Reexamination of helium fine structure

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In order to explain discrepancies between theoretical predictions and experimental data for the helium fine structure, we check and recalculate all theoretical contributions up to orders $m\,\alpha^7$ and $m^2/M\,\alpha^6$. The previous result for the $m\,\alpha^7$ correction is improved by a much more accurate calculation of relativistic corrections to the Bethe logarithm. The theoretical values of the $2^3P_0 - 2^3P_1$ and $2^3P_1 - 2^3P_2$ fine structure intervals in helium are, correspondingly, $\nu_{01} = 29\ 616\ 946.2(1.6)$ kHz and $\nu_{12} = 2\ 291\ 177.3(1.6)$ kHz, with the uncertainties being due to higher-order effects. For the small interval ν_{12}, the theoretical value agrees with the experimental data, whereas for the large interval ν_{01}, a discrepancy of about 3 standard deviations is present.

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I. INTRODUCTION

The fine structure splitting of the 2^3P level in helium has long been an attractive subject of theoretical and experimental studies. One of the reasons for this interest is that the fine structure, being an intrinsically relativistic effect, is proportional to α^2Ry and thus provides an opportunity for the determination of the fine structure constant α from a comparison of theoretical predictions with experimental data. A series of measurements of the helium fine structure has been performed during the last decade [1–7], with the current accuracy being on the level of 25 ppb. For theory, to reach an adequate level of precision in a description of a three-body system is a challenging problem.

Despite considerable calculational efforts of last years to provide an accurate theoretical determination of the fine structure of helium, the current status of theory can hardly be considered as satisfactory. Recent calculations [8, 9] demonstrated a significant discrepancy with the experimental data, the difference for the large (small) fine structure interval being about 10 (6) times larger than the total nonlogarithmic contribution to order $m\,\alpha^7$. It seems unlikely that such difference can be explained only by higher-order effects.

The theory of the helium fine structure up to order $m\,\alpha^6$ has been confirmed by at least two independent calculations and thus can be considered as established. The logarithmic part of the $m\,\alpha^7$ contribution has also been calculated independently. The only corrections that are not yet checked by different evaluations are the recoil contribution to order $m^2/M\,\alpha^6$ and the nonlogarithmic correction to order $m\,\alpha^7$. These corrections will be the main subject of the present investigation.

The theoretical description of the fine structure to order $m\,\alpha^7$ is a difficult task. Within the logarithmic accuracy, this was first done by Zhang *et al.* [10] and later confirmed by one of the authors (K.P.) [11]. An important part of the nonlogarithmic correction to order $m\,\alpha^7$ was calculated by K.P. and Sapirstein [12]. The problem of derivation of the complete set of effective spin-dependent operators to order $m\,\alpha^7$ was addressed by Zhang in a series of works [13–15] within the equal-time variant of the Bethe-Salpeter formalism. The derivation based on the dimensionally regularized NRQED was reported recently by K.P. [9], who noted several mistakes and inconsistencies in the previous derivation by Zhang.

In the present investigation, we give a detailed account of the derivation of the total contribution to order $m\,\alpha^7$, first reported in Ref. [9], and present a recalculation of all corrections up to orders $m^2/M\,\alpha^6$ and $m\,\alpha^7$. Particularly, we perform an evaluation of the relativistic correction to the Bethe logarithm, which improves significantly upon the first calculation in Ref. [12].

The paper is organized as follows. In Sec. II and III we give a short summary of the general formulas for the helium fine structure up to order $m\,\alpha^6$. The derivation of the $m\,\alpha^7$ correction is presented in Sec. IV. The next section describes the numerical approach and reports the numerical results. Sec. VI contains the summary of all contributions to the helium fine structure and the discussion of the present status of theory and experiment.

The relativistic units are used in this paper, $\hbar = c = \epsilon_0 = 1$ and $e^2 = 4\pi\alpha$.

II. LEADING-ORDER FINE STRUCTURE

The dominant contribution to the helium fine structure is induced by the spin dependent part of the Breit-Pauli Hamiltonian, which is, for an infinitely heavy nucleus,

$$
\begin{aligned}
H_{\rm fs} &= \frac{\alpha}{4\,m^2}\left(\frac{\vec\sigma_1\cdot\vec\sigma_2}{r^3} - 3\,\frac{\vec\sigma_1\cdot\vec r\,\vec\sigma_2\cdot\vec r}{r^5}\right)(1+a_e)^2 \\
&+ \frac{Z\alpha}{4m^2}\left[\frac{1}{r_1^3}\,\vec r_1\times\vec p_1\cdot\vec\sigma_1 + \frac{1}{r_2^3}\,\vec r_2\times\vec p_2\cdot\vec\sigma_2\right](1+2a_e) \\
&+ \frac{\alpha}{4\,m^2\,r^3}\bigg[\big[(1+2\,a_e)\,\vec\sigma_2 + 2\,(1+a_e)\,\vec\sigma_1\big]\cdot\vec r\times\vec p_2 \\
&\quad -\big[(1+2\,a_e)\,\vec\sigma_1 + 2\,(1+a_e)\,\vec\sigma_2\big]\cdot\vec r\times\vec p_1\bigg], \qquad (1)
\end{aligned}
$$

where $\vec r = \vec r_1 - \vec r_2$ and we have included the effects of the electron anomalous magnetic moment (amm) a_e,

$$
\begin{aligned}
a_e &= \frac{\alpha}{2\pi} - 0.328\,478\,965\left(\frac{\alpha}{\pi}\right)^2 \\
&+1.181\,241\,456\left(\frac{\alpha}{\pi}\right)^3 - 1.7283\,(35)\left(\frac{\alpha}{\pi}\right)^4 + \ldots \qquad (2)
\end{aligned}
$$

Expanding the amm prefactors in Eq. (1), $H_{\rm fs}$ can be written as a sum of operators contributing to different orders in α,

$$H_{\rm fs} = H^{(4)}_{\rm fs} + H^{(5)}_{\rm fs} + H^{(6)}_{\rm fs,amm} + H^{(7)}_{\rm fs,amm} + \ldots\,. \tag{3}$$

Here $H^{(4)}_{\rm fs}$ and $H^{(5)}_{\rm fs}$ yield the complete fine-structure contributions of order $m\,\alpha^4$ and $m\,\alpha^5$, respectively, whereas $H^{(6)}_{\rm fs,amm}$ and $H^{(7)}_{\rm fs,amm}$ are the amm parts of the corresponding higher-order operators.

The leading effect of the finite nuclear mass is conveniently divided into three parts, termed as the mass scaling, the mass polarization, and the recoil operators. The effect of the mass scaling is accounted for by including the prefactor $(m_r/m)^3$ into the operator $H_{\rm fs}$, where m_r is the reduced mass for the electron-nucleus system. The effect of the mass polarization can be accounted for to all orders by evaluating expectation values of all operators on the eigenfunctions of the Shrödinger Hamiltonian with the mass-polarization operator $(m_r/M)\,\vec{p}_1\cdot\vec{p}_2$ included. The third effect is induced by the recoil addition to the Breit-Pauli Hamiltonian,

$$\begin{aligned} H_{\rm fs,rec} &= \frac{Z\alpha}{2mM}\,\biggl[\frac{\vec{r}_1}{r_1^3}\times(\vec{p}_1+\vec{p}_2)\cdot\vec{\sigma}_1 \\ &\quad + \frac{\vec{r}_2}{r_2^3}\times(\vec{p}_1+\vec{p}_2)\cdot\vec{\sigma}_2\biggr]\,(1+a_e)\,. \end{aligned} \tag{4}$$

III. $m\,\alpha^6$ CONTRIBUTION

The $m\,\alpha^6$ contribution to the helium fine structure is a sum of the second-order perturbation corrections induced by the Breit-Pauli Hamiltonian and the expectation value of the effective fine-structure Hamiltonian to this order, $H^{(6)}_{\rm fs}$,

$$\begin{aligned} E^{(6)} &= \biggl\langle H_{\rm fs}\frac{1}{(E_0-H_0)'}H_{\rm fs}\biggr\rangle \\ &\quad + 2\,\biggl\langle H^{(4)}_{\rm nfs}\frac{1}{(E_0-H_0)'}H_{\rm fs}\biggr\rangle + \Bigl\langle H^{(6)}_{\rm fs}\Bigr\rangle\,. \end{aligned} \tag{5}$$

Here, $1/(E_0-H_0)'$ is the reduced Green function and $H^{(4)}_{\rm nfs}$ is the spin-independent part of the Breit-Pauli Hamiltonian,

$$\begin{aligned} H^{(4)}_{\rm nfs} &= -\frac{1}{8\,m^3}\,(p_1^4+p_2^4) + \frac{Z\,\alpha\,\pi}{2\,m^2}\,\bigl[\delta^3(r_1)+\delta^3(r_2)\bigr] \\ &\quad - \frac{\alpha}{2\,m^2}\,p_1^i\left(\frac{\delta^{ij}}{r}+\frac{r^i\,r^j}{r^3}\right)p_2^j\,, \end{aligned} \tag{6}$$

where we omitted a term with $\delta^3(r)$ since it vanishes for the triplet states. It is noteworthy that in Eq. (5) we include the operator $H_{\rm fs}$ [and not just $H^{(4)}_{\rm fs}$], thus accounting for the amm correction to the Breit-Pauli Hamiltonian. While this correction is of order $m\,\alpha^7$, it is convenient to calculate it together with the $m\,\alpha^6$ contribution because only simple changes in the prefactors are required.

$H^{(6)}_{\rm fs}$ consists of 15 operators first derived by Douglas and Kroll (DK) [16] in the framework of the Salpeter equation. These operators were later re-derived in a more simple way using the effective field theory in Refs. [11, 13]. The result is

$$H^{(6)}_{\rm fs} = \sum_{i=1}^{15} B_i\,, \tag{7}$$

where

$$\begin{aligned}
B_1 &= \frac{3\,Z}{8}\,\nabla_1^2\,\frac{1}{r_1^3}\,\vec{\sigma}_1\cdot(\vec{r}_1\times\vec{p}_1)\,, && (8)\\
B_2 &= -\frac{Z}{r^3\,r_1^3}\,\vec{\sigma}_1\cdot(\vec{r}_1\times\vec{r})\,(\vec{r}\cdot\vec{p}_2)\,, && (9)\\
B_3 &= \frac{Z}{2}\,\frac{1}{r^3\,r_1^3}\,(\vec{\sigma}_1\cdot\vec{r})\,(\vec{\sigma}_2\cdot\vec{r}_1)\,, && (10)\\
B_4 &= \frac{1}{2}\,\frac{1}{r^4}\,\vec{\sigma}_1\cdot(\vec{r}\times\vec{p}_2)\,, && (11)\\
B_5 &= -\frac{1}{2}\,\frac{1}{r^6}\,(\vec{\sigma}_1\cdot\vec{r})\,(\vec{\sigma}_2\cdot\vec{r})\,, && (12)\\
B_6 &= -\frac{5}{8}\,\nabla_1^2\,\frac{1}{r^3}\,\vec{\sigma}_1\cdot(\vec{r}\times\vec{p}_1)\,, && (13)\\
B_7 &= \frac{3}{4}\,\nabla_1^2\,\frac{1}{r^3}\,\vec{\sigma}_1\cdot(\vec{r}\times\vec{p}_2)\,, && (14)\\
B_8 &= \frac{i}{4}\,\nabla_1^2\,\frac{1}{r}\,\vec{\sigma}_1\cdot(\vec{p}_1\times\vec{p}_2)\,, && (15)\\
B_9 &= \frac{3\,i}{4}\,\nabla_1^2\,\frac{1}{r^3}\,(\vec{r}\cdot\vec{p}_2)\,\vec{\sigma}_1\cdot(\vec{r}\times\vec{p}_1)\,, && (16)\\
B_{10} &= \frac{3\,i}{8}\,\frac{1}{r^5}\,\vec{\sigma}_1\cdot(\vec{r}\times(\vec{r}\cdot\vec{p}_2)\,\vec{p}_1)\,, && (17)\\
B_{11} &= -\frac{3}{16}\,\frac{1}{r^5}\,\vec{\sigma}_2\cdot(\vec{r}\times(\vec{\sigma}_1\cdot(\vec{r}\times\vec{p}_1))\,\vec{p}_2)\,, && (18)\\
B_{12} &= -\frac{1}{16}\,\frac{1}{r^3}\,(\vec{\sigma}_1\cdot\vec{p}_2)\,(\vec{\sigma}_2\cdot\vec{p}_1)\,, && (19)\\
B_{13} &= -\frac{3}{2}\,\nabla_1^2\,\frac{1}{r^5}\,(\vec{\sigma}_1\cdot\vec{r})\,(\vec{\sigma}_2\cdot\vec{r})\,, && (20)\\
B_{14} &= \frac{i}{4}\,\nabla_1^2\,\frac{1}{r^3}\,(\vec{\sigma}_1\cdot\vec{r})\,(\vec{\sigma}_2\cdot\vec{p}_1)\,, && (21)\\
B_{15} &= -\frac{i}{8}\,\nabla_1^2\,\frac{1}{r^3}\,(\vec{\sigma}_1\cdot\vec{r})\,(\vec{\sigma}_2\cdot\vec{p}_2)\,. && (22)
\end{aligned}$$

The finite nuclear mass correction correction to the $m\,\alpha^6$ contribution can be divided into the mass scaling, the mass polarization, and the operator parts. The mass scaling prefactor is $(m_r/M)^4$ for the B_2, B_3, B_4, and B_5, $(m_r/M)^5$ for the other B_i operators, $(m_r/M)^6$ for the second-order corrections involving the first term in Eq. (6), and $(m_r/M)^5$ for all other second-order corrections. The mass polarization effect is most easily accounted for by including the mass polarization operator into the zeroth-order Hamiltonian. The operator part comes from recoil corrections to $H^{(4)}_{\rm fs}$, $H^{(4)}_{\rm nfs}$, and $H^{(6)}_{\rm fs}$. The recoil part of $H^{(4)}_{\rm fs}$ is given by Eq. (4). The spin-independent recoil part of the Breit-Pauli Hamiltonian is

$$H^{(4)}_{\rm nfs,rec} = -\frac{Z}{2}\,\frac{m}{M}\sum_{a=1,2} p_a^i\left(\frac{\delta^{ij}}{r_a}+\frac{r_a^i r_a^j}{r_a^3}\right)(p_1^j+p_2^j)\,. \tag{23}$$

Recoil corrections to the DK operators were studied by Zhang [15] and by K.P. and Sapirstein [17]. The result is given by the effective Hamiltonian

$$H^{(6)}_{\rm fs,rec} = \frac{m}{M}\sum_{i=1}^{8} V_i\,, \tag{24}$$

where

$$V_1 = \frac{iZ}{4}p_1^2\frac{1}{r_1}\vec\sigma_1\cdot(\vec p_1\times\vec p_2)\,, \tag{25}$$

$$V_2 = -\frac{iZ}{4}\,p_1^2\,\frac{\vec r_1}{r_1^3}\,(\vec\sigma_1\cdot\vec r_1\times\vec p_1)\cdot(\vec p_1+\vec p_2)\,, \tag{26}$$

$$V_3 = -\frac{3Z}{4}\,p_1^2\,\vec\sigma_1\cdot\frac{\vec r_1}{r_1^3}\times(\vec p_1+\vec p_2)\,, \tag{27}$$

$$V_4 = Z\,\vec\sigma_1\cdot\frac{\vec r}{r_1\,r^3}\times(\vec p_1+\vec p_2)\,, \tag{28}$$

$$V_5 = Z\,\vec\sigma_1\cdot\frac{\vec r}{r^3}\times\frac{\vec r_1}{r_1^3}\,(\vec r_1\cdot(\vec p_1+\vec p_2))\,, \tag{29}$$

$$V_6 = Z^2\,\vec\sigma_1\cdot\frac{\vec r_1}{r_1^3}\times\frac{\vec r_2}{r_2^3}\,(\vec r_1\cdot\vec p_1)\,, \tag{30}$$

$$V_7 = -\frac{Z^2}{2}\,\vec\sigma_1\cdot\frac{\vec r_1}{r_1^4}\times(\vec p_1+\vec p_2)\,, \tag{31}$$

$$V_8 = -\frac{Z^2}{4}\vec\sigma_1\cdot\frac{\vec r_2}{r_2^3}\,\vec\sigma_2\cdot\frac{\vec r_1}{r_1^3}\,. \tag{32}$$

IV. DERIVATION OF THE $m\,\alpha^7$ CONTRIBUTION

In this section we present a detailed derivation of the $m\,\alpha^7$ contribution to the helium fine structure. The corresponding results have already been presented in Ref. [9]. The derivation is based on the dimensionally regularized NRQED [18]. The general idea is that, in the situation when all relevant electron momenta are much smaller than the electron mass, an approximate QED Lagrangian can be used, obtained from the original full-QED Lagrangian by the Foldy-Wouthuysen (FW) transformation, as described in Appendix A. The standard FW transformation is generalized to the extended number of the space dimensions and also to account for the magnetic moment anomaly of the electron a_e. The regularization parameter ϵ, related to the space dimension $d = 3-2\,\epsilon$, plays the role of both an infrared and ultraviolet regulator and cancels out in the end of calculations.

