\,\delta_{ab}\left\langle\nabla_a^k\left[\frac{\delta^{ij}}{6\,r_a} - \frac{r_a^i\,r_a^j}{2\,r_a^3}\right]_\varepsilon\nabla_b^k\left[\frac{\delta^{ij}}{6\,r_b} - \frac{r_b^i\,r_b^j}{2\,r_b^3}\right]_\varepsilon\right\rangle\right]. \tag{46}$$

Spin-orbit contribution $E_{\rm secC}$ does not require any regularization,

$$E_{\rm secC} = \left\langle H_{\rm hfsC}\,\frac{1}{E-H}\,H_{\rm hfsC}\right\rangle$$
$$= E_{F2}\,\frac{1}{3}\,\sum_{a,b}\left\langle\frac{\vec r_a}{r_a^3}\times\vec p_a\,\frac{1}{E-H}\,\frac{\vec r_b}{r_b^3}\times\vec p_b\right\rangle, \tag{47}$$

and can be calculated directly in $d=3$ dimensions.

V. $E_{\rm diam}$

The diamagnetic contribution in natural units is

$$E_{\rm diam} = \sum_a\frac{e^2}{2\,m}\,\langle\vec{\mathcal{A}}(\vec r_a)^2\rangle\,, \tag{48}$$

where

$$e\,\vec{\mathcal{A}}(\vec r_a) = \frac{Z\,\alpha\,g}{4\,M}\,\sigma_N^{ij}\left[\frac{r_a^j}{r_a^3}\right]_\varepsilon. \tag{49}$$

After transforming to atomic units and performing the angular average, it becomes

$$E_{\rm diam} = E_{F2}\,\frac{1}{d}\,\sum_a\left\langle\frac{1}{r_a^4}\right\rangle_\varepsilon. \tag{50}$$

VI. $E_{\rm high}$

The high-energy contribution is obtained from the scattering amplitude, and is essentially the same as for the hydrogenic case. In momentum space and natural units, we have

$$V(\vec{q}) = -\frac{4\,\pi\,Z\,\alpha}{\vec{q}^{\,2}}\,\tilde{\rho}(q^2)\,, \tag{51}$$

$$V_{\rm hfs}(\vec{q}) = i\,4\,\pi\,Z\,\alpha\,\frac{g}{4\,M}\,\alpha^i\,\sigma_N^{ij}\,\frac{q^j}{q^2}\,\tilde{\rho}(q^2)\,. \tag{52}$$

Then,

$$\begin{aligned}E_{\rm high} = {}& \phi^2(0)\int\frac{d^dq_1}{(2\,\pi)^d}\int\frac{d^dq_2}{(2\,\pi)^d}\,V(\vec{q}_1-\vec{q}_2)\\ &\times\langle t|\gamma^0\,S_F(q_2-q_1)\,\gamma^0\,V_{\rm hfs}(-\vec{q}_1)\,S_F(q_2)\,\gamma^0\,V_{\rm hfs}(\vec{q}_2)\\ &+\gamma^0\,V_{\rm hfs}(-\vec{q}_1)\,S_F(q_1)\,\gamma^0\,S_F(q_2)\,\gamma^0\,V_{\rm hfs}(\vec{q}_2)\\ &+\gamma^0\,V_{\rm hfs}(-\vec{q}_1)\,S_F(q_1)\,\gamma^0\,V_{\rm hfs}(\vec{q}_2)\,S_F(q_1-q_2)\,\gamma^0|t\rangle\,,\end{aligned} \tag{53}$$

where S_F is the fermion propagator and $t=(m,\vec{0})$. Performing traces with Dirac matrices, one obtains

$$\begin{aligned}E_{\rm high} = {}& -\phi^2(0)\,(4\,\pi\,Z\,\alpha)^3\left(\frac{g}{2\,M}\right)^2\frac{4}{d\,(d-1)}\,\langle\vec{I}^{\,2}\rangle_\varepsilon\\ &\times\int\frac{d^dq_1}{(2\,\pi)^d}\int\frac{d^dq_2}{(2\,\pi)^d}\,\frac{\tilde{\rho}(q_1^2)\,\tilde{\rho}(q_2^2)\,\tilde{\rho}(q_3^2)}{q_1^2\,q_2^2\,q_3^2}\\ &\times\left(1+(d-2)\,\frac{(\vec{q}_1\cdot\vec{q}_2)\,(\vec{q}_2\cdot\vec{q}_3)\,(\vec{q}_3\cdot\vec{q}_1)}{q_1^2\,q_2^2\,q_3^2}\right),\end{aligned} \tag{54}$$

where $\vec{q}_3=\vec{q}_1-\vec{q}_2$. After transforming integral to the coordinate representation, it becomes

$$\begin{aligned}E_{\rm high} = {}& -\phi^2(0)\,(Z\,\alpha)^3\left(\frac{g}{4\,M}\right)^2\frac{16\,\langle\vec{I}^{\,2}\rangle_\varepsilon}{d\,(d-1)}\int d^dr\big[\mathcal{V}_\rho(r)^3-(d-2)\,\nabla^i\nabla^j\mathcal{V}^{(2)}_\rho(r)\,\nabla^j\nabla^k\mathcal{V}^{(2)}_\rho(r)\,\nabla^k\nabla^i\mathcal{V}^{(2)}_\rho(r)\big]\\ = {}& E_{\rm highA}+E_{\rm highB}\,,\end{aligned} \tag{55}$$

where $\mathcal{V}_\rho(r)$ and $\mathcal{V}^{(2)}_\rho(r)$ are defined in Appendix A. $E_{\rm highA}$ includes the $\vec{r}$ integral over a small region of the nuclear charge distribution, where we can set $d=3$. It is evaluated as

$$E_{\rm highA} = -\phi^2(0)\,(Z\,\alpha)^3\left(\frac{g}{4\,M}\right)^2\frac{8}{3}\,\langle\vec{I}^{\,2}\rangle\int^R d^3r\big[V_\rho(r)^3-\nabla^i\nabla^jV^{(2)}_\rho(r)\,\nabla^j\nabla^kV^{(2)}_\rho(r)\,\nabla^k\nabla^iV^{(2)}_\rho(r)\big]\,. \tag{56}$$

It is convenient at this point to use the explicit form of the nuclear charge distribution, which we chose to be dipole parametrization, the same as used in the hydrogenic case in Sec. II,

$$\tilde{\rho}(p^2) = \frac{\lambda^4}{(\lambda^2+p^2)^2}\,. \tag{57}$$

Thus, $d=3$ potentials become

$$4\,\pi\,\rho(r) = 4\pi\int\frac{d^3p}{(2\pi)^3}\tilde{\rho}(p^2)\,e^{i\vec{p}\cdot\vec{r}} = \frac{\lambda^3}{2}\,e^{-\lambda\,r}\,, \tag{58}$$

$$V_\rho(r) = 4\pi\int\frac{d^3p}{(2\pi)^3}\frac{\tilde{\rho}(p^2)}{p^2}e^{i\vec{p}\cdot\vec{r}} = \frac{1}{r}-\frac{e^{-\lambda\,r}}{r}-\frac{\lambda}{2}\,e^{-\lambda\,r}\,, \tag{59}$$

$$V^{(2)}_\rho(r) = 4\pi\int\frac{d^3p}{(2\pi)^3}\frac{\tilde{\rho}(p^2)\,e^{i\vec{p}\cdot\vec{r}}-1}{p^4} = -\frac{r}{2}-\frac{2}{\lambda^2\,r}+\frac{1}{2\,\lambda}\,e^{-\lambda\,r}+\frac{2}{\lambda^2}\,\frac{e^{-\lambda\,r}}{r}\,. \tag{60}$$

Now the r-integration in Eq. (56) can be performed analytically, with the result

$$E_{\rm highA} = -\phi^2(0)\,(4\,\pi\,Z\,\alpha)^3\left(\frac{g}{4\,M}\right)^2\frac{8}{3}\,\langle\vec{I}^{\,2}\rangle\,5\,\pi\left(-\frac{467}{540}+\frac{2\,\ln 2}{5}+\frac{3\,\ln 3}{10}-\ln\frac{r_C}{R}+\gamma\right), \tag{61}$$

where $r_C=2\sqrt{3}/\lambda$. It should be mentioned that the description of the nucleus through the elastic form-factors ρ_C and ρ_M here is not fully justified. It is because for high momenta $\sim\hbar/r_C$ the electron sees individual nucleons, rather than the nucleus as a whole. The detailed analysis of this contribution is complicated and should be performed together with other three-photon exchange corrections [21]. We will use the above form-factor result for comparison with direct numerical calculations for hydrogenic systems described in Sec. II, keeping in mind that for the 2^3S-2^1S transition in ^{3}He it is negligible.

The part $E_{\rm highB}$ of the high energy contribution involves integral outside of the nuclear region, thus we can assume the point nucleus and obtain

$$E_{\rm highB} = -\phi^2(0)\,(Z\,\alpha)^3\left(\frac{g}{4\,M}\right)^2\frac{16}{d\,(d-1)}\,\langle\vec{I}^{\,2}\rangle_\varepsilon\int_R d^dr\big[\mathcal{V}(r)^3-(d-2)\,\nabla^i\nabla^j\mathcal{V}^{(2)}(r)\,\nabla^j\nabla^k\mathcal{V}^{(2)}(r)\,\nabla^k\nabla^i\mathcal{V}^{(2)}(r)\big]$$

$$= \phi^2(0)\,(Z\,\alpha)^3 \left(\frac{g}{4\,M}\right)^2 \langle \vec{I}^{\,2}\rangle_\varepsilon\,[(4\,\pi)^\varepsilon\,\Gamma(1+\varepsilon)]^2\,\frac{40}{3}\,\pi\left(\frac{23}{30}+\frac{1}{4\,\varepsilon}+\ln R+\gamma\right), \tag{62}$$

and by convention the factor $[(4\,\pi)^\varepsilon\Gamma(1+\varepsilon)]^2$ is consistently pulled out from all the terms.