The fine structure contribution to order $m\,\alpha^7$ (α^5 Ry) can be written as [12]

$$E^{(7)} = \langle H^{(7)}_{\rm fs}\rangle + 2\left\langle H^{(4)}\frac{1}{(E_0-H_0)'}H^{(5)}\right\rangle + E_L, \tag{33}$$

where $H^{(i)}$ denotes the effective Hamiltonian to order $m\,\alpha^i$, $1/(E_0-H_0)'$ is the reduced Coulomb Green function, and E_L is the low energy contribution to be interpreted as the relativistic correction to the Bethe logarithm.

The second term in Eq. (33) that involves the second-order matrix element is the simplest. $H^{(4)}$ is the Breit-Pauli Hamiltonian and is the sum of the spin-dependent and the spin-independent parts, $H^{(4)} = H^{(4)}_{\rm fs} + H^{(4)}_{\rm nfs}$. The effective Hamiltonian to order $m\,\alpha^5$ is given by the sum $H^{(5)} = H^{(5)}_{\rm fs} + H^{(5)}_{\rm nfs}$, where the first part is the leading-order amm correction to the Breit-Pauli Hamiltonian defined by Eq. (3) and

$$H^{(5)}_{\rm nfs} = -\frac{7\,\alpha^2}{6\,\pi\,m^2}\,\frac{1}{r^3} + \frac{4}{3}\,\frac{Z\alpha^2}{m^2}\left[\frac{19}{30}+\ln(Z\alpha)^{-2}\right]\left[\delta^3(r_1)+\delta^3(r_2)\right]. \tag{34}$$

The amm part of $H^{(5)}$ has already been included into the $m\,\alpha^6$ correction described in the previous section. The remaining part of the second-order perturbation correction will be denoted as E_S and is given by

$$E_S = 2\left\langle H^{(4)}_{\rm fs}\,\frac{1}{(E_0-H_0)'}\,H^{(5)}_{\rm nfs}\right\rangle. \tag{35}$$

The effective operator $H^{(7)}_{\rm fs}$ consists of two parts: (i) the exchange terms, in which photons are exchanged between the two electrons, and (ii) the radiative corrections, in which one or several photons are emitted and absorbed by the same electron. They are calculated separately using different computational methods in the following subsections.

A. Photon exchange part

An important feature that leads to a considerable simplification of the calculation of the photon exchange part is the fact that the order being calculated is nonanalytic in α^2. For example, $H^{(5)}_{\rm nfs}$ consists of the two terms only, which can be derived from the two-photon exchange scattering amplitude. A similar statement holds for the photon exchange part of $H^{(7)}_{\rm fs}$: if $H^{(7)}_{\rm fs}$ is an effective Hamiltonian, it has to give the same scattering amplitude as in full QED. Due to the simple structure of $H^{(7)}_{\rm fs}$, the effective interaction can be unambiguosly extracted from this amplitude. The scattering amplitude is usually much simpler to calculate, than corrections within effective field approach, such as that used for the derivation of $H^{(6)}$. An important point here is that only the two-photon exchange diagrams contribute to $H^{(7)}_{\rm fs}$, the absence of the three-body effects being a result of an internal cancellation.

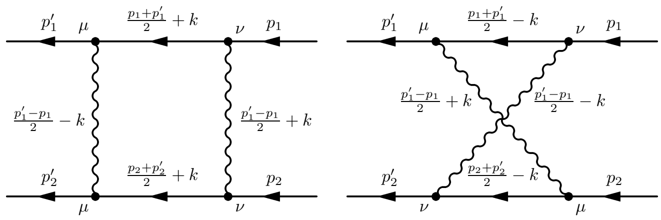

FIG. 1: The two-photon exchange scattering amplitude

So, we obtain the exchange contribution from the spin dependent part of the two-photon scattering amplitude, which is

$$\delta_1 H = \frac{i\, e^4}{(2\,\pi)^D} \int d^D k\, \frac{1}{(k+q/2)^2}\, \frac{1}{(k-q/2)^2} \Biggl[\bar u(p_1')\,\gamma^\mu\, \frac{1}{\not k + (\not p_1 + \not p_1')/2 - 1}\, \gamma^\nu\, u(p_1) + \bar u(p_1')\,\gamma^\nu\, \frac{1}{-\not k + (\not p_1 + \not p_1')/2 - 1}\, \gamma^\mu\, u(p_1)\Biggr] \times \bar u(p_2')\,\gamma^\nu\, \frac{1}{\not k + (\not p_2 + \not p_2')/2 - 1}\, \gamma^\mu\, u(p_2)\,, \tag{36}$$

where $q = p_1' - p_1$. There are three scales of the k integral that are responsible for the $m\,\alpha^7$ corrections: m, $m\,\alpha$, and $m\,\alpha^2$. Only the first two scales are accounted for in Eq. (36), whereas the third one, $k \sim m\,\alpha^2$, corresponds to a low-energy contribution and requires a separate treatment. Because of the dimensional regularization, the contribution of each energy scale can be obtained separately.

In our calculation, only the spin-dependent part of the scattering amplitude $\delta_1 H$ is needed. It is, however, not obvious what the spin dependent part is. In order to be consistent with the rest of the calculation, we employ the free FW transformation S,

$$\psi' = e^{i\,S}\,, \tag{37}$$

$$e^{-i\,S} = \frac{\not p + 1}{\sqrt{2\,E_p\,(E_p+1)}}\,, \tag{38}$$

which for small momentum takes a simple form

$$e^{-i\,S} \approx \frac{\not p + 1}{2}\,. \tag{39}$$

This leads us to the following projection operators

$$\bar u(p')\,Q\,u(p) = \mathrm{Tr}\,Q\,u(p)\otimes\bar u(p') \to \begin{cases} \mathrm{Tr}\,Q\,\left(\frac{\not p+1}{2}\right)\left(\frac{\gamma^0+I}{4}\right)\left(\frac{\not p'+1}{2}\right), \\ \sigma^{ij}\,\mathrm{Tr}\,Q\,\left(\frac{\not p+1}{2}\right)\left(\frac{\gamma^0+I}{2}\right)\frac{\sigma^{ij}}{4}\left(\frac{\not p'+1}{2}\right), \end{cases} \tag{40}$$

which identify the spin-independent and spin-dependent parts of the matrix element of the arbitrary operator Q, respectively, with σ^{ij} defined by

$$\sigma^{ij} = \frac{i}{2}\,[\gamma^i\,,\,\gamma^j] \overset{d=3}{=} \epsilon^{ijk}\,\sigma^k\,. \tag{41}$$

We now perform an expansion of the integrand of the scattering amplitude $\delta_1 H$ in Eq. (36) for two scales, $k \sim m$ and $k \sim m\,\alpha$. Assuming $k \sim m$ and the external momenta $p \sim m\,\alpha$ and expanding the integrand in α, we obtain

$$\begin{aligned}\delta_1 H[m] = \alpha^2 \Biggl\{ & \sigma_1(j,q)\,\sigma_2(j,q)\,\left[-\frac{23}{36} + \frac{7}{12\,\epsilon}\right] \\ & + i\,[\sigma_1(p_1',p_1) + \sigma_2(p_2',p_2)]\,\left[-\frac{1}{6} - \frac{1}{4\,\epsilon}\right] \\ & + i\,[\sigma_1(p_2',p_2) + \sigma_2(p_1',p_1)]\left[\frac{1}{4}\right] \\ & + \frac{1}{8}\,\sigma_1(j,p_1+p_1')\,\sigma_2(j,p_2+p_2') \\ & - \frac{1}{8}\,\sigma_1(j,p_2+p_2')\,\sigma_2(j,p_1+p_1') \\ & + \frac{17}{72}\,\sigma_1(j,p_1-p_2+p_1'-p_2') \\ & \times \sigma_2(j,p_1-p_2+p_1'-p_2') \Biggr\}\,. \end{aligned} \tag{42}$$

A similar expansion with the assumption that $k \sim m\,\alpha$ leads to

$$\begin{aligned}\delta_1 H[m\alpha] = \alpha^2 \Biggl\{ & \sigma_1(j,q)\,\sigma_2(j,q)\,\left[-\frac{5}{12} - \frac{1}{4\,\epsilon} + \frac{1}{2}\,\ln(q)\right] \\ & + i\,[\sigma_1(p_1',p_1) + \sigma_2(p_2',p_2)]\,\left[\frac{7}{12} - \frac{1}{12\,\epsilon} + \frac{1}{6}\,\ln(q)\right] \\ & + i\,[\sigma_1(p_2',p_2) + \sigma_2(p_1',p_1)]\left[\frac{2}{3} - \frac{2}{3\,\epsilon} + \frac{4}{3}\,\ln(q)\right]\Biggr\}. \end{aligned} \tag{43}$$

The sum of $\delta_1 H[m]$ and $\delta_1 H[m\alpha]$ is

$$\begin{aligned}\delta_1 H = \alpha^2 \Biggl\{ & \sigma_1(j,q)\,\sigma_2(j,q)\,\left[-\frac{19}{18} + \frac{1}{3\,\epsilon} + \frac{1}{2}\,\ln(q)\right] \\ & + i\,[\sigma_1(p_1',p_1) + \sigma_2(p_2',p_2)]\,\left[\frac{5}{12} - \frac{1}{3\,\epsilon} + \frac{1}{6}\,\ln(q)\right] \\ & + i\,[\sigma_1(p_2',p_2) + \sigma_2(p_1',p_1)]\left[\frac{11}{12} - \frac{2}{3\,\epsilon} + \frac{4}{3}\,\ln(q)\right] \\ & + \frac{1}{8}\,\sigma_1(j,p_1+p_1')\,\sigma_2(j,p_2+p_2') \\ & - \frac{1}{8}\,\sigma_1(j,p_2+p_2')\,\sigma_2(j,p_1+p_1') \\ & + \frac{17}{72}\,\sigma_1(j,p_1-p_2+p_1'-p_2') \\ & \times \sigma_2(j,p_1-p_2+p_1'-p_2') \Biggr\}, \end{aligned} \tag{44}$$

where $\sigma(j,q) = \sigma^{ji}\,q^i$, and $q = \sqrt{\vec q^{\,2}}$.

The third scale $k \sim m\,\alpha^2$ requires a more accurate treatment since any number of the electron-nucleus Coulomb photon exchanges contribute to the same order. This low energy part can be represented in the Coulomb gauge as

$$E_{LE} = e^2 \int_0^\infty \frac{d^d k}{(2\,\pi)^d\,2\,k}\left(\delta^{ij} - \frac{k^i\,k^j}{k^2}\right) \times \delta\left\langle\phi\left|p_1^i\,\frac{1}{E_0 - H_0 - k}\,p_2^j\right|\phi\right\rangle + (1\leftrightarrow 2)\,, \tag{45}$$

where the symbol $\delta\,\langle\ldots\rangle$ stands for the first-order perturbation correction of the matrix element $\langle\ldots\rangle$ by the (d-dimension generalization of the) Breit-Pauli Hamiltonian $H^{(4)}$, which implies perturbations of the reference-state wave function ϕ, the energy E_0, and the zeroth-order Hamiltonian H_0.

The expression (45) involves the Coulomb Green function, which is not known for the arbitrary dimension. This problem is solved by splitting the integral over k into two parts,

$$\int_0^\infty dk = \int_0^\Lambda dk + \int_\Lambda^\infty dk\,, \tag{46}$$

with $\Lambda = m\,(Z\,\alpha)^2\,\lambda$ and λ being a dimensionless cutoff parameter. The two corresponding parts of Eq. (45) will be referred to as $\mathcal{E}_{LE}$ and $\delta_2 E$. It is assumed that in these parts the expansion is performed first in the small ϵ and next in the large λ. The first part $\mathcal{E}_{LE}$ has a finite limit at $d = 3$. It will be evaluated in Sec. IV E together with other low-energy contributions.

We now turn to the evaluation of the second part $\delta_2 E$. The spin-dependent part of the Breit-Pauli Hamiltonian in d dimensions is the sum of the electron-electron part H_{ee} and the electron-nucleus part H_{eN},

$$\begin{aligned}\delta H_{ee} \;=\; & \frac{e^2}{4\,m^2\,q^2}\,\big[i\,p_1'^{\,i}\,p_1{}^j(\sigma_1^{ij}+2\,\sigma_2^{ij}) \\ & +i\,p_2'^{\,i}\,p_2{}^j(\sigma_2^{ij}+2\,\sigma_1^{ij}) - \sigma_1^{ik}\,\sigma_2^{jk}\,q^i\,q^j\big]\,,\end{aligned} \tag{47}$$

$$\delta H_{eN} = -\frac{Z\,e^2}{4\,q^2}\,\big[i\,\sigma_1^{ij}\,p_1''^{i}\,p_1^j + i\,\sigma_1^{ij}\,p_2''^{i}\,p_2^j\big]\,. \tag{48}$$

Only the electron-electron part H_{ee} contribute to $\delta_2 E$. Since k is much larger than $H_0 - E_0$, we expand the integrand to yield

$$\begin{aligned}& \delta\left\langle\phi\left|p_1^i\,\frac{1}{E_0-H_0-k}\,p_2^j\right|\phi\right\rangle + (1\leftrightarrow 2) \\ &= \frac{1}{k^2}\,\delta\left\langle\phi\left|p_1^i\,(H_0-E_0)\,p_2^j\right|\phi\right\rangle + (1\leftrightarrow 2) \\ &= \frac{1}{k^2}\,\delta\left\langle\phi\left|[p_1^i,\,[H_0-E_0\,,\,p_2^j]]\right|\phi\right\rangle \\ &= \frac{2}{k^2}\,\left\langle\phi\left|[p_1^i,\,[V\,,\,p_2^j]]\,\frac{1}{(E_0-H_0)'}\,\delta H_{ee}\right|\phi\right\rangle \\ &+\frac{1}{k^2}\,\left\langle\phi\left|[p_1^i,\,[\delta H_{ee}\,,\,p_2^j]]\right|\phi\right\rangle\,.\end{aligned} \tag{49}$$

The first term in the above expression is the second-order perturbation correction, which is already included into E_S, Eq. (35). The contribution of the second term is

$$\delta_2 E = e^2\,\frac{d-1}{d}\int_\Lambda^\infty \frac{d^dk}{(2\,\pi)^d\,2\,k^3}\,\left\langle\phi\left|[p_1^i,\,[\delta H_{ee}\,,\,p_2^i]]\right|\phi\right\rangle\,. \tag{50}$$

After expanding this expression in $\epsilon = (3-d)/2$ and then in α, the result is represented by the expectation value of the effective operator $\delta_2 H$,

$$\begin{aligned}\delta_2 H \;=\; & \alpha^2\left[\frac{5}{9}+\frac{1}{3\,\epsilon}+\frac{2}{3}\,\ln[(Z\,\alpha)^{-2}]-\frac{2}{3}\,\ln(2\,\lambda)\right] \\ & \times[i\,\sigma_1(p_1',p_1)+i\,\sigma_2(p_2',p_2)+2\,i\,\sigma_1(p_2',p_2) \\ & +2\,i\,\sigma_2(p_1',p_1)-\sigma_1(j,q)\,\sigma_2(j,q)]\,.\end{aligned} \tag{51}$$

So, the contribution due to the photon exchange is given by the sum of the expectation values of $\delta_1 H$ and $\delta_2 H$ and by the low-energy contribution $\mathcal{E}_{LE}$.