The sum of both parts is independent on arbitrary cutoff R, and is

$$E_{\rm high} = (Z\,\alpha)^3 \left(\frac{g}{2\,M}\right)^2 \langle \vec{I}^{\,2}\rangle_\varepsilon\,\frac{10}{3}\,\pi\biggl(\frac{881}{540}-\frac{2\,\ln 2}{5}-\frac{3\,\ln 3}{10}+\frac{1}{4\,\varepsilon}+\ln r_C\biggr)\,\langle\delta^d(r)\rangle\,. \tag{63}$$

Transforming to atomic units by $\vec{r}\to(m\,\alpha)^{-1/(1+2\,\varepsilon)}\,\vec{r}$, one pulls out the factor $m^{(1-2\,\varepsilon)/(1+2\varepsilon)}\,\alpha^{2/(1+2\,\varepsilon)}$ from H and obtains the nonrelativistic Hamiltonian in atomic units. Similarly, for $H^{(6)}$ the common factor in atomic units

$$\eta = m^{(1-10\,\varepsilon)/(1+2\varepsilon)}\,\alpha^{6/(1+2\,\varepsilon)} \tag{64}$$

is pulled out from all the terms, which corresponds to the replacement $m\to 1, \alpha\to 1$, and

$$E_{\rm high} = E_{F2}\,\frac{10}{3}\,\pi\biggl(\frac{881}{540}-\frac{2\,\ln 2}{5}-\frac{3\,\ln 3}{10}+\frac{1}{4\,\varepsilon}+\ln m\,\alpha\,r_C\biggr)\sum_a Z\,\langle\delta^d(r_a)\rangle\,. \tag{65}$$

VII. COMPLETE RESULT

In order to eliminate $1/\varepsilon$ singularity, we transform all singular operators (in atomic units) to the same form,

$$\biggl\langle\biggl[\frac{\delta^{ij}}{r^3}-3\frac{r^i r^j}{r^5}\biggr]_\varepsilon\biggl[\frac{\delta^{ij}}{6\,r}-\frac{r^i\,r^j}{2\,r^3}\biggr]_\varepsilon\biggr\rangle = (1-\varepsilon)\left\langle\frac{1}{r^4}\right\rangle_\varepsilon, \tag{66}$$

$$\biggl\langle\nabla^k\biggl[\frac{\delta^{ij}}{6\,r}-\frac{r^i\,r^j}{2\,r^3}\biggr]_\varepsilon\nabla^k\biggl[\frac{\delta^{ij}}{6\,r}-\frac{r^i\,r^j}{2\,r^3}\biggr]_\varepsilon\biggr\rangle = \frac{(d-1)(d^2-2d+4)}{4d}\left\langle\frac{1}{r^4}\right\rangle_\varepsilon = \left(\frac{7}{6}-\frac{31}{18}\,\varepsilon\right)\left\langle\frac{1}{r^4}\right\rangle_\varepsilon + O(\varepsilon)\,, \tag{67}$$

and use [22]

$$\left\langle\frac{1}{r^4}\right\rangle_\varepsilon = \left\langle\frac{1}{r^4}\right\rangle + Z\,\langle\pi\delta^d(r)\rangle\left(-\frac{2}{\varepsilon}+8\right)+O(\varepsilon)\,, \tag{68}$$

where $\langle 1/r^4\rangle$ is defined as integral from a small radius a to infinity with the $1/a$ and $\ln a+\gamma$ terms subtracted out. The $1/\varepsilon$ singularity cancels out, and we obtain the final result for the hydrogenic atom as

$$\begin{aligned} E_{\rm hfs2} &= E_{\rm secA}+E_{\rm secB}+E_{\rm diam}+E_{\rm high} \\ &= E_{F2}\biggl[\frac{1}{9}\left\langle V^+\,\frac{1}{(E-H)'}\,V\right\rangle + \frac{1}{12}\left\langle V^{+ij}\,\frac{1}{E-H}\,V^{ij}\right\rangle + \frac{16}{9}\,\langle\pi\,\delta^3(r)\rangle\left\langle\frac{1}{r}\right\rangle + \frac{5}{12}\left\langle\frac{1}{r^4}\right\rangle \\ &\quad + \frac{Z^4}{n^3}\,\frac{10}{3}\biggl(\frac{1223}{540}-\frac{2\,\ln 2}{5}-\frac{3\,\ln 3}{10}+\ln m\,\alpha\,r_C\biggr)\biggr]\,. \end{aligned} \tag{69}$$

Using the following expectation values with hydrogenic nS-state wave functions,

$$\left\langle\frac{1}{r^4}\right\rangle = \frac{8\,Z^4}{n^3}\left[-\frac{5}{3}+\frac{1}{2\,n}+\frac{1}{6\,n^2}+\gamma+\Psi(n)-\ln\frac{n}{2}+\ln Z\right], \tag{70}$$

$$\left\langle V^+\,\frac{1}{(E-H)'}\,V\right\rangle = Z^4\left(-\frac{56}{3\,n^5}-\frac{24}{n^4}+\frac{8}{3\,n^3}\right), \tag{71}$$

$$\left\langle V^{+ij}\,\frac{1}{(E-H)}\,V^{ij}\right\rangle = Z^4\left(\frac{2}{9\,n^5}-\frac{2}{3\,n^3}\right), \tag{72}$$

we obtain for the hydrogenic nS state

$$E_{\rm hfs2}(n) = m\,(Z\,\alpha)^6\left(\frac{g\,m}{2\,M}\right)^2 I(I+1)\,\frac{10}{3\,n^2}\left[\frac{181}{270}-\frac{3}{10\,n}+\frac{1}{12\,n^2}+\frac{3}{10}\,\ln\frac{4}{3}-\ln(n)+\gamma+\Psi(n)+\ln m\,Z\,\alpha\,r_C\right]. \tag{73}$$

Specifically, for $1S$ state it reduces to

$$E_{\rm hfs2}(1) = m\,(Z\,\alpha)^6 \left(\frac{g\,m}{2\,M}\right)^2 I(I+1)\,\frac{10}{3}\,(0.540\,008 + \ln m\,Z\,\alpha\,r_C)\,, \tag{74}$$

which is in perfect agreement with the results of our numerical calculations described in Sec. II. Namely, the analytical constant term 0.540 008 in Eq. (73) agrees with the result obtained by fitting the all-order numerical data, $2.700(2)/5 = 0.540\,0\,(4)$.

The final result for the helium atom takes the form (in atomic units)

$$\begin{aligned} E_{\rm hfs2} = E_{F2}\biggl\{ & \sum_a \biggl[\frac{5}{12}\left\langle\frac{1}{r_a^4}\right\rangle + \frac{10}{3}\biggl(\frac{1223}{540} - \frac{2\,\ln 2}{5} - \frac{3\,\ln 3}{10} + \ln m\,\alpha\,r_C\biggr) Z\,\pi\,\langle\delta^3(r_a)\rangle\biggr] \\ & + \sum_{a,b}\biggl[\frac{1}{27}\left\langle\vec\sigma_a\,V_a^+\,\frac{1}{(E-H)'}\,\vec\sigma_b\,V_b\right\rangle + \frac{1}{36}\left\langle\vec\sigma_a\,V_a^{+ij}\,\frac{1}{E-H}\,\vec\sigma_b\,V_b^{ij}\right\rangle + \frac{1}{3}\left\langle\frac{\vec r_a}{r_a^3}\times\vec p_a\,\frac{1}{E-H}\,\frac{\vec r_b}{r_b^3}\times\vec p_a\right\rangle\biggr] \\ & + \frac{16}{27}\sum_{a,b}\vec\sigma_a\cdot\vec\sigma_b\,\langle\pi\,\delta^3(r_a)\rangle\left\langle\frac{1}{r_b}\right\rangle - \frac{16}{27}\sum_{a\neq b}\vec\sigma_a\cdot\vec\sigma_b\left\langle\frac{\pi\,\delta^3(r_a)}{r_b}\right\rangle + \frac{1}{18}\sum_{a\neq b}\vec\sigma_a\cdot\vec\sigma_b\left\langle\frac{1}{r_a^3\,r_b} - 3\,\frac{(\vec r_a\cdot\vec r_b)^2}{r_a^5\,r_b^3}\right\rangle\biggr\}\,, \end{aligned} \tag{75}$$

where E_{F2} is defined in Eq. (22), the operator V_a is defined in Eq. (37), and V_a^{ij} is defined in Eq. (44).

VIII. NUMERICAL RESULTS

We first consider the hydrogenlike atoms. Using Eq. (73), we obtain the second-order HFS correction to the $1S-2S$ transition to be 0.86 kHz for H, 0.05 kHz for D, and 6.84 kHz for He$^+$. Consequently, the contribution for the H − D isotope shift of the $1S-2S$ transition energy is 0.81 kHz, which is twice the previously assumed uncertainty [21]. We, however, do not update the charge radius difference determined from the H − D isotope shift, as the corresponding inelastic three-photon exchange contribution must also be considered, which could be as large as the elastic one calculated here. Notably, the inelastic two-photon exchange contribution has already been accounted for the H − D isotope shift in Refs. [21, 23, 24].