When calculating expectation values of effective operators between the triplet P states, some simplifications can be performed. The first one is that the expectation value of the Dirac δ function with both momenta on the right (left) hand side vanishes. The second one is that the expectation value of σ_1 is equal to that of σ_2. As a result, the sum of $\delta_1 H$ and $\delta_2 H$ can be written as

$$\begin{aligned}H_E \;&= \delta_1 H + \delta_2 H \\ &= \alpha^2\left[6+4\ln[(Z\,\alpha)^{-2}]-4\,\ln(2\,\lambda)+3\,\ln q\right]i\,\sigma_1(p_1',p_1) \\ &+\alpha^2\left[-\frac{23}{9}-\frac{2}{3}\,\ln[(Z\,\alpha)^{-2}]+\frac{2}{3}\,\ln(2\,\lambda)+\frac{1}{2}\,\ln q\right] \\ &\times\sigma_1(j,q)\,\sigma_2(j,q)\,.\end{aligned} \tag{52}$$

B. Radiative corrections

The $m\,\alpha^7$ contribution induced by the radiative corrections is also split into the high and low energy parts. We argue that the high energy part can be accounted for by using the electromagnetic form factors F_1 and F_2 and the Uehling correction to the Coulomb potential F_V,

$$\begin{aligned}F_1(-\vec q^{\,2}) \;&=\; 1+\frac{\alpha}{\pi}\left(\frac{1}{8}+\frac{1}{6\,\epsilon}\right)\vec q^{\,2}\,, \\ F_2(-\vec q^{\,2}) \;&=\; \frac{\alpha}{\pi}\left(\frac{1}{2}-\frac{1}{12}\,\vec q^{\,2}\right)\,, \\ F_V(-\vec q^{\,2}) \;&=\; \frac{\alpha}{\pi}\,\frac{1}{15}\,\vec q^{\,2}\,.\end{aligned} \tag{53}$$

In principle, there are also corrections quadratic in the electromagnetic field. However, one can demonstrate that such terms formed out of $\vec E$, $\vec B$, $\vec p$, and $\vec\sigma$ contribute only to higher orders and can be neglected.

Corrections induced by the slope of the electromagnetic form factors are obtained by rederiving the Breit-Pauli Hamiltonian, Eqs. (47) and (48), with employing modified electromagnetic vertices. The resulting effective operator is

$$\begin{aligned}\delta_3 H \;=\; & \pi\,Z\,\alpha(F_1'+2\,F_2'+F_V')i\,[\sigma_1(p_1'',p_1)+\sigma_2(p_2'',p_2)] \\ & -\pi\,\alpha(2\,F_1'+2\,F_2'+F_V')i\,[\sigma_1(p_1',p_1)+\sigma_2(p_2',p_2)] \\ & -2\,\pi\,\alpha(2\,F_1'+F_2'+F_V')i\,[\sigma_1(p_2',p_2)+\sigma_2(p_1',p_1)] \\ & +\pi\,\alpha(2\,F_1'+2\,F_2'+F_V')\,\sigma_1(j,q)\,\sigma_1(j,q)\,,\end{aligned} \tag{54}$$

where p'' is the momentum scattered off the Coulomb potential of the nucleus.

The low-energy part of the radiative contribution is written in a form similar to Eq. (45),

$$E_{LR} = e^2 \int_0^\infty \frac{d^d k}{(2\pi)^d\, 2\,k} \left(\delta^{ij} - \frac{k^i\, k^j}{k^2}\right) \times \delta \left\langle \phi \left| p_1^i \, \frac{1}{E-H-k}\, p_1^j \right| \phi \right\rangle + (1 \to 2)\,. \tag{55}$$

Here, δ denotes the first-order perturbation correction due to both parts of the Breit-Pauli Hamiltonian, the electron-electron part δH_{ee} in Eq. (47) and the electron-nucleus part δH_{eN} in Eq. (48). Introducing the splitting parameter λ, we separate E_{LR} into two parts, $\mathcal{E}_{LR}$ and $\delta_4 E$, which correspond to the first and the second term in Eq. (46), respectively.

The evaluation of $\delta_4 E$ is similar to that of the photon exchange part. It yields $\delta_4 E = \langle \delta_4 H \rangle$, where the effective Hamiltonian is

$$\begin{aligned} \delta_4 H \;=\; & \alpha^2 \left[\frac{5}{9} + \frac{1}{3\,\epsilon} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}] - \frac{2}{3}\,\ln(2\,\lambda)\right] \\ & \times \biggl[\frac{i\,Z}{2}\,\sigma_1(p_1'', p_1) + \frac{i\,Z}{2}\,\sigma_2(p_2'', p_2) \\ & -i\,\sigma_1(p_1', p_1) - i\,\sigma_2(p_2', p_2) - 2\,i\,\sigma_2(p_1', p_1) \\ & -2\,i\,\sigma_1(p_2', p_2) + \sigma_1(j,q)\,\sigma_2(j,q)\biggr]. \end{aligned} \tag{56}$$

The total radiative correction is the sum of $\delta_3 H$, $\delta_4 H$, and the low-energy contribution $\mathcal{E}_{LR}$. The sum of $\delta_3 H$ and $\delta_4 H$ can be simplified further by using the symmetry $1 \leftrightarrow 2$, with the result

$$\begin{aligned} H_R \;=\; & Z\,\alpha^2 \left[\frac{91}{180} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}] - \frac{2}{3}\,\ln(2\,\lambda)\right] i\,\sigma_1(p_1'', p_1) \\ & -\alpha^2 \left[\frac{21}{10} + 4\,\ln[(Z\,\alpha)^{-2}] - 4\,\ln(2\,\lambda)\right] i\,\sigma_1(p_1', p_1)\,, \\ & +\alpha^2 \left[\frac{73}{180} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}] - \frac{2}{3}\,\ln(2\,\lambda)\right] \\ & \times \sigma_1(j,q)\,\sigma_2(j,q)\,. \end{aligned} \tag{57}$$

C. *Q*-operators

It is convenient to consider the sum of Eqs. (52) and (57), $H_Q = H_E + H_R$, as several logarithmic terms cancel out. The results is

$$\begin{aligned} H_Q \;=\; & Z\,\alpha^2 \left[\frac{91}{180} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}] - \frac{2}{3}\,\ln(2\,\lambda)\right] \\ & \times i\,\sigma_1(p_1'', p_1) + \alpha^2 \left[\frac{39}{10} + 3\,\ln q\right] i\,\sigma_1(p_1', p_1) \\ & +\alpha^2 \left[-\frac{43}{20} + \frac{\ln q}{2}\right] \sigma_1(j,q)\,\sigma_2(j,q). \end{aligned} \tag{58}$$

For numerical calculations, we have to obtain the coordinate space representation of H_Q, which involves singular operators and requires a proper definition. We introduce the following operators

$$\int \frac{d^3 q}{(2\,\pi)^3}\, e^{i\,\vec{q}\cdot\vec{r}}\, 4\,\pi\,(1 - \ln q) = \frac{1}{r^3}\,, \tag{59}$$

$$\int \frac{d^3 q}{(2\,\pi)^3}\, e^{i\,\vec{q}\cdot\vec{r}}\, \frac{4\,\pi}{15} \left(q^i\,q^j - \frac{\delta^{ij}}{3}\,q^2\right) \left(\ln q - \frac{23}{15}\right) = \frac{1}{r^7} \left(r^i\,r^j - \frac{\delta^{ij}}{3}\,r^2\right). \tag{60}$$

The coordinate-space representation of these operators is defined through their integrals with the arbitrary function f that is smooth at origin,

$$\int d^3 r \frac{1}{r^3}\, f(\vec{r}) \equiv \lim_{\epsilon\to 0} \int d^3 r \left[\frac{1}{r^3}\,\theta(r-\epsilon) + 4\,\pi\,\delta^3(r)\,(\gamma + \ln\epsilon)\right] f(\vec{r})\,, \tag{61}$$

$$\begin{aligned} & \int d^3 r\, \frac{1}{r^7} \left(r^i\,r^j - \frac{\delta^{ij}}{3}\,r^2\right) f(\vec{r}) \equiv \lim_{\epsilon\to 0} \int d^3 r \\ & \left[\frac{1}{r^7} \left(r^i\,r^j - \frac{\delta^{ij}}{3}\,r^2\right) \theta(r-\epsilon) \right. \\ & \left. + \frac{4\,\pi}{15}\,\delta^3(r)\,(\gamma + \ln\epsilon) \left(\partial^i\,\partial^j - \frac{\delta^{ij}}{3}\,\partial^2\right)\right] f(\vec{r})\,, \end{aligned} \tag{62}$$

where we assume that r is expressed in atomic units.

With these definitions, the coordinate-space representation of H_Q is (in atomic units)

$$\begin{aligned} H_Q \;=\; & Z\,\alpha^7 \left(\frac{91}{180} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}] - \frac{2}{3}\,\ln(2\,\lambda)\right) \\ & \times \bigl(i\,\vec{p}_1 \times \delta^3(r_1)\,\vec{p}_1 \cdot \vec{\sigma}_1\bigr) \\ & +\alpha^7 \left(-\frac{83}{60} + \frac{\ln\alpha}{2}\right) (\vec{\sigma}_1 \cdot \vec{\nabla})\,(\vec{\sigma}_2 \cdot \vec{\nabla})\delta^3(r) \\ & -\alpha^7\, \frac{15}{8\,\pi}\, \frac{1}{r^7}\, (\vec{\sigma}_1 \cdot \vec{r})\,(\vec{\sigma}_2 \cdot \vec{r}) \\ & +\alpha^7 \left(\frac{69}{10} + 3\,\ln\alpha\right) i\,\vec{p}_1 \times \delta^3(r)\,\vec{p}_1 \cdot \vec{\sigma}_1 \\ & -\alpha^7\, \frac{3}{4\,\pi}\, i\,\vec{p}_1 \times \frac{1}{r^3}\,\vec{p}_1 \cdot \vec{\sigma}_1\,. \end{aligned} \tag{63}$$

The above equation is written in atomic units because the definitions (61) and (62) are formulated in this unit system. Other formulas in the present paper are written in relativistic units. The λ-dependent term in Eq. (63) cancels with the corresponding contribution in Eq. (122). The logarithmic in α part of H_Q agrees with the results of Refs. [10, 11].

D. Anomalous magnetic moment correction to the $m\,\alpha^6$ operators

The remaining contribution to $H^{(7)}_{\rm fs}$ is the amm correction to the spin-dependent $m\,\alpha^6$ operators. It does not lead to any divergences and therefore can be calculated without any regularization. The derivation of the amm part of $H^{(7)}_{\rm fs}$ is done with the help of the NRQED Hamiltonian obtained by the FW transformation of the Dirac Hamiltonian with the electron magnetic moment anomaly included. The resulting Hamiltonian, with higher-order spin-independent terms omitted, is [19]

$$\begin{aligned} H_{FW} \;=\;& \frac{\vec\pi^2}{2} + e\,A^0 - \frac{e}{2}\,(1+a_e)\,\vec\sigma\cdot\vec B - \frac{\vec\pi^4}{8} \\ & -\frac{e}{8}\,(1+2\,a_e)\,[\vec\nabla\cdot\vec E + \vec\sigma\cdot(\vec E\times\vec\pi - \vec\pi\times\vec E)] \\ & +\frac{e}{8}\big(\{\vec\sigma\cdot\vec B,\vec\pi^2\} + a_e\,\{\vec\pi\cdot\vec B,\vec\pi\cdot\vec\sigma\}\big) \\ & +\frac{(3+4\,a_e)}{32}\,\{\vec p^{\,2}, e\,\vec E\times\vec p\cdot\vec\sigma\}\,. \end{aligned} \tag{64}$$

We use the opportunity to correct the misprint in Ref. [9] where the last term was typed with an incorrect prefactor. As demonstrated in Ref. [20], all spin-dependent operators to order $m\,\alpha^6$ can be obtained from H_{FW}. The derivation of the amm correction to the $m\,\alpha^6$ operators is very much similar.

We start with the general expression for the one-photon exchange amplitude between the electron a and the electron b,

$$\begin{aligned} \langle\delta H\rangle =\;& e^2\int\frac{d^4k}{(2\,\pi)^4\,i}\,G_{\mu\nu}(k) \\ \times\Bigg\{&\bigg\langle\phi\bigg|\jmath^\mu_a(k)\,e^{i\,\vec k\cdot\vec r_a}\frac{1}{E_0-H_0-k^0+i\,\epsilon}\jmath^\nu_b(-k)\,e^{-i\,\vec k\cdot\vec r_b}\bigg|\phi\bigg\rangle \\ +&\bigg\langle\phi\bigg|\jmath^\mu_b(k)\,e^{i\,\vec k\cdot\vec r_b}\frac{1}{E_0-H_0-k^0+i\,\epsilon}\jmath^\nu_a(-k)\,e^{-i\,\vec k\cdot\vec r_a}\bigg|\phi\bigg\rangle\Bigg\}\,, \end{aligned} \tag{65}$$

where $G_{\mu\nu}$ is the photon propagator in the Coulomb gauge,

$$G_{\mu\nu}(k) = \begin{cases} -\frac{1}{\vec k^2}\,, & \mu=\nu=0\,, \\ \frac{-1}{k_0^2-\vec k^2+i\,\epsilon}\Big(\delta_{ij}-\frac{k_i k_j}{\vec k^2}\Big)\,, & \mu=i,\nu=j\,, \end{cases} \tag{66}$$

ϕ is an eigenstate of H_0 and $\jmath^\mu_a$ is the operator of the electromagnetic current for particle a. In the following, we will consider separately the exchange by the Coulomb G_{00} and the transverse G_{ij} photons. The expression for the electromagnetic current $\jmath^\mu$ is obtained from the Hamiltonian H_{FW} as a coefficient that multiplies the electromagnetic potential A_μ. The first terms of the nonrelativistic expansion of the current are

$$\jmath^0(\vec k) = 1 + \frac{i}{4\,m}\,\vec\sigma\cdot\vec k\times\vec p - \frac{1}{8\,m^2}\vec k^{\,2} + \ldots\,, \tag{67}$$

for the $\jmath^0$ component and

$$\vec\jmath(\vec k) = \frac{\vec p}{m} + \frac{i}{2\,m}\,\vec\sigma\times\vec k + \ldots\,, \tag{68}$$

for the $\vec\jmath$ component.

The main part of the calculation is performed in the nonretardation approximation, which consists in setting $k^0=0$ in the photon propagator $G_{\mu\nu}(k)$ and in the current $\jmath(k)$; the retardation corrections are considered separately. Employing the nonretardation approximation and the symmetry $k^0\leftrightarrow -k^0$, the integration over k^0 is carried out as

$$\frac{1}{2}\int\frac{d\,k^0}{2\,\pi\,i}\left[\frac{1}{-\Delta E-k^0+i\,\epsilon}+\frac{1}{-\Delta E+k^0+i\,\epsilon}\right] = -\frac{1}{2}\,. \tag{69}$$

The one-photon exchange amplitude in the nonretardation approximation thus is

$$\begin{aligned} \langle\phi|\delta H|\phi\rangle \;=\;& -e^2\int\frac{d^3k}{(2\,\pi)^3}\,G_{\mu\nu}(\vec k) \\ & \times\bigg\langle\phi\bigg|\jmath^\mu_a(\vec k)\,e^{i\,\vec k\cdot(\vec r_a-\vec r_b)}\,\jmath^\nu_b(-\vec k)\bigg|\phi\bigg\rangle\,. \end{aligned} \tag{70}$$

To the leading order, the current does not depend on $\vec k$ and the $\vec k$ integration gives the coordinate-space representation of the photon propagator in the nonretardation approximation,

$$\begin{aligned} G_{\mu\nu}(\vec r) \;=\;& \int\frac{d^3k}{(2\,\pi)^3}\,e^{i\,\vec k\cdot\vec r}\,G_{\mu\nu}(\vec k) \\ =\;& \frac{1}{4\,\pi}\begin{cases} -\frac{1}{r}\,, & \mu=\nu=0\,, \\ \frac{1}{2\,r}\Big(\delta_{ij}+\frac{r_i r_j}{r^2}\Big)\,, & \mu=i,\nu=j\,. \end{cases} \end{aligned} \tag{71}$$

One easily recognizes that in the nonrelativistic limit G_{00} is the Coulomb interaction. This term is already included in H_0, which means that the nonrelativistic Coulomb interaction has to be excluded from the perturbative expansion. Next-order terms resulting from the expansion of $\jmath^0$ and $\vec\jmath$ lead to the Breit-Pauli Hamiltonian.

We are interested in the expansion terms that yield effective operators of order $m\,\alpha^6\,a_e$. Their derivation is analogous to that of the $m\,\alpha^6$ Hamiltonian in Ref. [20], the only difference being that the corresponding amm prefactors should be retained. These prefactors will give us the required effective operator, which will be denoted as $H^{(6)}_{a_e}$. It is expressed as a sum of various contributions

$$H^{(6)}_{a_e} = \sum_{i=1}^{8}\delta H_i\,, \tag{72}$$

which are calculated in the following.

δH_1 is the correction due to the last term in H_{FW} in Eq. (64). This term involves only A^0 and its gradient, so the nonretardation approximation is valid here. δH_1 includes the Coulomb interaction between the electron and the nucleus and between the electrons. We denote by V the nonrelativistic interaction potential

$$V \equiv -\sum_a\frac{Z\,\alpha}{r_a} + \sum_{a>b}\sum_b\frac{\alpha}{r_{ab}}\,, \tag{73}$$

and by $\mathcal{E}_a$ the static electric field at the position of particle a

$$e\,\vec{\mathcal{E}}_a \equiv -\nabla_a V = -Z\,\alpha\,\frac{\vec r_a}{r_a^3} + \sum_{b\neq a}\alpha\,\frac{\vec r_{ab}}{r_{ab}^3}\,, \tag{74}$$

and write δH_1 as

$$\delta H_1 = \sum_a \frac{3+4\,a_e}{32\,m^4}\,\vec\sigma_a\cdot\Big(p_a^2\,e\,\vec{\mathcal{E}}_a\times\vec p_a + e\,\vec{\mathcal{E}}_a\times\vec p_a\,p_a^2\Big)$$
$$\stackrel{a_e}{=} a_e\left(-\frac{Z\,\alpha}{2}\,p_1^2\,\frac{\vec r_1}{r_1^3}\times\vec p_1\cdot\vec\sigma_1 + \frac{\alpha}{2}\,p_1^2\,\frac{\vec r}{r^3}\times\vec p_1\cdot\vec\sigma_1\right), \tag{75}$$

where by $\stackrel{a_e}{=}$ we denote that the equation is valid modulo terms independent on a_e.

δH_2 is the correction to the Coulomb interaction between electrons which comes from the 5$^{\rm th}$ term in H_{FW}, namely

$$-\frac{e}{8}\,(1+2\,a_e)\,\Big[\vec\nabla\cdot\vec E + \vec\sigma\cdot\big(\vec E\times\vec p - \vec p\times\vec E\big)\Big]. \tag{76}$$

If the interaction of both electrons is modified by this term, the nonretardation approximation holds and Eq. (70) yields

$$\delta H_2 = \sum_{a>b}\sum_b\int d^3k\,\frac{e^2}{k^2}\,\frac{(1+2\,a_e)^2}{64}\,\Big(k^2+2\,i\,\vec\sigma_a\cdot\vec p_a\times\vec k\Big)\,e^{i\,\vec k\cdot\vec r_{ab}}\,\Big(k^2+2\,i\,\vec\sigma_b\cdot\vec k\times\vec p_b\Big)$$
$$\stackrel{\rm fs}{=} e^2\,\frac{(1+2\,a_e)^2}{16}\int d^3k\left(i\,\vec\sigma_1\cdot\vec p_1\times\vec k\,e^{i\,\vec k\cdot\vec r} - \vec\sigma_1\cdot\vec p_1\times\vec k\,\frac{e^{i\,\vec k\cdot\vec r}}{k^2}\,\vec\sigma_2\cdot\vec k\times\vec p_2\right) \tag{77}$$
$$\stackrel{a_e}{=} a_e\left[\frac{3\,i}{2}\,\frac{\alpha}{r^5}\,\vec r\times(\vec r\cdot\vec p_2)\,\vec p_1\cdot\vec\sigma_1 - \frac{3}{4}\,\frac{\alpha}{r^5}\,\vec r\times(\vec r\times\vec p_1\cdot\vec\sigma_1)\,\vec p_2\cdot\vec\sigma_2 - \frac{\alpha}{4\,r^3}\,(\vec p_1\cdot\vec\sigma_2)\,(\vec p_2\cdot\vec\sigma_1)\right],$$

where by $\stackrel{\rm fs}{=}$ we denote the equation that is valid modulo spin independent terms. To make the comparison with previous calculations more transparent, we transformed operators to the same form as in the original DK derivation.

δH_3 is the relativistic correction to the transverse photon exchange. The first electron is coupled to $\vec A$ by the nonrelativistic term,

$$-\frac{e}{m}\,\vec p\cdot\vec A - \frac{e}{2\,m}\,\vec\sigma\cdot\vec B\,, \tag{78}$$

and the second one, by the relativistic correction, i.e., the last but one term in Eq. (64),

$$\frac{e}{8}\big(\{\vec\sigma\cdot\vec B,\vec\pi^2\} + a_e\,\{\vec\pi\cdot\vec B,\vec\pi\cdot\vec\sigma\}\big) \to \frac{e}{8}\,\big[p^2\,2\,\vec p\cdot\vec A + 2\,\vec p\cdot\vec A\,p^2 + \vec\sigma\cdot\vec B\,p^2 + p^2\,\vec\sigma\cdot\vec B + a_e\big(\vec p\cdot\vec B\,\vec p\cdot\vec\sigma + \vec p\cdot\vec\sigma\,\vec p\cdot\vec B\big)\big], \tag{79}$$

It is sufficient to calculate δH_3 in the nonretardation approximation, in which any correction can be simply obtained by replacing the magnetic field $\vec A$ by the static field $\vec{\mathcal{A}}_a$,

$$e\,\mathcal{A}_a^i \equiv \sum_{b\neq a}\left[\frac{\alpha}{2\,r_{ab}}\left(\delta^{ij}+\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right)p_b^j + \frac{\alpha\,(1+a_e)}{2}\,\frac{\big(\vec\sigma_b\times\vec r_{ab}\big)^i}{r_{ab}^3}\right]. \tag{80}$$

The result then is

$$\delta H_3 = \sum_a\frac{e}{8}\Big[2\,p_a^2\,\vec p_a\cdot\vec{\mathcal{A}}_a + 2\,\vec p_a\cdot\vec{\mathcal{A}}_a\,p_a^2 + p_a^2\,\vec\sigma_a\cdot\vec\nabla_a\times\vec{\mathcal{A}}_a + \vec\sigma_a\cdot\vec\nabla_a\times\vec{\mathcal{A}}_a\,p_a^2 + a_e\big(\vec p_a\cdot(\vec\nabla_a\times\vec{\mathcal{A}}_a)\,\vec p_a\cdot\vec\sigma_a + \vec p_a\cdot\vec\sigma_a\,\vec p_a\cdot(\vec\nabla_a\times\vec{\mathcal{A}}_a)\big)\Big] \tag{81}$$

$$\stackrel{DK}{=} \frac{e}{2}\big[2\,p_1^2\,\vec p_1\cdot\vec{\mathcal{A}}_1 + p_1^2\,\vec\nabla_1\times\vec{\mathcal{A}}_1\cdot\vec\sigma_1 + a_e\,\vec p_1\cdot\vec\sigma_1\,\vec p_1\cdot\vec\nabla_1\times\vec{\mathcal{A}}_1\big]$$
$$\stackrel{a_e}{=} a_e\,\alpha\left[\frac{1}{2}\,p_1^2\,\frac{\vec r}{r^3}\times\vec p_1\cdot\vec\sigma_1 + \frac{3}{4}\,p_1^2\,\frac{\vec r\cdot\vec\sigma_1\,\vec r\cdot\vec\sigma_2}{r^5} - \frac{1}{2}\,\vec p_1\cdot\vec\sigma_1\,\vec p_1\times\frac{\vec r}{r^3}\cdot\vec p_2 - \frac{1}{4}\,\vec p_1\cdot\vec\sigma_1\,\vec p_1\cdot\vec\sigma_2\,\frac{1}{r^3} + \frac{3}{4}\,\vec p_1\cdot\vec\sigma_1\,\vec p_1\cdot\vec r\,\frac{\vec r}{r^5}\cdot\vec\sigma_2\right]. \tag{82}$$

where by $\stackrel{DK}{=}$ we denote the equation which is valid on the level of the expectation value of the operator on the triplet-state wave functions. More explicitly, following Douglas and Kroll, we use the symmetry $(1 \leftrightarrow 2)$ of the wave function to replace terms involving σ_2 by terms with σ_1.

The effective operator δH_4 originates from the coupling

$$\frac{e^2\,(1+2\,a_e)}{8}\,\vec\sigma\cdot(\vec E\times\vec A-\vec A\times\vec E)\,, \tag{83}$$

present in the fifth term in Eq. (64). The resulting correction is obtained by replacing the fields $\vec E$ and $\vec A$ by the static fields produced by the other electrons, with the result

$$\begin{aligned}\delta H_4 &= \sum_a \frac{e^2\,(1+2\,a_e)}{8}\,\vec\sigma_a\cdot\Big[\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a-\vec{\mathcal{A}}_a\times\vec{\mathcal{E}}_a\Big]\\ &\stackrel{DK,a_e}{=} a_e\bigg(\frac{3}{4}\,\frac{Z\,\alpha^2}{2\,r_1^3\,r^3}\,\vec\sigma_1\cdot\vec r\,\vec\sigma_2\cdot\vec r_1-\frac{3}{4}\,\frac{\alpha^2}{r^6}\,\vec\sigma_1\cdot\vec r\,\vec\sigma_2\cdot\vec r\\ &\quad-\frac{Z\,\alpha^2}{2\,r_1^3\,r}\,\vec r_1\times\vec p_2\cdot\vec\sigma_1+\frac{Z\,\alpha^2}{2\,r_1^3\,r^3}\,\vec r\times\vec r_1\cdot\vec\sigma_1\,\vec r\cdot\vec p_2\\ &\quad+\frac{\alpha^2}{2\,r^4}\,\vec r\times\vec p_2\cdot\vec\sigma_1\bigg)\,.\end{aligned} \tag{84}$$

The effective operator δH_5 comes from the coupling

$$\frac{e^2}{2}\,\vec A^2\,, \tag{85}$$

present in the first term of Eq. (64). Again, in the nonretardation approximation, the field $\vec A_a$ can be replaced by the static field produced by the other electrons,

$$\delta H_5=\sum_a\frac{e^2}{2}\,\vec{\mathcal{A}}_a^2\stackrel{DK}{=}e^2\,\mathcal{A}_1^2\stackrel{a_e}{=}-a_e\,\frac{\alpha^2}{2\,r^4}\,\vec r\times\vec p_1\cdot\vec\sigma_1\,. \tag{86}$$

The effective operators δH_6 and δH_7 represent the single- and the double-spin part of the retardation correction to the nonrelativistic single transverse photon exchange. To calculate them, we have to return to the general expression for the one-photon exchange amplitude, Eq. (65), and take the transverse part of the photon propagator,

$$\begin{aligned}\delta E &= -e^2\int\frac{d^4k}{(2\,\pi)^4\,i}\,\frac{1}{(k^0)^2-\vec k^2+i\,\epsilon}\left(\delta^{ij}-\frac{k^i\,k^j}{\vec k^2}\right)\\ &\quad\times\left\langle\phi\middle|j_a^i(k)\,e^{i\,\vec k\cdot\vec r_a}\,\frac{1}{E_0-H_0-k^0+i\,\epsilon}\,j_b^j(-k)\,e^{-i\,\vec k\cdot\vec r_b}\middle|\phi\right\rangle\\ &\quad+(a\leftrightarrow b)\,.\end{aligned} \tag{87}$$

We assume that the product $j_a^i(k)\ j_b^j(-k)$ contains at most a single power of k^0. This allows one to perform the k^0 integration by encircling the only pole $k^0=|\vec k|$ on the $\mathrm{Re}(k^0)>0$ complex half-plane and obtain

$$\begin{aligned}\delta E &= e^2\int\frac{d^3k}{(2\,\pi)^3\,2\,k}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right)\\ &\quad\times\left\langle\phi\middle|j_a^i(k)\,e^{i\,\vec k\cdot\vec r_a}\,\frac{1}{E_0-H_0-k}\,j_b^j(-k)\,e^{-i\,\vec k\cdot\vec r_b}\middle|\phi\right\rangle\\ &\quad+(a\leftrightarrow b)\,,\end{aligned} \tag{88}$$

where $k=|\vec k|$. The retardation expansion of the electron propagator yields

$$\frac{1}{E_0-H_0-k}=-\frac{1}{k}+\frac{H_0-E_0}{k^2}-\frac{(H_0-E_0)^2}{k^3}+\ldots\,. \tag{89}$$

The first term here contributes to the Breit-Pauli Hamiltonian and the second term, to $E^{(5)}$. Taking the current j^i in the nonrelativistic form, the third expansion term is

$$\begin{aligned}\delta E &= \sum_{a\neq b}\sum_b(-e^2)\int\frac{d^3k}{(2\,\pi)^3\,2\,k^4}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right)\\ &\quad\times\bigg\langle\left(\vec p_a+\frac{1+a_e}{2}\,\vec\sigma_a\times\vec\nabla_a\right)^i e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\\ &\quad\times\left(\vec p_b+\frac{1+a_e}{2}\,\vec\sigma_b\times\vec\nabla_b\right)^j e^{-i\,\vec k\cdot\vec r_b}\bigg\rangle\,.\end{aligned} \tag{90}$$