Now let us consider the helium atom. For the singlet states the total electron spin vanishes and, therefore, $\vec\sigma_1\cdot\vec\sigma_2 = -3$, $(\vec\sigma_1-\vec\sigma_2)^2 = 12$. Using notations from Tables I and II, we write the complete result for the second-order HFS correction for singlet S states as

$$\begin{aligned} E_{\rm hfs2} = E_{F2}\biggl\{ & \frac{1}{9}\,S(^3S) + \frac{1}{12}\,S(^3D) + \frac{1}{3}\,S(^1P^e) \\ & + \frac{5}{3}\biggl(\frac{1223}{540} - \frac{2\,\ln 2}{5} - \frac{3\,\ln 3}{10} + \ln m\,\alpha\,r_C\biggr) Z\,Q_1 \\ & + \frac{8}{9}\,Q_3 + \frac{5}{6}\,Q_{57} - \frac{1}{3}\,Q_{65}\biggr\}\,. \end{aligned} \tag{76}$$

Our numerical calculations are carried out with the fully correlated exponential basis set by the method described in Ref. [25]. Numerical results for the first- and second-order matrix elements are summarized in Tables I and II. The contribution to the ionization energy is obtained by evaluating Eq. (76) and subtracting the corresponding result for He$^+(1S)$. Our final result for the 2^1S state of helium is expressed in the form

$$E_{\rm hfs2}[{\rm He}] - E_{\rm hfs2}[{\rm He}^+] = \frac{E_{F2}}{9}\,S_0\,\Bigl[1 + \delta(2^1S)\Bigr]\,, \tag{77}$$

where S_0 describes the leading $n = 2$ hyperfine mixing and is defined in Table II. The correction δ corresponds to the hyperfine mixing with $n \neq 2$ states,

$$\delta(2^1S) = -\,0.034\,25\,, \tag{78}$$

with the corresponding energy shift $\delta E_{\rm mix} = -2.075$ kHz.

For the triplet states the total electron spin is equal to 1, thus $\vec\sigma_1\cdot\vec\sigma_2 = 1$, $(\vec\sigma_1-\vec\sigma_2)^2 = 4$, $(\vec\sigma_1+\vec\sigma_2)^2 = 8$. Using notations from Tables I and II, the complete result for the second-order HFS correction for triplet S states can be expressed as

$$\begin{aligned} E_{\rm hfs2} = E_{F2}\biggl\{ & \frac{2}{27}\,S(^3S) + \frac{1}{27}\,S(^1S) + \frac{1}{18}\,S(^3D) + \frac{1}{36}\,S(^1D) \\ & + \frac{5}{3}\biggl(\frac{1223}{540} - \frac{2\,\ln 2}{5} - \frac{3\,\ln 3}{10} + \ln m\,\alpha\,r_C\biggr) Z\,Q_1 \\ & + \frac{1}{3}\,S(^3P^e) + \frac{5}{6}\,Q_{57} + \frac{32}{27}\,Q_1\,Q_{53} - \frac{8}{27}\,Q_3 + \frac{1}{9}\,Q_{65}\biggr\}\,. \end{aligned} \tag{79}$$

With numerical results for the first- and second-order matrix elements from Tables I and II, we obtain the contribution to the ionization energy of the 2^3S state as

$$E_{\rm hfs2}[{\rm He}] - E_{\rm hfs2}[{\rm He}^+] = -\,\frac{E_{F2}}{27}\,S_0\,\Bigl[1 + \delta(2^3S)\Bigr]\,, \tag{80}$$

where

$$\delta(2^3S) = 0.015\,08\,, \tag{81}$$

with the corresponding energy shift $\delta E_{\rm mix} = -0.305$ kHz for the 2^3S state.

TABLE I. Expectation values of various operators for the 2^1S and 2^3S states, in atomic units.

		2^1S	2^3S
Q_1	$4\pi\delta^3(r_1)$	16.455 169	16.592 071
Q_3	$4\pi\delta^3(r_1)/r_2$	5.593 744	4.648 724
Q_{53}	$1/r_1$	1.135 408	1.154 664
Q_{57}	$1/r_1^4$	25.531 680	25.511 838
Q_{65}	$[r_1^2 r_2^2 - 3(\vec{r}_1\cdot\vec{r}_2)^2]/(r_1^5 r_2^3)$	0.015 024	0.001 629

TABLE II. Second-order matrix elements for 2^1S and 2^3S states of He, in atomic units.

State	Term	Expression	Symmetry	Value
	S_0	$\langle 2^1S\vert 4\pi[\delta^3(r_1)-\delta^3(r_2)]\vert 2^3S\rangle^2\,[E_0(2^1S)-E_0(2^3S)]^{-1}$		29 015.120
2^1S	$S(^3S)$	$\left\langle\left(V_1^+ - V_2^+\right)\frac{1}{(E_0-H_0)'}\left(V_1 - V_2\right)\right\rangle$	^3S	27 703.473 2
	$S(^3D)$	$\left\langle\left(V_1^{ij+} - V_2^{ij+}\right)\frac{1}{(E_0-H_0)'}\left(V_1^{ij} - V_2^{ij}\right)\right\rangle$	$^3D^e$	−7.356 2
	$S(^1P^e)$	$\left\langle\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1+\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)\frac{1}{(E_0-H_0)'}\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1+\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)\right\rangle$	$^1P^e$	−0.012 469
2^3S	$S(^3S)$	$\left\langle\left(V_1^+ + V_2^+\right)\frac{1}{(E_0-H_0)'}\left(V_1 + V_2\right)\right\rangle$	^3S	−658.648 8
	$S(^1S)$	$\left\langle\left(V_1^+ - V_2^+\right)\frac{1}{(E_0-H_0)'}\left(V_1 - V_2\right)\right\rangle$	^1S	−29 425.198 9
	$S(^3D)$	$\left\langle\left(V_1^{ij+} + V_2^{ij+}\right)\frac{1}{(E_0-H_0)'}\left(V_1^{ij} + V_2^{ij}\right)\right\rangle$	$^3D^e$	−7.463 4
	$S(^1D)$	$\left\langle\left(V_1^{ij+} - V_2^{ij+}\right)\frac{1}{(E_0-H_0)'}\left(V_1^{ij} - V_2^{ij}\right)\right\rangle$	$^1D^e$	−7.458 3
	$S(^3P^e)$	$\left\langle\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1+\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)\frac{1}{(E_0-H_0)'}\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1+\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)\right\rangle$	$^3P^e$	−0.004 694

IX. 2^3S-2^1S ISOTOPE SHIFT

In our previous calculation of the isotope shift of the $2^3S - 2^1S$ transition energy of helium [22], the second-order HFS contribution was accounted for approximately by taking the leading $n=2$ mixing contributions S_0 and neglecting $\delta(2^1S)$ and $\delta(2^3S)$ in Eqs. (77) and (80). It was recently pointed out by Qi and coworkers [17] that these contributions are in fact significant and shift the theoretical predictions for the isotope shift beyond the previously estimated error bars. We now extend our previous theory by accounting for the complete second-order HFS correction calculated in the previous sections.

The individual theoretical contributions to the $^3\mathrm{He} - {}^4\mathrm{He}$ isotope shift of the 2^1S–2^3S centroid energies are summarized in Table III, in comparison with results of Qi and coworkers [17]. All numerical values apart from $\delta\mathcal{E}_{\rm mix}$ are taken from our previous investigation [22]. Note that the entries α^6, α^7, and $\alpha^5\mathcal{E}_{\rm pol}$ were not independently reproduced by Qi and coworkers but taken from our work [22]. The deviation from Qi and coworkers for $\delta\mathcal{E}_{\rm mix}$ is due to the fact that they did not calculate the complete second-order HFS correction but used an approximate representation for it. Otherwise, we observe very good agreement with their calculation.

The primary source of uncertainty arises from the α^7 term, which is estimated basing on the mass scaling of the hydrogenic A_{72} coefficient. A calculation of the full α^7 correction for the helium atom is quite challenging and has not been attempted so far. Another open challenge is the inelastic second-order HFS contribution. However, given that the leading (electric dipole) polarizability correction is only 0.2 kHz, it can be argued to be negligible at the current level of precision.

The theory for the point nucleus summarized in Table III needs to be complemented by the description of the energy shift arising due to the nuclear mean square charge radius r_C. Generalizing the expression for the finite nuclear size (fs) effect for the hydrogenic energy levels [21] to the helium case, we obtain

$$
\begin{aligned}
E_{\rm fs}[^A\mathrm{He}] = {} & \frac{2}{3}\,Z\,\alpha^4\,m\,\frac{r_C^2}{\bar{\lambda}^2}\,\sum_a \langle\,\pi\,\delta^3(r_a)\rangle_M \\
& \times\Big\{1-(Z\,\alpha)^2\Big[\ln\Big(Z\,\alpha\,\frac{r_C}{\bar{\lambda}}\Big)+\beta\Big] \\
& + \alpha\,(Z\,\alpha)\,(4\,\ln 2-5)\Big\} \equiv C_A\,r_C^2\,, \qquad (82)
\end{aligned}
$$

where $\bar{\lambda} = 386.159$ fm is the reduced Compton wavelength, the expectation value of the δ function is calculated for the case of the finite-mass nucleus, and the nonlogarithmic relativistic correction $\beta = -0.41$ is obtained from Ref. [21], assuming the $1S$ state and the dipole charge distribution model. The last term in the brackets of Eq. (82) is the radiative fs correction [28].

It should be pointed out that, because of the nuclear mass dependence, the fs effect to the isotope shift is not exactly proportional to the difference of the squared radii (as was assumed in Ref. [17]) but has a small contribution

TABLE III. Breakdown of theoretical contributions to the ^{3}He$-^4$He isotope shift of the 2^1S–2^3S centroid transition frequencies, for the point nucleus, in kHz. $\mathcal{E}_{\rm mix}$ is the mixing contribution induced by S_0. $\delta\mathcal{E}_{\rm mix}$ comes from $\delta(2^1S)$ and $\delta(2^3S)$ terms in Eqs.(77) and (80). $\mathcal{E}_{\rm pol}$ is the leading nuclear polarizability contribution at the order α^5 (two-photon exchange), see Refs. [26, 27]. Physical constants are from Ref. [28].