This is the most complicated term among the amm corrections, so we describe its evaluation in detail. The correction is split into the double spin part δE_6 and the single spin part δE_7,

$$\delta E\stackrel{\text{fs}}{=}\delta E_6+\delta E_7\,. \tag{91}$$

The double spin part is

$$\begin{aligned}\delta E_6 &= \sum_{a\neq b}\sum_b\left(-\frac{e^2}{8}\right)(1+a_e)^2\int\frac{d^3k}{(2\,\pi)^3}\\ &\quad\times\frac{(\vec\sigma_a\times\vec k)\cdot(\vec\sigma_b\times\vec k)}{k^4}\left\langle e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\,e^{-i\,\vec k\cdot\vec r_b}\right\rangle.\end{aligned} \tag{92}$$

We use the commutation identity

$$\begin{aligned}&\left\langle e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\,e^{-i\,\vec k\cdot\vec r_b}\right\rangle+(a\leftrightarrow b)\\ &\quad=\left\langle\Big[e^{i\,\vec k\cdot\vec r_a},\Big[(H_0-E_0)^2,e^{-i\,\vec k\cdot\vec r_b}\Big]\Big]\right\rangle\\ &\quad=-\frac{1}{2}\left\langle\big[p_a^2,[p_b^2,e^{i\,\vec k\cdot\vec r_{ab}}]\big]\right\rangle\end{aligned} \tag{93}$$

to express this correction as the expectation value of the effective operator δH_6,

$$\begin{aligned}\delta H_6 &\stackrel{\text{fs}}{=} \frac{\alpha\,(1+a_e)^2}{32}\left[p_1^2,\left[p_2^2\,,\,\sigma_1^i\,\sigma_2^j\,\frac{r^i\,r^j}{r^3}\right]\right]\\ &\stackrel{a_e}{=} a_e\bigg[\frac{3\,\alpha}{4}\,p_1^2\,\frac{\vec\sigma_1\cdot\vec r\,\vec\sigma_2\cdot\vec r}{r^5}+\frac{\alpha}{4}\,p_1^2\,\frac{i}{r^3}\bigg((\vec r\cdot\vec\sigma_2)\,\vec\sigma_1\\ &\quad+(\vec r\cdot\vec\sigma_1)\,\vec\sigma_2-\frac{3\,(\vec\sigma_1\cdot\vec r)\,(\vec\sigma_2\cdot\vec r)}{r^2}\,\vec r\bigg)\cdot\vec p_2\bigg]\,.\end{aligned} \tag{94}$$

The single spin part is

$$\begin{aligned}\delta E_7 &= \sum_{a\neq b}\sum_b\left(-\frac{i\,e^2}{4}\right)(1+a_e)\int\frac{d^3k}{(2\,\pi)^3\,k^4}\\ &\quad\times\Big\langle e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\,e^{-i\,\vec k\cdot\vec r_b}\,\vec\sigma_a\times\vec k\cdot\vec p_b\\ &\quad-\vec p_a\cdot\vec\sigma_b\times\vec k\,e^{i\,\vec k\cdot\vec r_a}\,(H_0-E_0)^2\,e^{-i\,\vec k\cdot\vec r_b}\Big\rangle\,.\end{aligned} \tag{95}$$

With the help of the integral formula

$$\int d^3k\,\frac{4\,\pi\,\vec{k}}{k^4}\,e^{i\,\vec{k}\cdot\vec{r}} = \frac{i}{2}\,\frac{\vec{r}}{r}\,, \tag{96}$$

one obtains

$$\begin{aligned}
\delta H_7 &= \sum_{a>b}\sum_b \frac{\alpha\,(1+a_e)}{4}\biggl\{\biggl[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_a^2}{2}\biggr]\cdot\bigl[V,\vec{p}_b\bigr] + \biggl[\frac{p_b^2}{2},\biggl[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_a^2}{2}\biggr]\biggr]\cdot\vec{p}_b \\
&\quad -\bigl[\vec{p}_a,V\bigr]\cdot\biggl[p_b^2,\vec{\sigma}_b\times\frac{\vec{r}_{ab}}{r_{ab}}\biggr] - \vec{p}_a\cdot\biggl[\frac{p_a^2}{2},\biggl[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_b^2}{2}\biggr]\biggr]\biggr\} \\
&\overset{DK,a_e}{=} a_e\left(\frac{\alpha^2}{2}\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r^4}\times\vec{p}_1 + \frac{Z\,\alpha^2}{2\,r}\,\vec{\sigma}_1\cdot\frac{\vec{r}_1}{r_1^3}\times\vec{p}_2 + \frac{Z\,\alpha^2}{2}\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r^3}\times\frac{\vec{r}_1}{r_1^3}\,(\vec{r}\cdot\vec{p}_2)\right. \\
&\quad \left. +\frac{\alpha}{2}\,p_1^2\,\frac{i}{r}\,\vec{\sigma}_1\cdot\vec{p}_2\times\vec{p}_1 - \frac{\alpha}{2}\,p_1^2\,\frac{i}{r^3}\,(\vec{r}\cdot\vec{p}_2)\,(\vec{r}\times\vec{p}_1)\cdot\vec{\sigma}_1\right).
\end{aligned} \tag{97}$$

The effective operator δH_8 represents the retardation correction to the single transverse photon exchange contribution, in which one vertex is nonrelativistic, Eq. (48), whereas the second comes from the fifth term in Eq. (64),

$$-\frac{e\,(1+2\,a_e)}{8}\,\vec{\sigma}\cdot\bigl(\vec{E}\times\vec{p}-\vec{p}\times\vec{E}\bigr)\,. \tag{98}$$

With the help of Eq. (88), one obtains

$$\begin{aligned}
\delta E_8 &= \sum_{a\neq b}\sum_b e^2\,(1+2\,a_e)\int\frac{d^3k}{(2\,\pi)^3}\left(\delta^{ij}-\frac{k^i\,k^j}{k^2}\right) \\
&\quad\times\frac{i}{16}\left\langle\left(e^{i\,\vec{k}\cdot\vec{r}_a}\,\vec{p}_a\times\vec{\sigma}_a + \vec{p}_a\times\vec{\sigma}_a\,e^{i\,\vec{k}\cdot\vec{r}_a}\right)^i\right. \\
&\quad\left.\times\frac{1}{E_0-H_0-k}\left(\vec{p}_b-\frac{i}{2}\,\vec{\sigma}_b\times\vec{k}\right)^j e^{-i\,\vec{k}\cdot\vec{r}_b}\right\rangle + \text{h.c.}\,.
\end{aligned} \tag{99}$$

In the expansion of $1/(E_0-H_0-k)$ in Eq. (89) the first term vanishes because of the Hermitian conjugation and the second term contributes to order $m\,\alpha^6\,a_e$. After commuting (H_0-E_0) on the left, one obtains the effective operator δH_8,

$$\begin{aligned}
\delta H_8 &= (1+2\,a_e)\sum_a\biggl\{\frac{e^2}{8}\,\vec{\sigma}_a\cdot\bigl(\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a-\vec{\mathcal{A}}_a\times\vec{\mathcal{E}}_a\bigr) + \frac{i\,e}{16}\Bigl[\vec{\mathcal{A}}_a\cdot\vec{p}_a\times\vec{\sigma}_a+\vec{p}_a\times\vec{\sigma}_a\cdot\vec{\mathcal{A}}_a\,,p_a^2\Bigr]\biggr\} \\
&\overset{DK,a_e}{=} \delta H_5 + a_e\biggl[-\frac{i\,\alpha}{2}\,p_1^2\,\frac{1}{r}\,\vec{p}_2\times\vec{p}_1\cdot\vec{\sigma}_1 - \frac{i\,\alpha}{2}\,p_1^2\,\frac{1}{r^3}\,(\vec{r}\cdot\vec{p}_2)\,(\vec{r}\times\vec{p}_1)\cdot\vec{\sigma}_1 + \frac{9\,\alpha}{8}\,p_1^2\,\frac{(\vec{\sigma}_1\cdot\vec{r})\,(\vec{\sigma}_2\cdot\vec{r})}{r^5} \\
&\quad -\frac{3\,i\,\alpha}{4}\,p_1^2\left(\frac{\vec{r}}{r^3}\cdot\vec{\sigma}_1\right)(\vec{p}_1\cdot\vec{\sigma}_2) - \frac{\alpha}{2}\,p_1^2\,\frac{\vec{r}}{r^3}\times\vec{p}_2\cdot\vec{\sigma}_1 - \frac{\alpha}{2}\,p_1^2\,\frac{\vec{r}}{r^3}\times\vec{p}_1\cdot\vec{\sigma}_1\biggr].
\end{aligned} \tag{100}$$

Finally, after some rearrangement, the total amm correction can be expressed as the expectation value of 17 operators,

$$E_H = \langle H_{a_e}^{(6)}\rangle = \sum_{i=1}^{17}\langle\mathcal{H}_i\rangle\,, \tag{101}$$

where

$$\mathcal{H}_1 = -\frac{Z}{4}\,p_1^2\,\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1\cdot\vec{\sigma}_1\,, \tag{102}$$

$$\mathcal{H}_2 = -\frac{3\,Z}{4}\,\frac{\vec{r}_1}{r_1^3}\times\frac{\vec{r}}{r^3}\cdot\vec{\sigma}_1\,(\vec{r}\cdot\vec{p}_2)\,, \tag{103}$$

$$\mathcal{H}_3 = \frac{3\,Z}{4}\,\frac{\vec{r}}{r^3}\cdot\vec{\sigma}_1\,\frac{\vec{r}_1}{r_1^3}\cdot\vec{\sigma}_2\,, \tag{104}$$

$$\mathcal{H}_4 = \frac{1}{2\,r^4}\,\vec{r}\times\vec{p}_2\cdot\vec{\sigma}_1\,, \tag{105}$$

$$\mathcal{H}_5 = -\frac{3}{4\,r^6}\,\vec{r}\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2\,, \tag{106}$$

$$\mathcal{H}_6 = \frac{1}{4}\,p_1^2\,\frac{\vec{r}}{r^3}\times\vec{p}_1\cdot\vec{\sigma}_1\,, \tag{107}$$

$$\mathcal{H}_7 = -\frac{1}{4}\,p_1^2\,\frac{\vec{r}}{r^3}\times\vec{p}_2\cdot\vec{\sigma}_1\,, \tag{108}$$

$$\mathcal{H}_8 = -\frac{Z}{4\,r}\,\frac{\vec{r}_1}{r_1^3}\times\vec{p}_2\cdot\vec{\sigma}_1\,, \tag{109}$$

$$\mathcal{H}_9 = -\frac{i}{2}\,p_1^2\,\frac{1}{r^3}\,\vec{r}\cdot\vec{p}_2\,\vec{r}\times\vec{p}_1\cdot\vec{\sigma}_1\,, \tag{110}$$

$$\mathcal{H}_{10} = \frac{3\,i}{4\,r^5}\,\vec{r}\times(\vec{r}\cdot\vec{p}_2)\,\vec{p}_1\cdot\vec{\sigma}_1\,, \tag{111}$$

$$\mathcal{H}_{11} = -\frac{3}{8\,r^5}\,\vec{r}\times(\vec{r}\times\vec{p}_1\cdot\vec{\sigma}_1)\,\vec{p}_2\cdot\vec{\sigma}_2\,, \tag{112}$$

$$\mathcal{H}_{12} = -\frac{1}{8\,r^3}\,\vec{p}_1\cdot\vec{\sigma}_2\,\vec{p}_2\cdot\vec{\sigma}_1\,, \tag{113}$$

$$\mathcal{H}_{13} = \frac{21}{16}\,p_1^2\,\frac{1}{r^5}\,\vec{r}\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2\,, \tag{114}$$

$$\mathcal{H}_{14} = -\frac{3\,i}{8}\,p_1^2\,\frac{\vec{r}}{r^3}\cdot\vec{\sigma}_1\,\vec{p}_1\cdot\vec{\sigma}_2\,, \tag{115}$$

$$\mathcal{H}_{15} = \frac{i}{8}\,p_1^2\,\frac{1}{r^3}\,\big(\vec{r}\cdot\vec{\sigma}_2\,\vec{p}_2\cdot\vec{\sigma}_1 + (\vec{r}\cdot\vec{\sigma}_1)\,(\vec{p}_2\cdot\vec{\sigma}_2) - \frac{3}{r^2}\,\vec{r}\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2\,\vec{r}\cdot\vec{p}_2\big)\,, \tag{116}$$

$$\mathcal{H}_{16} = -\frac{1}{4}\,\vec{p}_1\cdot\vec{\sigma}_1\,\vec{p}_1\times\frac{\vec{r}}{r^3}\cdot\vec{p}_2\,, \tag{117}$$

$$\mathcal{H}_{17} = \frac{1}{8}\,\vec{p}_1\cdot\vec{\sigma}_1\,\big(-\vec{p}_1\cdot\vec{\sigma}_2\,\frac{1}{r^3} + 3\vec{p}_1\cdot\vec{r}\,\frac{\vec{r}}{r^5}\cdot\vec{\sigma}_2\big)\,. \tag{118}$$

The operators above are intentionally written in a form very similar to that for the DK operators given by Eqs. (8)-(22). For most of $\mathcal{H}_i$, there is an one-to-one correspondence with the DK operators, all the difference being the overall prefactors. There are only three exceptions. The first one is that our operator $\mathcal{H}_8$ cancels out in the DK calculation, while DK operator $\mathcal{H}_8$ cancels out in our calculations. The other two are related to the different spin structure of the next to last term in Eq. (64), which leads to the operators $\mathcal{H}_{16}$ and $\mathcal{H}_{17}$.

E. Low-energy contribution

The low-energy part E_L comes from the photon momenta region $k < \Lambda$, Λ being the cutoff parameter introduced by Eq. (46). E_L is a sum of the low-energy contributions due to the photon exchange ($\mathcal{E}_{LE}$ in Section IV A), due to the radiative corrections ($\mathcal{E}_{LR}$ in Section IV B), and an additional uv-finite contribution that was not considered in previous sections. E_L can be conveniently derived from the low energy form of the electromagnetic interaction Hamiltonian [21],

$$H_I = \sum_a \left(-e\,\vec{r}_a\cdot\vec{E} - \frac{e}{2\,m}\,\sigma_a^i\,r_a^j\,B^i_{,j} - \frac{e}{4\,m^2}\,\vec{\sigma}_a\cdot\vec{E}_a\times\vec{p}_a\right). \tag{119}$$

This choice of the starting point for the derivation is more convenient than the general nonrelativistic Hamiltonian in Eq. (A9) since it makes transparent the high degree of cancellation between various terms. Specifically, the contributions of the second and the third terms in H_I cancel each other and only the first term contributes to E_L,

$$E_L = \frac{2}{3}\,\alpha\int_0^\Lambda \frac{d^3k}{(2\,\pi)^3\,2\,k}\,k^2 \times\delta\left\langle\phi\left|(\vec{r}_1+\vec{r}_2)\,\frac{1}{E-H-k}\,(\vec{r}_1+\vec{r}_2)\right|\phi\right\rangle, \tag{120}$$

where $\delta\langle\ldots\rangle$ denotes the correction to the matrix element $\langle\ldots\rangle$ due to the Breit-Pauli Hamiltonian $H^{(4)}_{\rm fs}$. Using the relation

$$\big[H,\vec{r}_1+\vec{r}_2\big] = -\frac{i}{m}(\vec{p}_1+\vec{p}_2)+\frac{1}{4\,m^2}\,\big[\vec{p}_1\times\vec{\sigma}_1+\vec{p}_2\times\vec{\sigma}_2, H_0-E_0\big], \tag{121}$$

E_L can be transformed to the following compact form,

$$E_L = -\frac{2\,\alpha}{3\,\pi}\,\delta\left\langle\phi\right|(\vec{p}_1+\vec{p}_2)\,(H-E)\ln\left[\frac{2(H-E)}{(Z\,\alpha)^2}\right](\vec{p}_1+\vec{p}_2)\left|\phi\right\rangle + \ln(2\,\lambda)\,\frac{2}{3}\,Z\,\alpha^2\,\langle i\,\vec{p}_1\times\delta^3(r_1)\,\vec{p}_1\cdot\vec{\sigma}_1\rangle$$
$$+\frac{i\,Z^2\,\alpha^3}{3\,\pi}\left\langle\phi\right|\left(\frac{\vec{r}_1}{r_1^3}+\frac{\vec{r}_2}{r_2^3}\right)\times\frac{(\vec{\sigma}_1+\vec{\sigma}_2)}{2}\ln\left[\frac{2(H_0-E_0)}{(Z\,\alpha)^2}\right]\cdot\left(\frac{\vec{r}_1}{r_1^3}+\frac{\vec{r}_2}{r_2^3}\right)\left|\phi\right\rangle, \tag{122}$$

where the term with the second order matrix element has been dropped out, as all such terms are included in E_S. The term with $\ln(2\,\lambda)$ in Eq. (122) cancels out with the corresponding contribution in H_Q in Eq. (63).