Contribution	$(m/M)^1$	$(m/M)^2$	$(m/M)^3$	Sum	Qi *et al.*
α^2	$-8\,026\,758.512$	$-4\,958.331$	5.070	$-8\,031\,711.773$	$-8\,031\,711.78$
α^4	$-2\,496.229$	2.076	—	$-2\,494.153$	$-2\,494.16$
α^5	56.605	0.000(47)	—	56.605(47)	56.59
α^6	2.732[a]	—	—	2.732	2.73[b]
$\alpha^6\,\mathcal{E}_{\rm mix}$	—	80.765	0.000(70)	80.765(70)	80.76
$\alpha^6\,\delta\mathcal{E}_{\rm mix}$	—	-1.770	—	-1.770	-1.37
α^7	$-0.210(105)$			$-0.210(105)$	$-0.21(11)$[b]
$\alpha^5\,\mathcal{E}_{\rm pol}$	0.198(20)	—	—	0.198(20)	0.20(2)[b]
Total				$-8\,034\,067.607(136)$	$-8\,034\,067.24(19)$

[a] Agrees with our former estimate of 2.75 (69) [13],
[b] Taken from Ref. [22].

beyond this. We therefore write the fs contribution to the ^{3}He $-$ ^{4}He isotope shift as

$$\begin{aligned} E_{\rm fs}[^3{\rm He}-{}^4{\rm He}] &= C_3\,r_3^2 - C_4\,r_4^2 \\ &= \frac{C_3+C_4}{2}\left[r_3^2-r_4^2\right] + \frac{C_3-C_4}{2}\left[r_3^2+r_4^2\right] \\ &\equiv C\left[r_3^2-r_4^2\right] + D\left[r_3^2+r_4^2\right], \end{aligned} \tag{83}$$

where $r_A \equiv r_C[^A{\rm He}]$ and the last line is the definition of the coefficients C and D. Their numerical values are given in Table IV .

We are now in the position to determine the mean square charge radius difference of the helium isotopes, $\delta r^2 = r^2[^3{\rm He}] - r^2[^4{\rm He}]$ by comparing the theory prediction with the measured transition frequencies. Table IV summarizes all experimental and theoretical input required for the determination. Our result for the mean square charge radius difference of $\delta r^2 = 1.067\,8\,(7)$ fm^2 agrees within $1.3\,\sigma$ with the muonic value of $1.063\,6\,(31)$ fm^2 [14].

X. SUMMARY

We have derived the complete elastic second-order hyperfine-interaction correction of order α^6 to the centroid energy levels of hydrogen-like and helium-like ions. The resulting formulas have been verified through comparisons with our all-order numerical calculations for hydrogen-like ions. Numerical calculations have been performed for the 2^1S and 2^3S states of atomic helium, extending the previous approximate treatment of this effect by Qi *et al.* [17].

The obtained results impact the determination of the nuclear charge radii difference between ^{3}He and ^{4}He, largely resolving the previously reported disagreement between the muonic and electronic helium determinations [14, 15]. From the measured isotope shift of the 2^1S-2^3S transition energy we obtain the mean square charge radius difference of ^{3}He and ^{4}He, which is only $1.3\,\sigma$ away from the muonic value. Given the difficulty of estimating the nuclear polarizability uncertainties in muonic atoms, we consider this to be good agreement.

Remarkably, the determination of δr^2 from the electronic helium spectroscopy is four times more accurate than that from the muonic helium. This is the consequence of the fact that the inelastic nuclear effects for muonic atoms are much more significant than in the electronic ones. The observed agreement between electronic and muonic measurements supports the reliability of nuclear charge radius determinations from muonic atoms, suggesting that they could be successfully extended to heavier nuclei, which is the objective of the QUARTET collaboration [29].

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Appendix A: Dimensional regularization

This appendix is based on Ref. [22]. In order to extend spin-$\frac{1}{2}$ into d dimensions, we define antisymmetric tensor

$$\sigma^{ij} = \frac{i}{2}[\gamma^i, \gamma^j]\,, \tag{A1}$$

which in the three-dimensional limit simplifies to

$$\sigma^{ij} \overset{d\to 3}{=} 2\,\epsilon^{ijk} s^k. \tag{A2}$$

TABLE IV. Determination of the nuclear charge difference δr^2 from the measurement of ${}^3\mathrm{He}-{}^4\mathrm{He}$ isotope shift in the 2^1S-2^3S transition, in kHz unless specified otherwise. Physical constants are from Ref. [28].