V. NUMERICAL EVALUATION AND THE RESULTS

A. Nonrelativistic wave function

In order to obtain the nonrelativistic wave function, we use the technique by Korobov [22, 23], in which the spatial part of the triplet P states is represented as

$$\vec{\phi}(\vec{r}_1,\vec{r}_2) = \sum_{i=1}^{N} c_i \times\left[\vec{r}_1\exp(-\alpha_i\,r_1-\beta_i\,r_2-\gamma_i\,r)-(1\leftrightarrow 2)\right], \tag{123}$$

where $r=|\vec{r}_1-\vec{r}_2|$. Real nonlinear parameters α_i, β_i, and γ_i are chosen quasirandomly from the intervals

$$\begin{aligned}\alpha_i &\in [A_1,A_2]\,,\\ \beta_i &\in [B_1,B_2]\,,\\ \gamma_i &\in [C_1,C_2]\,,\end{aligned} \tag{124}$$

with the parameters $A_{1,2}$, $B_{1,2}$, and $C_{1,2}$ being subjects of a variational optimization. In order to enforce the proper behavior of the wave function (123) in the limits $r_1\to\infty$, $r_2\to\infty$, and $r\to\infty$, the nonlinear parameters are subjected to the condition

$$\{\alpha_i+\beta_i,\alpha_i+\gamma_i,\beta_i+\gamma_i\} > \sqrt{2E_{\rm io}}\,, \tag{125}$$

where $E_{\rm io}$ is the ionization energy of the atom. In order to reproduce the behavior of the exact wave function for small values of $r_{1,2}$ and r, the variational parameters $A_{1,2}$, $B_{1,2}$, and $C_{1,2}$ are allowed to take negative values. To make the basis set more flexible, multiple sets of the variational parameters $A_{1,2}$, $B_{1,2}$, and $C_{1,2}$ are introduced. Namely, the double basis set was used in this work for the determination of the nonrelativistic wave function, and the triple basis set was used in calculations of corrections to the Bethe logarithm and second-order corrections.

The calculation of matrix elements of the nonrelativistic Hamiltonian is performed with the use of the simple formula for the master integral:

$$\frac{1}{16\,\pi^2}\int d^3r_1\int d^3r_2\,\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1\,r_2\,r} = \frac{1}{(\alpha+\beta)(\beta+\gamma)(\gamma+\alpha)}. \tag{126}$$

Integrals with any additional powers of r_i in the numerator can be obtained by differentiating with respect to the corresponding parameter α, β, or γ. Matrix elements of relativistic corrections involve additional inverse powers of r_1, r_2, and r. They can be obtained by integrating with respect to the corresponding parameter. In fact, all matrix elements required for the evaluation of the relativistic, QED, and the finite nuclear mass corrections can be expressed in terms of the rational, logarithmic, and dilogarithmic functions of α, β, and γ.

The procedure of generating the nonrelativistic wave function looks now as follows. For the initial set of parameters $A_{1,2}$, $B_{1,2}$, and $C_{1,2}$, the nonlinear parameters α_i, β_i, and γ_i with $i=1,\ldots,N$ are distributed quasirandomly. Then, the $N\times N$ matrix of the nonrelativistic Hamiltonian H_0 is evaluated. The linear coefficients c_i and the reference-state eigenvalue E_0 are determined by using the inverse iteration method, with the LDU decomposition employed for the inversion of the Hamiltonian matrix. Then the procedure is repeated for a different set of parameters $A_{1,2}$, $B_{1,2}$, and $C_{1,2}$, looking for the minimum value of the energy E_0. The minimization problem is rather noisy, as the functional contains many local minima. So, the simplest simplex-like algorithms of minimization are probably the most appropriate for this task. Our calculations were performed in the quadruple, sixtuple, and octuple arithmetics, which were implemented in Fortran 95 by libraries written by V. Korobov [24].

Our result for the nonrelativistic energy of helium for the triplet P state and the infinite nuclear mass is (in atomic units)

$$E(2^3P) = -2.133\,164\,190\,779\,283\,205\,146\,96\,^{+0}_{-10}\,. \tag{127}$$

This value is the upper variational bound for the energy obtained with $N=6600$ basis functions, and the uncertainty is the extrapolated lower bound. The value in Eq. (127) is by about 4 decimals more precise than the previously best result of Ref. [8].

B. Angular momentum algebra

In the approach employed in the present investigation as well as in the previous studies by K.P. and coauthors [12, 28], all the angular momentum algebra is performed in Cartesian coordinates. Tensor product of the ^3P wave functions is represented [37] in terms of the spatial wave functions and the spin operator $\vec{s} = (\vec{\sigma}_1 + \vec{\sigma}_2)/2$ as

$$|^3P_0\rangle\langle^3P_0| = |i\rangle\langle j| \left(\delta^{ij}\,\frac{s^2}{2} - s^j\,s^i\right), \quad (128)$$

$$\frac{1}{3}\sum_m |^3P_1,m\rangle\langle^3P_1,m| = |i\rangle\langle j|\,\frac{1}{2}\,s^i\,s^j\,, \quad (129)$$

$$\frac{1}{5}\sum_m |^3P_2,m\rangle\langle^3P_2,m| = |i\rangle\langle j|\,\frac{1}{10} \quad (130)$$

$$\times\left(2\,s^2\,\delta^{ij} - 3s^i\,s^j + 2\,s^j\,s^i\right), \quad (131)$$

where $|j\rangle$ denotes the state with the Cartesian index j and the normalization of the spatial wave functions is

$$\langle i|j\rangle = \delta^{ij}/3. \quad (132)$$

For the calculation of the second order matrix elements one needs formulae for the spin product

$$s^i\,s^j\,s^k = \delta^{jk}\,s^i + \frac{i}{2}\,\epsilon^{jkl}\,s^i\,s^l + \frac{i}{2}\,\epsilon^{ikl}\,s^j\,s^l + \frac{i}{2}\,\epsilon^{ijl}\,s^k\,s^l\,, \quad (133)$$

and for spin traces

$$\mathrm{Tr}\,s^i = 0\,, \quad (134)$$

$$\mathrm{Tr}\,s^i\,s^j = 2\,\delta^{ij}\,, \quad (135)$$

$$\mathrm{Tr}\,s^i\,s^j\,s^k = i\,\epsilon^{ijk}\,, \quad (136)$$

$$\mathrm{Tr}\,s^i\,s^j\,s^k\,s^l = \delta^{ij}\,\delta^{kl} + \delta^{jk}\,\delta^{il}\,. \quad (137)$$

Using these formulae, all matrix elements can be reduced to a form involving the spatial wave functions only. For example, matrix elements of the operators in the Breit-Pauli Hamiltonian can be expressed as

$$\langle\vec{Q}\cdot\vec{s}\rangle_J = i\,\epsilon_{jkl}\,\langle j|Q^k|l\rangle\,u_J \quad (138)$$

$$\langle\vec{s}\cdot\hat{Q}\cdot\vec{s}\rangle_J = \langle j|Q^{jl}|l\rangle\,v_J \quad (139)$$

where $\hat{Q}$ is an arbitrary symmetric and traceless tensor ($Q^{jl} = Q^{lj}$ and $Q^{kk} = 0$) and

$$u_J = (1, 1/2, -1/2), \quad (140)$$

$$v_J = (-1, 1/2, -1/10)\,, \quad (141)$$

for $J = 0, 1, 2$ respectively.

C. Leading-order fine structure

The dominant contribution to the fine structure comes from the spin-dependent part of the Breit-Pauli Hamiltonian $H_{\rm fs}$ given by Eq. (1). With including the nuclear recoil effect, the leading-order contribution to the fine structure in helium is

$$E_{\rm fs}(J) = \langle H_{\rm fs}\rangle_J$$

$$= \left(\frac{m_r}{m}\right)^3\frac{\alpha^4}{4}\Big[-E_1\,(1+a_e)^2\,v_J + E_2\,(1+2\,a_e)\,u_J + E_3\left(1+\frac{4}{3}\,a_e\right)u_J + \frac{m}{M}\,E_4\,(1+a_e)\,u_J\Big]\,. \quad (142)$$

The corresponding results for the large and the small fine structure interval are

$$\nu_{01} = \left(\frac{m_r}{m}\right)^3\alpha^2 R_\infty c\Big[\frac{3E_1}{4}(1+a_e)^2 + \frac{E_2}{4}(1+2a_e) + \frac{E_3}{4}(1+\frac{4}{3}a_e) + \frac{m}{M}\frac{E_4}{4}(1+a_e)\Big]\,, \quad (143)$$

$$\nu_{12} = \left(\frac{m_r}{m}\right)^3\alpha^2 R_\infty c\Big[-\frac{3E_1}{10}(1+a_e)^2 + \frac{E_2}{2}(1+2a_e) + \frac{E_3}{2}(1+\frac{4}{3}a_e) + \frac{m}{M}\frac{E_4}{2}(1+a_e)\Big]\,, \quad (144)$$

where the constants E_i are given by (in atomic units)

$$E_1 = 2\left\langle j\middle|3\,\frac{r^j\,r^i}{r^5} - \frac{\delta^{ji}}{r^3}\middle|i\right\rangle, \quad (145)$$

$$E_2 = 2\,Z\,\epsilon_{jki}\left\langle j\middle|\left(\frac{\vec{r}_1}{r_1^3}\times\vec{\nabla}_1\right)^k\middle|i\right\rangle, \quad (146)$$

$$E_3 = -3\,\epsilon_{jki}\left\langle j\middle|\left(\frac{\vec{r}}{r^3}\times(\vec{\nabla}_1-\vec{\nabla}_2)\right)^k\middle|i\right\rangle, \quad (147)$$

$$E_4 = 4\,Z\,\epsilon_{jki}\left\langle j\middle|\left(\frac{\vec{r}_1}{r_1^3}\times(\vec{\nabla}_1+\vec{\nabla}_2)\right)^k\middle|i\right\rangle. \quad (148)$$

Our numerical results for the constants E_i are

$$E_1 = 0.180\,220\,618\,632\,744\,(10)\,, \quad (149)$$

$$E_2 = -0.277\,401\,358\,712\,829\,(10)\,, \quad (150)$$

$$E_3 = 0.411\,999\,963\,626\,094\,(25)\,, \quad (151)$$

$$E_4 = 0.241\,945\,125\,695\,21\,(6)\,. \quad (152)$$

These results are obtained with including the mass polarization term into the zeroth-order Hamiltonian and thus contain effects of the second and higher orders in m/M.

D. $m\,\alpha^6$ contribution

The contribution of order $m\,\alpha^6$ to the fine structure of helium is represented by Eq. (5). The most difficult part of its numerical evaluation is associated with the second-order contributions. First calculations of the second-order corrections to the helium fine structure were performed by Hambro [25] and Lewis and Serafino [26]. Two decades later, Yan and Drake [27] did these calculations to a much higher accuracy and demonstrated that the first results were much less accurate than it was claimed. The nuclear recoil and the amm effects were included into the second-order corrections in Ref. [8].

An independent evaluation of the second-order corrections (including the amm part but not the recoil effect) was performed by K.P. and Sapirstein [28]. In the present work, we re-calculate all $m\,\alpha^6$ corrections, with the intention to independently check the numerical convergence of the previous results and, more importantly, to check the nuclear recoil effect on the second-order corrections, which was previously calculated only by Drake.

The second-order corrections in Eq. (5) are of two kinds: the symmetric and the non-symmetric one. The symmetric contributions are the most numerous ones since they involve the ^3P, ^1P, ^3D, ^1D, and ^3F intermediate states. The derivation of the calculational formulas for them is relatively straightforward along the lines presented in Sec. V B.

The numerical evaluation of the symmetric second-order contributions was performed by employing the variational optimization of the nonlinear parameters of the basis set for the Green function. Convergence of numerical results is rather slow for the ^3P intermediate states because of the singular character of the Breit interaction. The convergence can be improved by introducing singular functions into the basis set, as in Ref. [27]. We, however, prefer to exploit the flexibility of the basis set (123) and emulate the missing basis functions by using very large exponents. In order to effectively span large regions of nonlinear parameters, we used non-uniform distributions of the kind [29]

$$\alpha_i = A_1 + (t_i^{-a} - 1)A_2\,, \tag{153}$$

with $a = 2$ and 3, where the variable t_i has a uniform quasirandom distribution over the interval $(0, 1)$.

The non-symmetric second-order contributions involve only the ^3P intermediate states. Care should be taken in the numerical calculation of this part due to the presence of singular operators, namely the Dirac δ and the $\vec{p}^{\,4}$ operators. While a straightforward numerical evaluation is possible, a much better convergence is obtained by transforming the singular operators to a more regular form.

The treatment of the second-order correction involving the δ operator is based on the global representation of the δ function introduced by Drachman [30],

$$\begin{aligned}\langle 0|4\pi\,\delta^3(r_1)|n\rangle & \\ = \left\langle 0\left|\frac{2}{r_1}(f_n+f_0) + \sum_{a=1,2}\vec{\nabla}_a\cdot\frac{2}{r_1}\vec{\nabla}_a\right|n\right\rangle\,, &\end{aligned} \tag{154}$$

where

$$f_k = E_k - V + \frac{m_r}{M}\,\vec{\nabla}_1\cdot\vec{\nabla}_2\,, \tag{155}$$

and $V = -Z/r_1 - Z/r_2 + 1/r$. Noting that $f_n = E_n - E_0 + f_0$, one can cancel the $E_n - E_0$ factor with the denominator of the reduced Green function in the second-order matrix element. Using the completeness of the eigenfunctions, we obtain the regularized expression for the second-order correction,

$$\begin{aligned}&\left\langle 4\pi\left[\delta^3(r_1)+\delta^3(r_2)\right]\,\frac{1}{(E_0-H_0)'}\,H_{\rm fs}\right\rangle \\ &= \left\langle\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\,4f_0\,\frac{1}{(E_0-H_0)'}\,H_{\rm fs}\right\rangle \\ &+ \sum_{a=1,2}\left\langle\vec{\nabla}_a\cdot\left(\frac{2}{r_1}+\frac{2}{r_2}\right)\vec{\nabla}_a\,\frac{1}{(E_0-H_0)'}\,H_{\rm fs}\right\rangle \\ &- \left\langle\left(\frac{2}{r_1}+\frac{2}{r_2}\right)\,H_{\rm fs}\right\rangle + \left\langle\frac{2}{r_1}+\frac{2}{r_2}\right\rangle\langle H_{\rm fs}\rangle\,.\end{aligned} \tag{156}$$

A regularized expression for the second-order correction with the operator $-1/8(\vec{p}_1^{\,4}+\vec{p}_2^{\,4})$ can be derived by using the identity

$$-\frac{1}{8}\,(\vec{p}_1^{\,4}+\vec{p}_2^{\,4}) = -\frac{1}{8}\,(\vec{p}_1^{\,2}+\vec{p}_2^{\,2})^2 + \frac{1}{4}\,\vec{p}_1^{\,2}\vec{p}_2^{\,2} \tag{157}$$

and employing the Schrödinger equation to transform the first term, as described in Ref. [8].

For the numerical evaluation of the non-symmetric contributions we used the set of nonlinear parameters obtained by merging two subsets, one obtained by the variational optimization of the symmetric second-order Breit correction and another, by an optimization of the symmetric correction for the model perturbation $\delta V = 1/r_1^2 + 1/r_2^2$. The model potential δV corresponds to the most singular part of the regularized δ operator.

The numerical results for the $m\,\alpha^6$ second-order corrections are presented in Table I. Our values for these corrections in the non-recoil limit (both with and without the amm part) agree well with the results by Drake [8]. In the recoil part of the second-order corrections, we observe some deviation from Drake's results. To localize the source of the discrepancy, we separate the recoil contributions into 3 parts, which are unduced by the mass scaling, the mass polarization, and the recoil operators. The corresponding contributions to the ν_{01} interval from the ^3P intermediate states are $3.26 - 3.66 - 0.69 = -1.09$ kHz, to be compared with Drake's values of $3.25 - 3.66 - 0.06 = -0.47$ kHz. Analogous contributions to the ν_{12} interval are $1.17 - 1.87 + 0.91 = 0.21$ kHz, to be compared with Drake's values of $1.17 - 2.15 + 0.91 = -0.07$ kHz. The contributions to the ν_{01} interval from the ^1P intermediate states are $-4.54 - 7.68 + 2.93 = -9.29$ kHz, to be compared with Drake's values of $-4.52 - 7.66 + 1.87 = -10.31$ kHz. The total difference between our results and those by Drake is rather small numerically and does not influence significantly the comparison of theory with the experimental data.

E. Relativistic correction to the Bethe logarithm

The relativistic correction to the Bethe logarithm is given by Eq. (122). The two λ-independent parts in the right-hand side of this equation will be referred to as the E_{L1} and E_{L2} corrections, respectively. We will start our discussion with

TABLE I: Second-order contributions to order $m\,\alpha^6$ for the large (ν_{01}) and small (ν_{12}) fine-structure intervals in helium, including the recoil and the amm corrections. Units are kHz.

State	ν_{01}			ν_{12}		
		recoil	amm		recoil	amm
^3P	$-4894.29(2)$	-1.09	-14.40	-1569.62	0.21	-3.20
^1P	6595.64	-9.29	23.28	-6595.64	9.29	-23.28
^3D	26.33	-0.01	0.07	50.50	-0.03	0.16
^1D				22.20	0.05	0.05
^3F				52.24	-0.01	0.24
Sum	1727.68(2)	-10.39	8.96	-8040.32	9.51	-26.02
Drake [8]	1727.58(4)	$-10.81(4)$	8.95	$-8040.38(5)$	10.19(11)	-26.02

the simpler part E_{L2}. For the numerical evaluation, it is convenient to transform this correction to the equivalent form,

$$E_{L2} = -\frac{\alpha}{3\,\pi}\int_0^\infty dk\left[k^2\,L_2(k) - A_2\right], \tag{158}$$

where

$$L_2(k) \;=\; -i\left\langle(\vec p_1+\vec p_2)\times\frac{1}{H_0+k-E_0}\,(\vec p_1+\vec p_2)\cdot\vec s\right\rangle, \tag{159}$$

and A_2 is the leading term of the large-k asymptotic expansion of $k^2 L_2(k)$, which has the form

$$k^2\,L_2(k) = A_2 + \frac{B_2}{k^{3/2}} + \frac{C\,\ln k}{k^2} + \frac{D}{k^2} + \frac{E}{k^{5/2}} + \ldots\,. \tag{160}$$

The two leading asymptotic constants are evaluated to be

$$A_2 \;=\; Z\left\langle\left(\frac{\vec r_1}{r_1^3}+\frac{\vec r_2}{r_2^3}\right)\times(\vec p_1+\vec p_2)\cdot\vec s\right\rangle, \tag{161}$$

$$B_2 \;=\; -i\,\frac{4\,\pi\,Z^2}{3\,\sqrt{2}}\,\langle\vec p_1\times\delta^3(r_1)\,\vec p_1\cdot\vec s+\vec p_2\times\delta^3(r_2)\,\vec p_2\cdot\vec s\rangle\,. \tag{162}$$

Here we correct the overall sign in Eqs. (159) and (161) as compared to Ref. [12]. It is noteworthy that the k^{-2} asymptotic behavior of $L_2(k)$ arises through an internal cancellation of the three angular-momentum contributions ($^3S^e$, $^3P^e$, and $^3D^e$, where e stands for the even parity), since each of them separately falls off as k^{-1} only.

In order to accurately perform the integration in Eq. (158), we transform this expression to the following form

$$E_{L2} = -\frac{\alpha}{3\,\pi}\left\{\int_0^\kappa dk\,k^2\,L_2(k) + \int_\kappa^\infty dk\,\left[k^2\,L_2(k) - A_2 - \frac{B_2}{k^{3/2}}\right] - A_2\kappa + \frac{2B_2}{\sqrt{\kappa}}\right\}, \tag{163}$$

where κ is a free parameter.

In the numerical evaluation of E_{L2}, we exploit the fact that the integrand $L_2(k)$ obeys the variational principle, similarly to that for the Bethe logarithm [31]. In fact, each angular-momentum contribution to $L_2(k)$ has the same form as for the Bethe logarithm, the difference being only the prefactors coming from the angular-momentum algebra. (It is important that the difference in the prefactors leads to the disappearance of the k^{-1} term in the large-k asymptotics of $L_2(k)$.) In order to perform the integration over k in Eq. (163), one needs to know the function $L_2(k)$ for a wide region of k. As noted in Ref. [32], there is no need to perform the full variational optimization of the basis for each value of k. The idea is that, having got the optimized set of nonlinear parameters for the basis at $k = k_1$ and $k = k_2$, for all k in between one can use the basis obtained by merging together the two optimized sets. The asymptotic behavior of the integrand $L_2(k)$ for large k, together with its value at $k = 0$, $L_2(0) = -\langle(\vec r_1+\vec r_2)\times(\vec p_1+\vec p_2)\cdot\vec s\rangle$, served as useful tests of the numerical procedure.

The general evaluation scheme is as follows. First, we perform a careful optimization of nonlinear basis-set parameters for several distinct scales of k: $k_i = 10^i$, with $i = 1,\ldots,i_{\rm max}$ and $i_{\rm max} = 4$. The optimization is carried out with incrementing the size of the basis, until the prescribed accuracy is achieved. The size of the optimized basis employed in actual calculations varied from $N = 600$ for $k_1 = 10$ to $N = 1600$ for the $^3D^e$ wave and $k_4 = 10^4$, yielding the numerical accuracy of about 10 digits for $L_2(k)$. For each particular value of $k \le 10^{i_{\rm max}}$, the calculational basis is obtained by merging the optimized bases for the two closest k_i points, thus essentially doubling the number of the basis functions. According to our experience, such merging usually yields an additional digit of accuracy.

The integral over $k \in [0,\kappa]$ in Eq. (163) was calculated analytically, after performing the full diagonalization of the Hamiltonian matrix and using the spectral representation of the propagator. This allowed us to avoid problems associated with the pole on the real axis coming from the 2^3S state. The parameter κ was set to $\kappa = 10$. The integral over $k \in [\kappa,\infty)$ was separated into two parts, $k < 10^{i_{\rm max}}$ and $k > 10^{i_{\rm max}}$. The first part was evaluated by using the Gauss-Legendre quadratures, after the change of variables $t = 1/k^2$. The second part was evaluated by fitting the integrand to the form

$$k^2\,L_2(k) - A_2 - \frac{B_2}{k^{3/2}} = \frac{\ln k}{k^2}\,W_1\left(\frac{1}{k}\right) + \frac{1}{k^2}\,W_2\left(\frac{1}{\sqrt{k}}\right), \tag{164}$$

where $W(x)$ denotes a polynomial of x. For fitting, we used the function $L_2(k)$ stored on the interval $k = 1, \ldots, 100$. The total number of fitting parameters in the above expression was about $9 - 11$. The optimal form of the fitting function was selected by demanding it to reproduce the known asymptotic constants A_2 and B_2 for the function $L_2(k)$. The error due to the fitting procedure was estimated by comparing the integration results for the fitted function and for the numerical integrand outside the fitting region, i.e., for $k \in [10^2, 10^4]$.

Our results for the asymptotic constants A_2 and B_2 are

$$A_2 = 0.120\,944\,339\,354\,433\,(8)\, u_J\,, \tag{165}$$

$$B_2 = -0.982\,581\,108\,(2)\, u_J\,. \tag{166}$$

The final result for the E_{L2} correction to the helium fine structure is (in units $m\,\alpha^7$)

$$E_{L2} = 0.067\,682\,1(5)\, u_J\,, \tag{167}$$

This is in reasonable agreement with the value obtained previously in Refs. [12, 28], which is $-0.06775(5)\, u_J$, except for the overall sign, which we correct here.

We now turn to the evaluation of the E_{L1} correction. In terms of the integral over the photon momentum, it is written as

$$E_{L1} = -\frac{2\alpha}{3\,\pi} \lim_{K\to\infty} \left[\int_0^K dk\, k\, L_1(k) - A_1\, K - B_1\, \ln K \right], \tag{168}$$

where

$$\begin{aligned} L_1(k) &= 2 \left\langle H_{\rm fs}^{(4)}\, \frac{1}{(E_0 - H_0)'}\, (p_1^i + p_2^i)\, \frac{1}{H_0 + k - E_0} \right. \\ &\quad \left. \times\, (p_1^i + p_2^i) \right\rangle + \left\langle (p_1^i + p_2^i)\, \frac{1}{H_0 + k - E_0} \right. \\ &\quad \left. \times \left[\langle H_{\rm fs}^{(4)} \rangle - H_{\rm fs}^{(4)} \right] \frac{1}{H_0 + k - E_0}\, (p_1^i + p_2^i) \right\rangle, \end{aligned} \tag{169}$$

and A_1 and B_1 are the leading terms of the large-k asymptotic expansion of the integrand,

$$k\, L_1(k) = A_1 + \frac{B_1}{k} + \frac{C}{k^{3/2}} + \frac{D\, \ln k}{k^2} + \frac{E}{k^2} + \ldots\,, \tag{170}$$

with

$$A_1 = 2 \left\langle H_{\rm fs}^{(4)}\, \frac{1}{(E_0 - H_0)'} (\vec p_1 + \vec p_2)^2 \right\rangle, \tag{171}$$

$$\begin{aligned} B_1 &= -\left\langle H_{\rm fs}^{(4)}\, \frac{1}{(E_0 - H_0)'}\, 4\,\pi\, Z\, [\delta^3(r_1) + \delta^3(r_2)] \right\rangle \\ &\quad - \frac{i\,\pi\, Z}{2}\, \langle \vec p_1 \times \delta^3(r_1)\, \vec p_1 \cdot \vec s + \vec p_2 \times \delta^3(r_2)\, \vec p_2 \cdot \vec s \rangle\,. \end{aligned} \tag{172}$$

At $k = 0$, the integrand L_1 can be evaluated analytically to yield $L_1(0) = 0$.

For the numerical evaluation, Eq. (168) is written in the form similar to Eq. (163),

$$\begin{aligned} E_{L1} &= -\frac{2\alpha}{3\,\pi} \left\{ \int_0^\kappa dk\, k\, L_1(k) \right. \\ &\quad \left. + \int_\kappa^\infty dk \left[k\, L_1(k) - A_1 - \frac{B_1}{k} \right] - A_1 \kappa - B_1\, \ln \kappa \right\}. \end{aligned} \tag{173}$$

The main difference of the numerical evaluation of E_{L1} from that of E_{L2} is that the integrand $L_1(k)$, contrary to $L_2(k)$, does not obey the variational principle [i.e., there is no functional whose minimum yields the exact value of $L_1(k)$]. Because of this, in evaluation of E_{L1} we have to use the variational optimization results for the nonlinear basis-set parameters obtained for E_{L2}. This is a serious drawback since it is clear that the optimal set of parameters for the integrand $L_2(k)$ is not exactly optimal for $L_1(k)$, because of an additional singularity introduced by the perturbing Hamiltonian $H_{\rm fs}^{(4)}$. After some numerical experimenting, we found that this additional singularity can be well accounted for if the calculational basis for each k is not just doubled by merging two sets optimized for two scales k_1 and k_2, but tripled, with the third part obtained from the second one by (alternatively) scaling the parameters α_i and β_i by a factor $g = 10$. This trick was inspired by the method described in Ref. [33].

With this modification, our numerical evaluation of E_{L1} was done similarly to that for E_{L2}. Because of the tripling of the basis set, we used the optimized parameters with somewhat smaller number of the basis functions but increased the high-energy cutoff parameter up to $k_5 = 10^5$. Our results for the asymptotic constants A_1 and B_1 are

$$A_1 = -0.028\,038\,047\,8\,(10)\, u_J + 0.054\,037\,866\,(4)\, v_J\,, \tag{174}$$

$$B_1 = -0.169\,127\,85\,(20)\, u_J + 0.146\,477\,680\,(2)\, v_J\,. \tag{175}$$

The final result for the E_{L1} correction to the helium fine splitting is (in units $m\,\alpha^7$)

$$E_{L1} = -0.107\,664\,(6)\, u_J + 0.118\,404\,4\,(4)\, v_J\,. \tag{176}$$

The spin-orbit part of the above result is by about 25% larger than the previously reported value of Ref. [12] of $-0.0817(20)u_J$, whereas the spin-spin part is by about 10% larger that the previous value of $0.0959(4)v_J$. The reason for this deviation lies in the insufficient accuracy of the previous calculations.

VI. SUMMARY AND DISCUSSION

The summary of all contributions available for the fine structure of helium is given in Table II. Numerical results are presented for the large ν_{01} and the small ν_{12} intervals, defined

TABLE II: Summary of individual contributions to the helium fine structure. Units are kHz.

	ν_{01}	ν_{12}
$E^{(4)}$	29 618 418.54	2 297 717.82
$E^{(6)}$	$-1\,556.97(2)$	$-6\,544.93$
$E^{(7)}$[log]	82.59	-10.09
Subtotal	29 616 944.16(2)	2 291 162.80
Drake [8]	29 616 943.40(6)	2 291 163.40(13)
E_Q[nolog]	21.73	7.42
E_H	-4.21	4.05
E_S[nolog]	11.42	-1.21
E_{L1}	-31.51	-4.99
E_{L2}	4.61	9.22
$E^{(7)}$[nolog]	2.04	14.48
Higher orders	± 1.6	± 1.6
Total theory	$29\,616\,946.20 \pm 1.6$	$2\,291\,177.28 \pm 1.6$
Experiment [7]		2 291 177.53(35)
Experiment [5]	29 616 951.66(70)	2 291 175.59(51)
Experiment [4]	29 616 950.9(9)	
Experiment [6]	29 616 952.7(1.0)	2 291 168.(11.)

by

$$\nu_{01} = \big[E(2^3P_0) - E(2^3P_1)\big]/h\,, \tag{177}$$

$$\nu_{12} = \big[E(2^3P_1) - E(2^3P_2)\big]/h\,. \tag{178}$$

The parameters used in our calculations are: $\alpha^{-1} = 137.035\,999\,679(94)$, $cR_\infty = 3\,289\,841\,960\,361(22)$ kHz, and $m/M = 1.370\,933\,555\,70 \times 10^{-4}$. In the table, the correction $E^{(4)}$ is given by Eqs. (143) and (144) and the correction $E^{(6)}$, by Eq. (5). $E^{(7)}$[log] denotes the sum of the logarithmic parts of E_S and E_Q. The corrections E_Q, E_H, and E_S are given by Eqs. (63), (101), and (35), respectively. The complete listing of numerical results for individual terms contributing to E_Q and E_H can be found in Ref. [9] and is not repeated here. The relativistic corrections to the Bethe logarithm E_{L1} and E_{L2} are given by Eqs. (168) and (158), respectively.