$E({}^3\mathrm{He}, 2^1S^{F=1/2} - 2^3S^{F=3/2})$	192 504 914 418.96(17)	Exp. [15]
$-E({}^4\mathrm{He}, 2^1S - 2^3S)$	−192 510 702 148.72(20)	Exp. [30]
$\delta E_{\mathrm{hfs}}(2^3S^{3/2})$	−2 246 567.059(5)	Exp. [31, 32]
$-\delta E_{\mathrm{iso}}(2^1S - 2^3S)$ (point nucleus)	8 034 067.607 (136)	Theory, Table III
Sum	−229.21(14)	
C	−214.758 kHz/fm^2	this work
D	0.017 kHz/fm^2	this work
$\delta r^2 = r^2({}^3\mathrm{He}) - r^2({}^4\mathrm{He})$	1.067 8(7) fm^2	this work
	1.069 3(15) fm^2	Ref. [17]
	1.075 7(15) fm^2	previous [22, 33]
	1.063 6(6)$_{\mathrm{exp}}$(30)$_{\mathrm{theo}}$ fm^2	$\mu^{3,4}\mathrm{He}^+$ Lamb shift [14]

Since we consider only corrections to energy and neglect the hyperfine splitting, we may perform the angular average

$$\sigma_a^{ij}\,\sigma_b^{kl} \to \sigma_a^{ij}\,\sigma_b^{ij}\,\frac{\delta^{ik}\,\delta^{jl} - \delta^{il}\,\delta^{jk}}{d\,(d-1)}\,, \tag{A3}$$

$$\sigma_a^{ij}\,\sigma_b^{il} \to \sigma_a^{ij}\,\sigma_b^{ij}\,\frac{\delta^{jl}}{d}\,. \tag{A4}$$

For $a=b$,

$$\sigma^{ij}\,\sigma^{ij} = d\,(d-1)\,. \tag{A5}$$

We will not always have spin 1/2 for the nucleus. In the dimensional regularization, we will pretend that $I=1/2$ and use σ_N^{ij}. However, instead of the above identity, we will consistently use the notation

$$\sigma_N^{ij}\sigma_N^{ij} \equiv 8\,\langle\vec{I}^{\,2}\rangle_\varepsilon\,, \tag{A6}$$

and drop the subscript ε once all $1/\varepsilon$ terms are canceled out.

Throughout our calculations, we extensively used the following result for the general d-dimensional integral,

$$\Omega_d = \frac{2\,\pi^{d/2}}{\Gamma(d/2)}\,, \tag{A7}$$

$$\int \frac{d^dp}{(2\pi)^d}\,\frac{4\pi}{p^n}\,e^{i\vec{p}\cdot\vec{r}} = 2^{2-n}\pi^{1-d/2}\,\frac{\Gamma\left(\frac{d-n}{2}\right)}{\Gamma\left(\frac{n}{2}\right)}\,r^{n-d}\,. \tag{A8}$$

Two special cases are of particular importance (with $d = 3-2\,\varepsilon$):

$$\mathcal{V}(r) = \int \frac{d^dp}{(2\pi)^d}\,\frac{4\pi}{p^2}\,e^{i\vec{p}\cdot\vec{r}} = \frac{C_1}{r^{1-2\varepsilon}}\,, \tag{A9}$$

$$\mathcal{V}^{(2)}(r) = \int \frac{d^dp}{(2\pi)^d}\,\frac{4\pi}{p^4}\,e^{i\vec{p}\cdot\vec{r}} = C_2\,r^{1+2\varepsilon}\,, \tag{A10}$$

where

$$C_1 = \pi^{\varepsilon-1/2}\Gamma(1/2-\varepsilon)\,, \tag{A11}$$

$$C_2 = \frac{1}{4}\pi^{\varepsilon-1/2}\Gamma(-1/2-\varepsilon)\,. \tag{A12}$$

We define also the associated potentials:

$$\mathcal{V}_\rho = 4\pi\int \frac{d^dp}{(2\pi)^d}\,\frac{\tilde\rho(p^2)}{p^2}\,e^{i\vec{p}\cdot\vec{r}}, \tag{A13}$$

$$\mathcal{V}^{(2)}_\rho = 4\pi\int \frac{d^dp}{(2\pi)^d}\,\frac{\tilde\rho(p^2)}{p^4}\,e^{i\vec{p}\cdot\vec{r}}, \tag{A14}$$

and in $d=3$

$$V_\rho = 4\pi\int \frac{d^3p}{(2\pi)^3}\,\frac{\tilde\rho(p^2)}{p^2}\,e^{i\vec{p}\cdot\vec{r}}, \tag{A15}$$

$$V^{(2)}_\rho = 4\pi\int \frac{d^3p}{(2\pi)^3}\,\frac{\tilde\rho(p^2)\,e^{i\vec{p}\cdot\vec{r}} - 1}{p^4}. \tag{A16}$$

Asymptotic forms of these potentials at $r\to\infty$ are:

$$\mathcal{V}_\rho \to \mathcal{V} + \text{local terms}, \tag{A17}$$

$$\mathcal{V}^{(2)}_\rho \to \mathcal{V}^{(2)} + \tilde\rho'(0)\mathcal{V} + \text{local terms}\,, \tag{A18}$$

and in $d=3$

$$V_\rho \to \frac{1}{r} + \text{local terms}, \tag{A19}$$

$$V^{(2)}_\rho \to -\frac{r}{2} + \frac{\tilde\rho'(0)}{r} + \text{local terms}. \tag{A20}$$

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