The result for $E^{(4)}$ in Table II is consistent with that of Ref. [9] after accounting for the newer value of the fine structure constant. The result for $E^{(6)}$ differs slightly from the corresponding value in Ref. [9], mainly because of the change in the recoil second-order Breit correction, which was previously calculated only by Drake [8]. As can be seen from the table, different theoretical predictions that include contributions up to order $m\,\alpha^7 \log\alpha$ and $m^2/M\,\alpha^6$ (entry "Subtotal") agree at a sub-kHz level with each other.

The nonlogarithmic correction to order $m\,\alpha^7$ has not been checked independently. The compilation of results presented for this correction in Ref. [8] is in part based on the derivation by Zhang [13–15], which was shown to be not entirely consistent [9], and in part includes calculational results by K.P. and Sapirstein [12].

Table II shows that the calculational error of our results is almost negligible as compared to the experimental uncertainty. There is, however, a much larger theoretical error induced by the higher-order corrections. It was believed previously [10, 12] that the higher-order $m\,\alpha^8$ effects contribute well under the 1 kHz level. Particularly, the analysis presented in Ref. [12] identified several $m\,\alpha^8$ corrections that are enhanced by $\ln(Z\alpha)$ but nevertheless contribute only about 0.1 kHz. In the present investigation, we found several nonlogarithmic corrections that might contribute at the 1 kHz level.

The first contribution comes from the mixing between the $^3P_1$ and $^1P_1$ levels. The nonrelativistic $2^1P_1 - 2^3P_1$ energy difference of 61.3×10^6 MHz acquires the relativistic correction of -17.1×10^3 MHz. If we consider the $m\,\alpha^6$ second-order Breit correction to the energy of the 2^3P_1 state with the 2^1P_1 intermediate states, the modification of the $2^1P_1 - 2^3P_1$ energy difference by relativistic effects alters the value of the correction by about 1 kHz. We thus estimate the theoretical uncertainty of the ν_{01} and ν_{12} fine structure intervals due to the mixing between the $^3P_1$ and $^1P_1$ levels as ± 1.0 kHz. It should be mentioned, however, that all corrections due to the mixing cancel identically in the sum of the large and small intervals, $\nu_{02} = \nu_{01} + \nu_{12}$. It is, therefore, likely that the theoretical value for the interval ν_{02} is more accurate than that for the interval ν_{01} and ν_{12} separately.

The largest identified $m\,\alpha^8$ contribution to the interval ν_{02} comes from the one-photon exchange diagram, which was evaluated to all orders in $Z\alpha$ but to the leading order in $1/Z$ in Ref. [34]. The result obtained in that work for ν_{02} is $0.1033\,m\,\alpha^8\,Z^7$. Because of the Z^7 enhancement, the numerical contribution for helium is quite large, 13.1 kHz. This is, however, only the leading term of the $1/Z$ expansion; the complete contribution for helium is going to be much smaller because of the screening. In order to estimate the screening effect, we compare the complete contribution to order $m\,\alpha^6$ for ν_{02} in helium, which is -8.11 MHz, with the corresponding one-photon exchange term, which gives 86.4 MHz. The resulting estimate is ± 1.2 kHz.

The total theoretical error due to the higher-order effects specified in Table II for the ν_{01} and ν_{12} intervals is obtained by adding quadratically the two error estimates discussed above. We observe that for the small interval, the theoretical value agrees well with the experimental results, whereas for the large interval, a disagreement of about 3 standard deviations is present. It should be noted that the present theoretical uncertainties are much larger than those specified in previous investigations, the reason being that in most previous cases, the uncertainties represented the calculational errors only.

Commenting on the situation when theory agrees with experiment for one fine-structure interval and disagrees for another, we have to state that we do not have any satisfactory explanation for it. All effects contributing to one interval contribute also to the other, both contributions being comparable in magnitude. We thus see no reason why a theoretical prediction for one interval should be significantly more accurate than for the other. Presuming that the experimental value for the ν_{01} interval is correct, we have to conclude that the excellent agreement of our theoretical value for the ν_{12} interval with the latest measurement by Borbely *et al.* [7] is probably accidental.

Finally, we present separately the theoretical result for the sum of the large and the small fine structure intervals in helium, $\nu_{02}(\text{theo}) = 31\,908\,123.5\,(1.2)$ kHz. For the reason discussed above, its uncertainty is smaller than for the ν_{01} and ν_{12} intervals. The theoretical value disagrees with the experimental result of $\nu_{02}(\text{exp}) = 31\,908\,126.78\,(94)$ kHz [5] by about 2 standard deviations.

To conclude, we performed an evaluation of the helium fine structure that is complete to orders $m\,\alpha^7$ and $m^2/M\,\alpha^6$. Our results for the $m\,\alpha^4$, $m\,\alpha^5$, and $m\,\alpha^6$ contributions agree with those reported in previous investigations at a sub-kHz level. The present evaluation of the relativistic corrections to the Bethe logarithm significantly improves upon the original calculation. The corresponding results reduce the previously reported discrepancy between the theoretical predictions and the experimental results. However, the remaining difference for the ν_{01} interval is larger than the estimated contribution of the higher-order effects. This discrepancy needs to be resolved in order to make possible the determination of the fine structure constant by means of the helium spectroscopy.

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[1] F. Minardi, G. Bianchini, P. C. Pastor, G. Giusfredi, F. S. Pavone, and M. Inguscio, Phys. Rev. Lett. **82**, 1112 (1999).
[2] J. Castillega, D. Livingston, A. Sanders, and D. Shiner, Phys. Rev. Lett. **84**, 4321 (2000).
[3] C. H. Storry, M. C. George, and E. A. Hessels, Phys. Rev. Lett. **84**, 3274 (2000).
[4] M. C. George, L. D. Lombardi, and E. A. Hessels, Phys. Rev. Lett. **87**, 173002 (2001).
[5] T. Zelevinsky, D. Farkas, and G. Gabrielse, Phys. Rev. Lett. **95**, 203001 (2005).
[6] G. Giusfredi, P. C. Pastor, P. D. Natale, D. Mazzotti, C. de Mauro, L. Fallani, G. Hagel, V. Krachmalnicoff, and M. Inguscio, Can. J. Phys. **83**, 301 (2005).
[7] J. S. Borbely, M. C. George, L. D. Lombardi, M. Weel, D. W. Fitzakerley, and E. A. Hessels, Phys. Rev. A, in press.
[8] G. W. F. Drake, Can. J. Phys. **80**, 1195 (2002).
[9] K. Pachucki, Phys. Rev. Lett. **97**, 013002 (2006).
[10] T. Zhang, Z.-C. Yan, and G. W. F. Drake, Phys. Rev. Lett. **77**, 1715 (1996).
[11] K. Pachucki, J. Phys. B **32**, 137 (1999).
[12] K. Pachucki and J. Sapirstein, J. Phys. B **33**, 5297 (2000).
[13] T. Zhang, Phys. Rev. A **54**, 1252 (1996).
[14] T. Zhang, Phys. Rev. A **53**, 3896 (1996).
[15] T. Zhang, Phys. Rev. A **56**, 270 (1997).
[16] M. Douglas and N. Kroll, Ann. Phys. (NY) **82**, 89 (1974).
[17] K. Pachucki and J. Sapirstein, J. Phys. B **36**, 803 (2003).
[18] A. Yelkhovsky, Phys. Rev. A **64**, 062104 (2001).
[19] U. D. Jentschura, A. Czarnecki, and K. Pachucki, Phys. Rev. A **72**, 062102 (2005).
[20] K. Pachucki, Phys. Rev. A **71**, 012503 (2005).
[21] K. Pachucki, Phys. Rev. A **69**, 052502 (2004).
[22] V. I. Korobov and S. V. Korobov, Phys. Rev. A **59**, 3394 (1999).
[23] V. I. Korobov, Phys. Rev. A **61**, 064503 (2000).
[24] V. I. Korobov, *private communication.*
[25] L. Hambro, Phys. Rev. A **5**, 2027 (1972); **6**, 865 (1972); **7**, 479 (1973).
[26] M. L. Lewis and P. H. Serafino, Phys. Rev. A **18**, 867 (1978).
[27] Z.-C. Yan and G. W. F. Drake, Phys. Rev. Lett. **74**, 4791 (1995).
[28] K. Pachucki and J. Sapirstein, J. Phys. B **35**, 1783 (2002).
[29] K. Pachucki, J. Phys. B **35**, 3087 (2002).
[30] R. J. Drachman, J. Phys. B **14**, 2733 (1981).
[31] C. Schwartz, Phys. Rev. **123**, 1700 (1961).
[32] J. Komasa, Phys. Rev. A **65**, 012506 (2001).
[33] V. I. Korobov, Phys. Rev. A **69**, 054501 (2004).
[34] P. J. Mohr, Phys. Rev. A **32**, 1949 (1985).
[35] C. Itzykson and J. Bernard Zuber, *Quantum Field Theory* (McGraw-Hill, New York, 1980).
[36] K. Pachucki, Phys. Rev. A **74**, 022512 (2006).
[37] G. Łach and K. Pachucki, Phys. Rev. A **64**, 042510 (2001).

Appendix A: Foldy-Wouthuysen transformation in d-dimensions

The Foldy-Wouthuysen (FW) transformation [35] is the nonrelativistic expansion of the Dirac Hamiltonian in an external electromagnetic field. Following Ref. [36] we extend this transformation to the case where the dimension d of space is arbitrary. The Dirac Hamiltonian in an external electromagnetic field is

$$H = \vec{\alpha}\cdot\vec{\pi} + \beta\,m + e\,A^0\,, \tag{A1}$$

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

$$\alpha^i = \begin{pmatrix} 0 & \sigma^i \\ \sigma^i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \tag{A2}$$

and

$$\{\sigma^i, \sigma^j\} = 2\,\delta^{ij}\,I. \tag{A3}$$

The FW transformation S [35] leads to a new Hamiltonian

$$H_{\rm FW} = e^{i\,S}\,(H - i\,\partial_t)\,e^{-i\,S}\,, \tag{A4}$$

which decouples the upper and the lower component of the Dirac wave function up to a specified order in the $1/m$ expansion. Here we calculate $H_{\rm FW}$ up to terms contributing to the $m\,\alpha^6$ correction to the energy. We use a convenient form of the FW operator S, which can be written as

$$S = -\frac{i}{2\,m}\biggl\{\beta\,\vec\alpha\cdot\vec\pi-\frac{1}{3\,m^2}\,\beta\,(\vec\alpha\cdot\vec\pi)^3 +\frac{1}{2\,m}\,[\vec\alpha\cdot\vec\pi\,,\,e\,A^0-i\,\partial_t]+\frac{\beta}{5\,m^4}\,(\vec\alpha\cdot\vec\pi)^5 -\frac{\beta\,e}{4\,m^2}\,\vec\alpha\cdot\dot{\vec E}+\frac{i\,e}{24\,m^3}\,[\vec\alpha\cdot\vec\pi,[\vec\alpha\cdot\vec\pi,\vec\alpha\cdot\vec E]] -\frac{i\,e}{3\,m^3}\,\bigl\{(\vec\alpha\cdot\vec\pi)^2\,,\,\vec\alpha\cdot\vec E\bigr\}\biggr\}. \tag{A5}$$

The FW Hamiltonian is expanded in a power series in S

$$H_{\rm FW}=\sum_{j=0}^{6}\mathcal{H}^{(j)}+\ldots \tag{A6}$$

where

$$\begin{aligned}\mathcal{H}^{(0)} &= H,\\ \mathcal{H}^{(1)} &= [i\,S\,,\mathcal{H}^{(0)}-i\,\partial_t],\\ \mathcal{H}^{(j)} &= \frac{1}{j}\,[i\,S\,,\mathcal{H}^{(j-1)}]\,,\ \ \text{for } j=2\ldots6,\end{aligned} \tag{A7}$$

and higher order terms with $j>6$ are neglected. The calculation of nested commutators is rather tedious but the result is simply

$$\begin{aligned}H_{\rm FW} &= e\,A^0+\frac{(\vec\sigma\cdot\vec\pi)^2}{2\,m}-\frac{(\vec\sigma\cdot\vec\pi)^4}{8\,m^3}+\frac{(\vec\sigma\cdot\vec\pi)^6}{16\,m^5}\\ &\quad -\frac{i\,e}{8\,m^2}\,[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]-\frac{e}{16\,m^3}\,\bigl\{\vec\pi\,,\,\partial_t\vec E\bigr\}\\ &\quad -\frac{i\,e}{128\,m^4}\,[\vec\sigma\cdot\vec\pi,[\vec\sigma\cdot\vec\pi,[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]]]\\ &\quad +\frac{i\,e}{16\,m^4}\,\Bigl\{(\vec\sigma\cdot\vec\pi)^2\,,\,[\vec\sigma\cdot\vec\pi,\vec\sigma\cdot\vec E]\Bigr\}.\end{aligned} \tag{A8}$$

There is some arbitrariness in the operator S, which means that $H_{\rm FW}$ is not unique. The standard approach [35] relies on the subsequent use of several FW transformations and yields a result that agrees with the $d=3$ limit of Eq. (A8) up to a transformation with an additional even operator.

Our aim is to obtain a Hamiltonian suitable for calculations of the $m\,\alpha^7$ contributions to energy levels of an arbitrary light atom. In this case one can neglect the vector potential $\vec A$ in all terms having m^4 and m^5 in the denominator. Less obviously, one can also neglect terms with $\vec\sigma\cdot\vec A\,\vec\sigma\cdot\dot{\vec E}$ and $\vec B^2$. This is because they are of second order in electromagnetic fields, which additionally contain derivatives, and thus contribute only to higher orders. After these simplifications, $H_{\rm FW}$ takes the form

$$\begin{aligned}H_{\rm FW} &= e\,A^0+\frac{\pi^2}{2\,m}-\frac{e}{4\,m}\,\sigma^{ij}\,B^{ij}-\frac{\pi^4}{8\,m^3}\\ &\quad -\frac{e}{8\,m^2}\Bigl(\vec\nabla\cdot\vec E+\sigma^{ij}\,\bigl\{E^i\,,\,\pi^j\bigr\}\Bigr)\\ &\quad +\frac{e}{16\,m^3}\bigl\{\sigma^{ij}B^{ij}\,,\,p^2\bigr\}-\frac{e}{16\,m^3}\,\bigl\{\vec p\,,\,\partial_t\vec E\bigr\}\\ &\quad +\frac{3\,e}{32\,m^4}\,\bigl\{\sigma^{ij}\,E^i\,p^j\,,\,p^2\bigr\}+\frac{e}{128\,m^4}\,[p^2,[p^2,A^0]]\\ &\quad -\frac{3\,e}{64\,m^4}\,\bigl\{p^2\,,\,\nabla^2A^0\bigr\}+\frac{p^6}{16\,m^5},\end{aligned} \tag{A9}$$

where

$$\sigma^{ij} = \frac{1}{2\,i}\,[\sigma^i\,,\,\sigma^j], \tag{A10}$$

$$B^{ij} = \partial^i\,A^j-\partial^j\,A^i, \tag{A11}$$

$$E^i = -\nabla^iA^0-\partial_tA^i. \tag{A12}$$